Ministerie van Verkeer en Waterstaat

Rijkswaterstaat

Second Intercalibration Round in the framework of Bonn-OSINET -Round Robin 2007

The comparison of six HFO samples

29 April 2008

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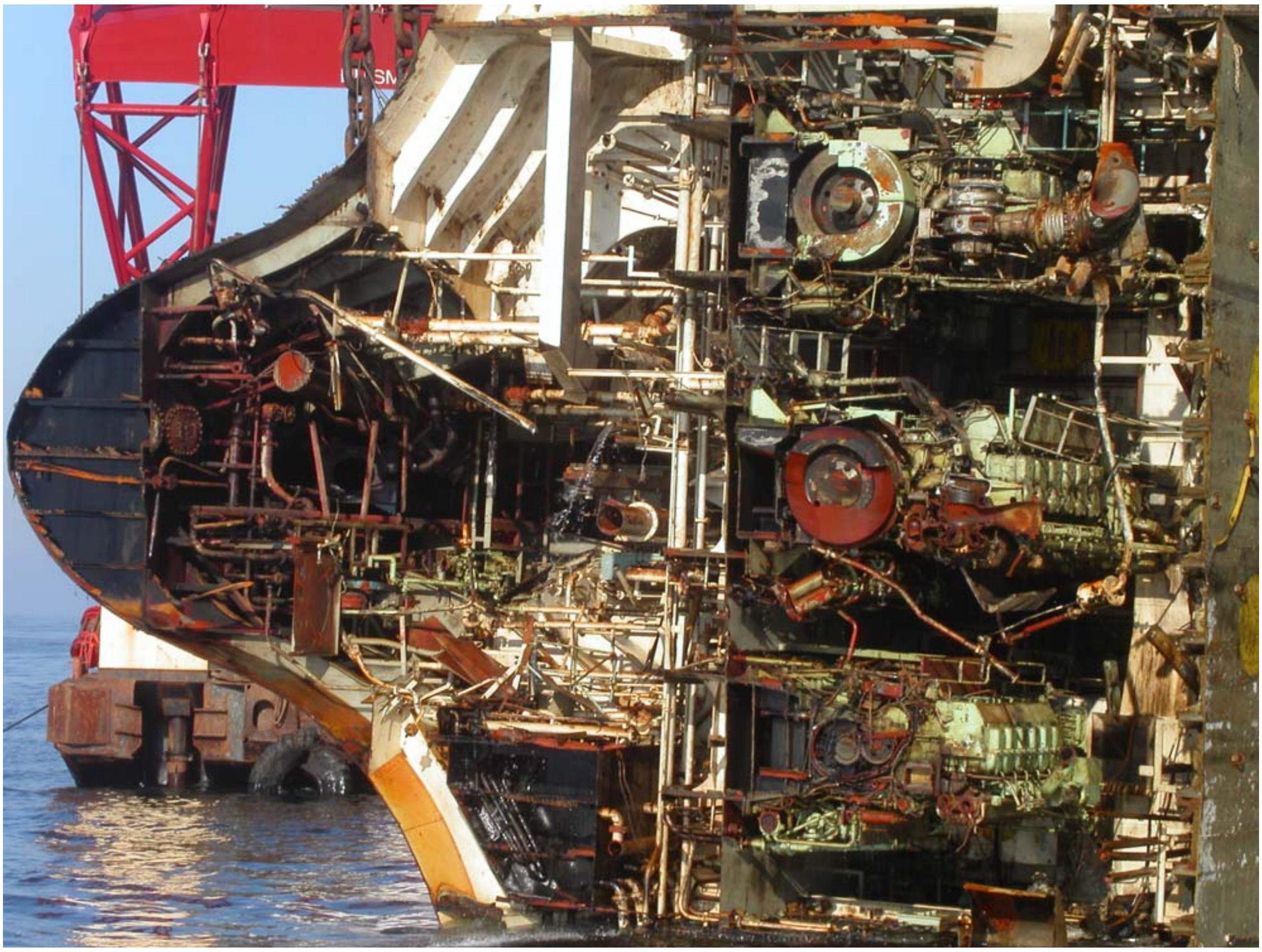
The results of nineteen international laboratories



Front page:
The hot tap oil recovery system is being deployed on the TRICOLOR.

Second page:
The engine room of the TRICOLOR, sliced by the cutting wire of the CBT, surfaces above the waterline.

From http://www.tricolorsalvage.com/ :

Welcome to TRICOLORSALVAGE.COM

The 'TRICOLOR' is a 1987 built Norwegian flagged vehicle carrier, which, in the early hours of 14 December 2002, was struck by 'Kariba', a 1982 built Bahamian flagged container ship in the French Exclusive Economic Zone some 20 miles north of the French coast in the English channel.

TRICOLOR sank as a result of the impact of the striking and was eventually declared a total loss. In December 2002 French authorities ordered the TRICOLOR to be removed, as it was perceived to represent a danger to shipping and the environment.

This site is a source of information about the development, background and progress of the remarkable wreck removal of the TRICOLOR, one of the biggest wrecks ever to be removed.

Colofon

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Contents

Executive summary

RIZA and BSH have organized a round robin in 2007 for oil spill identification (RR2007), where 21 international laboratories participated of which 19 send in a report. The goal of RR2007 was to practice and improve CEN/TR 15522-2 (published December 2006), to check the own laboratory's method and to learn from the results of other labs.

Six samples of the Tricolor – Vicky incident (source, beach and artificially weathered HFO samples) have been sent to the participants. Four spill samples (Sp 3, 4, 5, 6) had to be compared with two possible source samples (So 1 and S 2). The conclusions are summarized in the table.

Participant	So1_Sp3	So1_Sp4	So1_Sp5	So1_Sp6	So2_Sp3	So2_Sp4	So2_Sp5	So2_Sp6
AU_EC_CES	NM	NM	M	PbM	NM	NM	NM	NM
AU_NSWDECC	NM	NM	PbM	NM	NM	NM	NM	NM
BR_Petrobas	NM -4	NM -4	M +4	M +4	NM -4	PbM +2	NM -4	NM -4
CA_EC_ALET	NM -3	NM -3	M +2	M +2	NM -3	Inc -1	NM -3	NM -3
CA_ESTD	NM -4	NM -4	PbM +3	PbM +2	NM -3	PbM +3	NM -4	NM -4
CA_PESC_EC	-3	-3	+2	+2	-3	+1	-3	-3
CN_NCSEMC	NM -4	NM -4	PbM +3	NM -2	NM -4	PbM +2	NM -4	NM -4
DE_BSH	NM -4	NM -4	M +4	M +4	NM -4	NM -4	NM -4	NM -4
EE_EERC	NM -4	NM -4	M +4	NM -2	NM -4	PbM +3	NM -2	NM -3
ES_CEDEX	NM	NM	M	M	NM	M	NM	NM
ES_CSIC	NM -4	NM -4	M +4	M +4	PbNM -3	PbM +3	NM -4	NM -4
FI_NBI	Inc 0	NM -3	PbM	Inc 0	Inc 0	PbM +2	NM -3	NM -3
FR_CEDRE	-4	-4	3	-4	-4	2	-4	-4
LV_LVA	NM -2	NM -2	M +4	NM -1	NM -3	PbM +1	NM -3	NM -1
NL_NFI	-4	-4	3	-4	-4	-4	-4	-4
NL_RIZA	NM -4	NM -4	M +4	M +3	NM -4	NM -4	NM -4	NM -4
NO_Sintef	NM -4	NM -4	M +4	M +4	NM -4	PbM +3	NM -4	NM -4
SE_SKL	-4	-4	+2	+1	-4	-3	-4	-4
US_OSPR	NM	NM	M	M	NM	M	NM	NM

Comparison level assignment according to CEN /TR 15522-2

NM= non match	Inc = inconclusive	M = match
PbNM = possible non-match	PbM = probable match	

Comparison level assignment according to SKL (Sweden)

+4 to -4

The participants were asked to use the comparison level assignment used in CEN/TR 15522-2 and /or the method used by the forensic lab SKL (SE).

The source samples 1 (tank Vicky) and 2 (tank Tricolor), and the spill samples 3 (from water 24-01-2003) and 4 (beach 05-02-2003) were received from BMM (BE). The spill samples 5 and 6 were prepared from source 1 by artificial weathering (evaporation; Sp5: 120 min. at 120°C; Sp6: 120 min at 120°C followed by 90 min at 150°C).

The results of RR2007 have been discussed during the annual workshop of the Bonn_OSINET expertgroup. (7-9 Nov. 2007 in Trondheim, NO).

All participants have correctly found at least a probable match between Source I and Spill 5.
Many participants could not identify spill 6.
Many participants concluded a probable match of Spill 4 with Source 2, although differences were present.

Together with the samples the participants were asked to fill in a spreadsheet file with height and area values for a range of compounds and to copy a set of chromatograms into a PowerPoint presentation. The spreadsheet file was prepared in such a way that the samples could be compared based on ratio comparison and weathering plots.

The data received were in line with the fact that sample 1 and spill 5 contained the same oil.

But in nearly all cases they were also in line with the fact that samples 1 and 6 contained the same oil.
As sample 6 was heavily evaporated, this finding is mainly based on the PW- or weathering plots.
Thus weathering plots, which are one of the three main points (levels) in the Nordtest-method NTChem001 (and described there in detail) were newly recognized as being of great value in case there are doubts as to whether observed differences in compound relations are caused by weathering or not:

> The third level, the weathering check, is a way of representing the data measured in order to ascertain whether an observed difference between the samples compared is significant or not (NTChem001).

But those weathering plots also pronounced the differences between sample 2 and spill 4:
Very obviously, weathering was not an issue with regard to spill 4, and plotting the values of sample 4 in percentage of those in sample 2 should have resulted in a straight line of all points at 100%.
This was not the case. Merely “clouds” of points could be seen in all PW-plots, and a best-fit line or -curve could not be drawn.
Participants having concluded a probable match between sample 2 and sample 4:

- did not find all differences,
- did not present objective/provable explanations for those differences.
- assumed a different amount of cutterstock in the two samples.

In chapter 2 of this report the individual results of the participants are discussed and the original conclusions shown, while in chapter 3 the interlaboratory results are discussed.
The complete original reports are published on the Bonnagreement website: http://www.bonnagreement.org/. at the Bonn-OSINET section.

During the workshop 5 working groups were formed to study the following issues:

WG_1	Pre-injection Clean-up - Reason for why not using fractionation: F1/F2: sat/aro (?)
WG_2	Harmonization of chromatographic conditions Quality management - Instrumental aspects
WG_3	Selection of CR's Further refinement of Gerhards table (WP3) - Selection of compound ratios
WG_4	Common Data-base possibility / needs for it - at which level ? - Multivariate Treatment
WG_5	Conclusion definitions. Further refinements of suggested terms - Statistics

Coordinator	Gerhard Dahlmann
Time frame	First quarter of 2008

1. Introduction

1.1 Letter of 10-5-07

On 10-5-07 these instructions have been send by email:
Instructions round robin2007v2.doc

Dear colleague,

This is the second oil spill identification intercalibration round within the Bonn-OSINET expert group. We have several new participants, so a short introduction might be useful.

Note
For literal quotations of parts of reports, publications and letters, in this report the typesetting of the text to the right is used

The Bonnagreement (www.bonnagreement.org) is an organization of a group of countries around the North Sea to help each other in combating pollution in the North Sea Area from maritime disasters and chronic pollution from ships and offshore installations.

After several international disasters, it became clear that each country has a lab for oil spill identification, but that each lab has his own method and experience resulting in different conclusions and advises.
Therefore it was decided in September 2005 to establish an expert group in order to come to
- a common method
- mutual assistance
- an oil database.

RIZA(NL) and BSH(DE) started in 2004 an annual round robin for oil spill identification with the intension to learn from each other. The method applied was free and original reports have been made available for all participants.
In 2006 the round robin has been implemented in the Bonnagreement expert group.
As a result both members of the expert group and other labs from all over the world participate in the round robin.

Samples and analysis method
Last week I have send 6 samples to all participants. Please inform me when you didn’t receive the samples in the meantime.
Note: Gerhard has given me today the addresses of Susan Sugarman, Wayne Grunlund, and Krista Mötz. I have send them the samples today.

The samples are indicated with Source 1 , 2 and Spill 3, 4, 5 and 6.
All samples are filtered extracts at a conc. of 100 mg/ml in DCM in order to be able to send all participants the same samples. The samples should be analysed and compared according to CEN/TR 15522-2 published in nov 2006.
We like to ask you to analyse and compare the two source samples with the four spill samples and send in a report by email.

The resulting report should not only consist of a simple yes or no, but also reasons why a decision has been taken. The original reports will be combined in a final report, together with an evaluation of the results.

During the meeting of the expert group of November 2006 in Hamburg the results of RR2006 and the CEN/TR have been discussed.
Together with this letter the minutes of the meeting, the final report of RR2006, and a document, written by Gerhard on request of the meeting, dealing with ratios. The last document is intended to help an analyst to select the correct ratios for each oil type. You will find comments from me in this document. It is still under discussion.
Please feel free to give comments in your report on these documents and the CEN/TR.

Last year we have additionally asked you to enter values and chromatograms into a spreadsheet. In this way it was possible to evaluate the st dev of ratios and to study the differences between labs.
For this year we have the same intentions, but we are still working on the spreadsheet.

So we like to ask you to start the analysis and to write your report. You will receive in about two weeks a spreadsheet file to fill in heights and areas of a series of peaks, that will be used to test a range of ratios.

Time schedule

May:	Delivery of the samples.
before August:	Reports have been returned.
End of August:	Final report will be sent to the participants.
September :	Annual meeting of the Bonn OSInet expert group in Trondheim.

We hope it will be possible for everybody to analyse the samples and make a report within two months, although we know that most of us will have a vacation in that period.

The attachments can be found in the directory:
RR2007\attachments letter 10-5-07

1.2 Letter of 22-5-07

Two weeks later these instructions have been send by email:
Spreadsheet Instructions round robin2007final.doc

Dear colleagues,
as indicated already, RR2007 is conducted in two steps: 1. Intra-laboratory comparison, i.e. compare the spill samples with the source samples by using your normal analytical method and send a report.
2. For the inter-laboratory comparison, we kindly ask you to measure some peaks in the samples you have received and to insert the values into the attached Excel-spreadsheet (please replace the existing values as these were only inserted for testing).
In addition, please fill in your own analytical parameters and the mass-chromatograms, from which the measurements were made into the PowerPoint-file, which is also attached. Here you can find already the analytical parameters used by RIZA and BSH, and the mass-chromatograms of source 1 produced by RIZA, which may be used for finding the right peaks in the samples.
We want to extract as much information as possible from this RR2007, so we ask for heights and areas of peaks, measurements of small peaks and overlapping peaks, and values of summarised areas of isomeric compound patterns.
Please fill in the values into the table “results” of the Excel-file.
One absolute prerequisite of this test is that you fill in the values into this table totally unbiased –just like a skilled organic analytical chemist would do it. We are, of course, aware that an analyst experienced in oil spill identification will come to the right conclusion without comparing compound ratios, as described in NTChem001 and the ASTM-standards. The mere visual comparison of the many compound clusters of oils, described here, has been used successfully over tenth of years.
But your experience in oil spill identification should in no case influence the values you insert into table “results”. We are working on a more “objective” methodology, and thus need unbiased tests.

This does not mean however that you should not have a look into the many other tables of this excel spreadsheet afterwards, where the calculated ratios are present as soon as you have filled in the table “results”.
You will find here that the two source samples are compared with each of the four spill samples (h=height used, a=area used). The calculated differences of the compound ratios are given in form of a table but also in form of a bar-chart, where the repeatability of 14% based on an RSD of 5% is used as a match criterion.
Please interpret the differences here (pronounced by a “flag” or shown by a bar exceeding the 14% line in the graph). These differences may be either “true” differences or they may have been caused by weathering of the spilled oil and/or analytical variations. May be, you even come to a different conclusion, when you look at these results?

Please give us also your opinion about the value of the calculated parameters in connection with their ease of determination (time and efforts needed), and also your opinion about the match criterion itself.
You will find also a PW (Percentage weathering) plot on all pages that shows the relative intensity of each peak after normalization on hopane of the spill sample compared to the source sample, sorted on retention time. Due to RIZA's experience, it helps to assess weathering and homogeneity of samples to be compared (comparable to a PW plot of the GC-FID results). Your opinion?

We are sure that you will like this RR2007, and we are very glad about the great, world-wide interest in this test (see list of addresses, attached). Obviously, we can work now on our program 24 hours a day around the world.

The attachments can be found in the directory:
RR2007\attachments letter 22-5-07

1.3 Email of 12-6-07

On 12-6-07 an additional request dealing with **conclusion definitions** has been send for comment to the participants by email

Dear all,

We would like to ask you to take part in a discussion about the presentation of the final result/conclusion of an oil case.
You will find a letter with instructions and 9 annexes showing idea's, experiences and suggestions of some of our colleagues.

The attachment can be found in the directory:
RR2007\attachment email 12-6-07

1.4 Letter of 16-8-07

To inform the participants on the status of the Round Robin and to give information about the meeting in Trondheim the letter **Deadline and workshop RR2007v3.doc** was send on 16-08-2007 by email together with an improved spreadsheet template.
The letter and the template including an area/height table can be found in the directory:
RR2007\attachment email 15-8-07

1.5 Sample preparation

In RR2004 three gas oil samples from a real case were used. The "solution" to this case was not known, which was regarded as a disadvantage by some of the participants.
This year bunker oil (HFO) from the Tricolor case was used and to be able to know some of the answers, two of the spill samples were artificially prepared from one of the source samples.

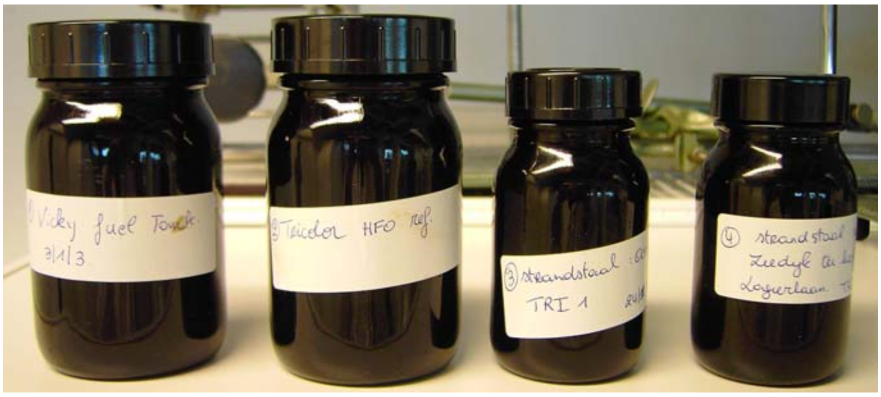


Fig 1 HFO samples used for the round robin and selected by Marijke Neyts and Patrick Roose (BMM).

Source sample 1 is from one of the tanks of the Vicky and Source sample 2 from one of the tanks of the Tricolor. More information about the Tricolor incident can be found in the directory of **BE_MUMM_Roose** (Kerkhof et al). Information about removing the Tricolor from the bottom of the sea can be found on http://www.tricolorsalvage.com/

Two samples from different places on the beach were used as Spill samples:
Spill 3: Waterborne oil taken between the sandbanks Buitenratel and Oostdijk(at the height of De Panne) 24/01/2003, expected to have come from the Tricolor.
Spill 4: Oil from the beach (at the height of Middelkerke; L. Logierlaan) 05/02/2003, expected to have come from the Tricolor.

Whether the spill samples originate from one of the tanks of the Tricolor, Vicky or another ship is unknown.
To create two spill samples from a known source, Source sample 1 has been artificially weathered at two levels.
Two glass Petri dishes, containing about 4 g of Source I each, stayed in a ventilated oven (Heraeus UT12) for 2 hours at a temperature of 120°C. After removing the Petri dish of Spill sample 5 the other dish stayed in the oven at 150°C for another 2 hours to create Spill sample 6 The remaining oil of each dish (about 3 gram was left on the dish of Spill 6) was dissolved in dichloromethane and filtered over a glass fibre filter to remove small particles visible and, to be sure, dried with Na_2SO_4.

The resulting "case" contains two "known" spill samples that are artificially weathered in a short time by means of evaporation and at temperatures that are quite unrealistic for "normal" spill samples, although thin layers of oil in the sun can also lose low boiling compounds very fast.
It will be interesting to see whether this "high temperature" treatment has effect on the more stable compounds used for oil spill identification.

Note
Per Daling (Sintef) indicated at the workshop that he has heated bunker oil up to 500°C and didn't see changes of the composition of the oil sample.

1.6 Results

Results from 19 labs were returned and could be evaluated. 2 participants apologized for not being able to conduct the analyses in time due to unexpected bigger problems in their labs.

RR2007 suffered from obvious (human) errors. Much time was spent by contacting most of the participants individually and asking them for checking their data again (up to 4 times in one case).
This is not common practice in comparable intercalibration rounds, which are, for example, conducted between labs involved in environmental monitoring. But several labs just started in oil spill identification and/or did not conduct proper quality management.

In addition, errors were a little bit provocated as overall 432 values form the six samples had to be measured and to be inserted into an excel table. The often used Chemstation-software, for example does not include both areas and heights of peaks in integration-tables, and inserting all values individually by hand required several hours of hard and concentrated working. On the other hand, the technique of "copy and paste" did not require less attendance (especially, when groups of peaks were taken, because the compounds in the integration tables were not sorted in the same order as the compounds in the excel table "results", which had to be filled).

But RR2007 must be seen in the light of the discussion about a common methodology, and the revision of the CEN Technical Report as decided at the Bonn_OSINET06-meeting in Hamburg.
Fortunately, such bigger efforts (e.g. the determination of both heights and areas of peaks) are not needed in an actual case.

From former discussions and the meeting in Hamburg questions arose about:

- the use of an additional table for oil type dependent ratios
- the use of a PW plot for GCMS results.
- the use of combined ratios
- conclusion definitions
- ratio dependency of column phase and column lengths
- the use of height or area for the calculation of peak ratios (with the use of ratios in interlaboratory databases in mind)

- the prescription of analytical parameters, including column length, phase, temperature program, carrier flow etc. (with the use of the ratios in interlaboratory databases in mind)
- the use of ratio's from different masses.
- the use of summary integration of groups of PAH's.
- an additional chapter about the use of multivariate techniques in oil spill identification (PCA, COSI).
- the use of quantitative analysis.

Answers were thus expected partly by comparing the produced data, partly by comments/opinions of the participants -in addition to general suggestions for a common methodology, which could be expected from the individual practices of the many participants.

1.7 Final report

All results (report, spreadsheet file and powerpoint file) were received by email. The information of the individual participants is summarized and commented in chapter 2.

The reports will not be discussed in great detail with the intention that all individual reports are available and all participants can compare their own method with others.

The interlaboratory results are discussed in chapter 3.
The area/height results of the spreadsheet files are used to take decisions to come to a common method for the Bonn agreement contracting parties. The power point files contain chromatograms including integration lines and are used to check performance and integration.

A concept report has been send to all participants before the annual Bonn-OSINET workshop in Trondheim Norway on 7-9-November 2007. The concept report has been used as guidance for the workshop.

The final report including the individual results and additional information, has been published in the Bonn-OSINET section of the Bonnagreement website after the workshop, to be able to incorporate the findings of this meeting.

Gerhard and Paul

2. Individual results

In this chapter a summary of the results of each participant will be given. The participants are listed based on country code followed by the abbreviation of the institute. All original results, separated in directories and indicated in the same way, can be downloaded from http://www.bonnagreement.org/.

Each participant is introduced shortly and the method(s) used to analyze the samples are summarized. The conclusion is an exact copy of the conclusion found in the original report.
Maria Plaza (ES-CEDEX) has generated PCA plots from the ratios of the participants. The pdf file **MultivariateStatistic.pdf** shows all results and can be found in the directory of ES-CEDEX. Copies of the results for each participant have been added to this chapter and the use of multivariate statistics is discussed in section 3.6.

Finally for most of the participants additional notes/remarks can be found.

For result evaluation, especially the tables in the Excel-spreadsheet behind the table “results” were used. Those tables were automatically filled as soon as the values were inserted into the table “results”. Here the ratios were produced from the original height- and area measurements, and compared between the source - and the spill samples. The red “flags”, the diagrams showing the relative differences of the ratios and the “weathering plots” gave a rapid overview of the measured data. The consistency of observed peculiarities with the original mass-chromatograms and the analytical parameters was checked.

Although these tables are primarily used for testing (use of height or area, small peaks etc.), of course also peculiarities of the individual analytical practices became obvious.
But corresponding notes/remarks should in no case be regarded as bad criticism, but rather as a contribution to a discussion. Participants are invited to further take part in this discussion, and help to improve the final version of this report.

The results are evaluated especially with regard to the comparison of samples 1, 5 , 6 and samples 2 and 4, by taking into account that:
- samples 1, 5 and 6 contained the same oil
- samples 2 and 4 definitely show differences (Are these differences recognized, and if so, how are these differences explained?)

2.1 AU_EC_CES

Contact:
Syed Hasnain and Ivo Tence
Environmental Chemistry_Center for Environmental Sciences
EPA Victoria
Ernest Jones Drive, Macleod VIC 3085, Melbourne
AUSTRALIA

Organization

Environment Protection Authority Victoria's http://www.epa.vic.gov.au/ is a governamental organization with the purpose is to protect, care for and improve the Australian environment.

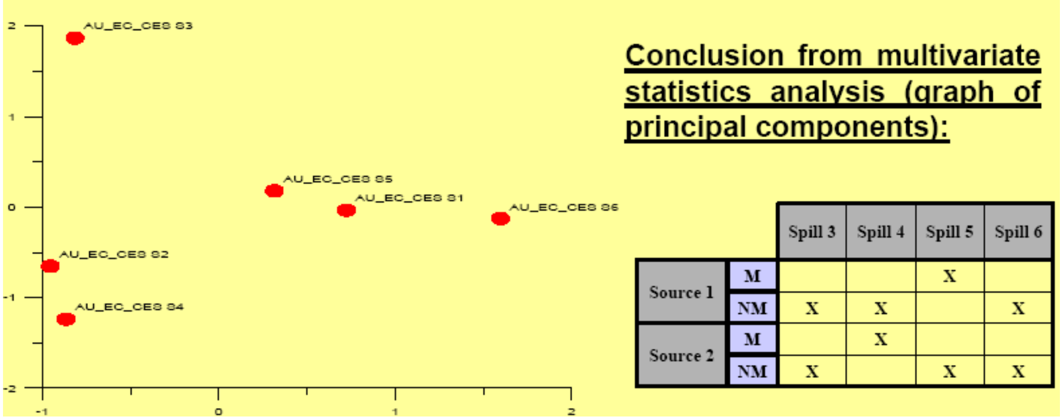
Sample handling

The samples have been diluted to 10 mg/ml and were analyzed with GC-FID and GC-MS. Powerpoint files of both the GC-FID and GC-MS files were send with the report.

Original Conclusions

Sample number	Source 1	Source 2
Source 1	---	Non Match
Source 2	Non Match	---
Spill 3	Non Match	Non Match
Spill 4	Non Match	Non Match
Spill 5	Match	Non Match
Spill 6	Probable Match	Non Match

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	
	NM	X	X		X
Source 2	M		X		
	NM	X		X	X

NOTE
PCA plot of the ratios delivered by AU_EC_CES and calculated by Maria Plaza of ES-CEDEX.

Comments/Remarks

A correct match is found between samples 1, 5 and 6.
All conclusions are comprehensibly explained.

The report firstly describes the samples individually and then each source sample is compared with each spill sample in detail. Ratio's have been calculated from the larger peaks. Smaller ones like

C28(22R+S), C28(22R+S), C29ba and C30g were only used for visual comparison.

Syed's PW-plots of the matching samples, which can be found in the spreadsheet file **AU_EC_CES_RR 2007v5.xls** on the sheets **1_5h, 1_6h, 1_5a (see Fig 2) , 1_6a** show a peculiarity:

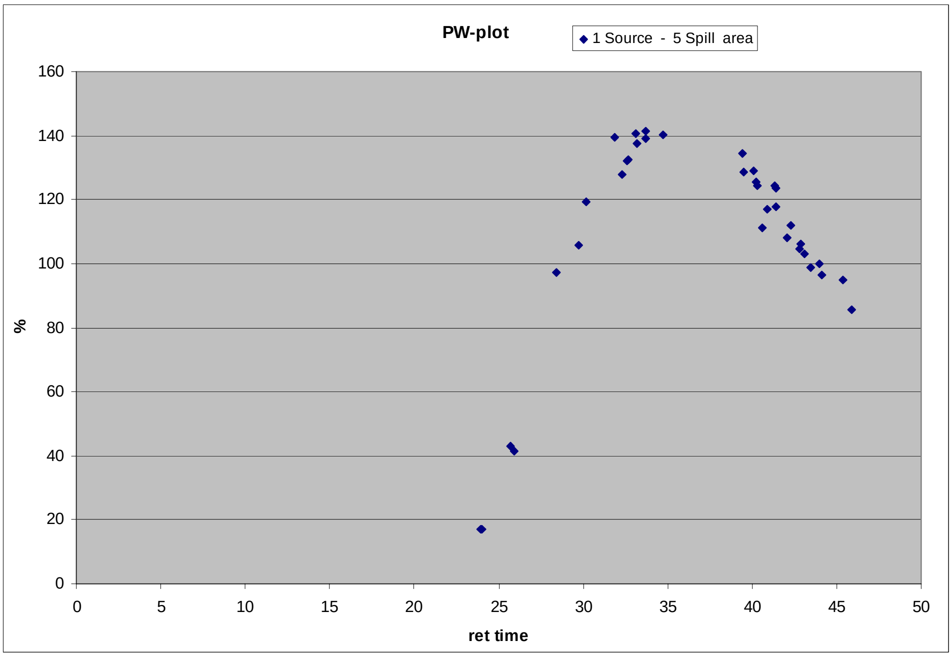


Fig 2
Pw-plot of EPA Victoria for the comparison of Source 1 with Spill 5 based on area.

For an explanation of the PW-plot see section 3.4.

Normally the non-weathered compounds in spill sample 5 should have the same height/area as the same compounds in the source sample 1. But in Fig 2 the concentration of the biomarkers varies from 85 to 140% in a steady line indicating that the values of the first eluting biomarkers in the spill sample are elevated compared to the biomarkers of the source sample. No explanation for this strange behavior could be found.
The final temperature of 290°C, which is the lowest value for all participants, is reached two minutes before the elution of hopane 30ab. It could be possible that the higher boiling compounds in the samples remain on the column thus influencing the next analyzes.

In an email discussion Ivo Tence indicated:

1.Treatement
We do not do any pretreatment of extracts and do not fractionate into fractions. We normally prepare extracts of oils in hexane in order to precipitate asphaltenes and then inject approximatley 10000 mg/L solution as per ASTM method. As your samples came in dichloromethane we would not have done asphaltene precipitation. Syed only diluted them to 10000 mg/L.

2.Sensitivity

I observed a gradual decrease in abundance of 191 ion to about 35% response (comparing sample 1 to sample 5 duplicate) over a 20 hour period during the GC sequence . I did not see any large changes in retention time and conclude that there was no leak in GC system. Due to a GC/computer malfunction I could not compare a QC oil sample at end of sequence.
A PAH QC sample run about same time as sample 5, showed a 40% reduction in area response for late eluting benzoperylene peak and a 3% reduction for middle eluting fluoranthene peak when compared to start.

For a further discussion of the pretreatment of samples see section 3.5

Conclusion:
The PW-plot works only well when the analytical system is stable during the series. A good method to be aware of the stability of the system is to analyze a standard (e.g. Brent) before and after the samples and to compare them before starting to evaluate the samples

2.2 AU_NSWDECC

Contact:
Steve Fuller
NSW Dept. Environment and Conservation
Dock 1 Weeroona Road
Lidcombe NSW 1825 Australia

Organization

The Department of Environment and Climate Change www.environment.nsw.gov.au is a new agency formed on 27 April 2007. With the change, the former Department of Environment and Conservation is taking on new and renamed programs to build a broader organisation able to respond to the unprecedented challenge presented by climate change. The new department brings together a range of conservation and natural resources science and programs, including native vegetation, biodiversity and environmental water recovery to provide an integrated approach to natural resource management.

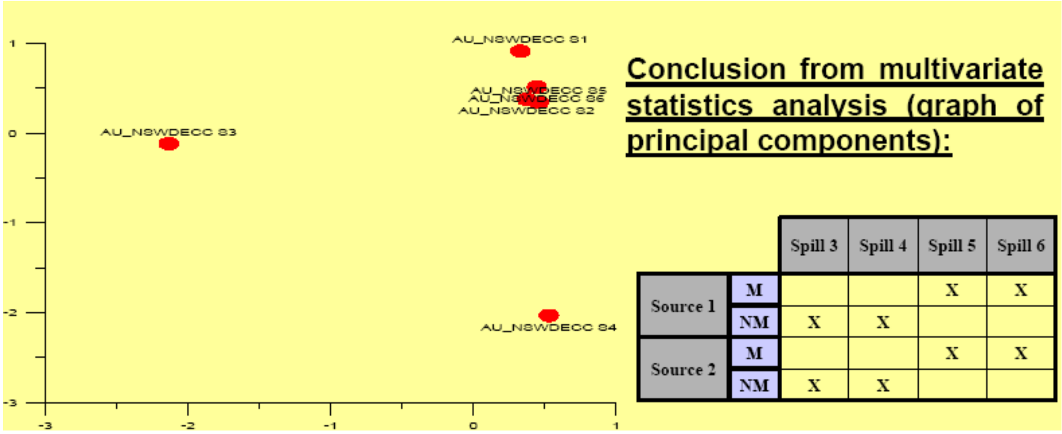
Sample handling

Due to the nature of the supplied samples and sample volume, the full suite of testing procedures was not able to be employed. All samples were analysed by GC/MS using direct dilution with DCM as the only sample preparation. Additional analysis procedures such as metals analysis and stable isotope analysis were not performed. Samples were analysed by in-house method OMSOFP1. An aliquot of each of the oils was carefully dried under nitrogen and reconstituted with cyclohexane for screening by fluorescence spectrophotometry.
The oils were screened by a Saturn 2000 GC/MS for examination of the hydrocarbon profiles. PAHs and DBTs analysis was carried out by a Saturn 2000 ion trap in SIS mode and biomarkers were determined using an Agilent 6890/5973 MSD.

Original Conclusions

Source 1 (200700856) was found to be a PROBABLE MATCH with Spill 5 (200700860).
Spill samples 3, 4 and 6 were found to be a NON MATCH with Source 1.
All spill samples were found to be a NON MATCH with Source 2.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M			X	X
	NM	X	X		

Comments/Remarks

Steve indicates that his method is under development:

Our laboratory does not have formal responsibilities for analysis of marine oil spills – our main focus is on refined products, particularly light fuel oils. The in-house fingerprinting method does not utilise biomarkers to the extent of the CEN methodology. For this exercise we have attempted to identify as many biomarker components are possible, using the SINTEF 0436 reference sample as a guide.

We are keen to expand our methods to better deal with crude oils and heavy fuel oils.

His report shows results of a fluorescence analysis with an evaluation by means of PCA. The results show differences between all samples except for the four replicates of Source 1. The method is fast and looks good, but has probably problems with weathered samples.

The oil proficiency report RR2007 is based on the analyses of the samples on different instruments as explained by Steve:

The screening method (including alkane hydrocarbon measurements) is done on an ion trap with a DB-1 column. No FID analysis is employed.

The routine analysis method for PAHs and DBT is on the same ion trap with a DB-1 column. The biomarker work was performed on an Agilent 6890/5973 equipped with a DB-5 MS column. This was necessary in order to be able to compare data with the SINTEF reference oil.

The analysis on different instruments can have effect on the PW plots, because the area's are normalized on the area's of hopane 30ab. The effect is visual in the PW-plots of e.g. the samples So1-Sp5 (Fig 3), where all compounds are normalized on hopane (bigger scattering of the points).

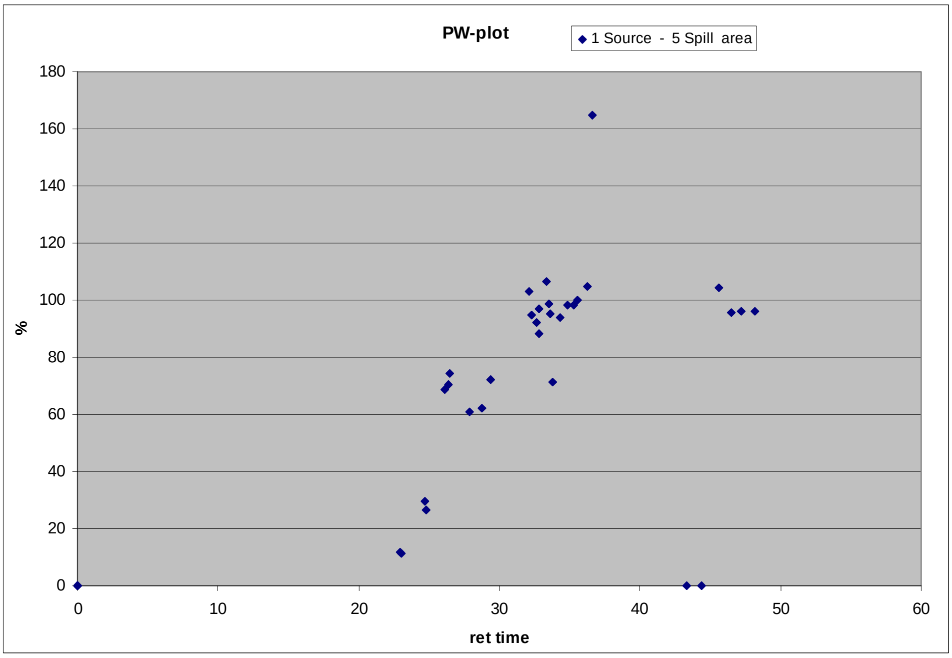


Fig 3
PW-plot of matching samples analyzed on different instruments

Steve Fuller has made an additional document **AU_NSWDECC_rr2007 CEN method results.doc** dealing with the CEN method available in the directory of AU_NSWDECC.

Based on this document we have had an email discussion:

Paul:

You have made an additional document about the validity of the ratios.

I think that you mean that one of the peaks in the ratio is difficult to reliably integrate, due to baseline variance, co-eluting or distorted peaks.

You mention different ratios for the different comparisons, based on the flag criterion.

I'm surprised that you even mention ratios like Ts/30ab and Tm/30ab (eg 1vs3 area)

In 1vs5 Ts and Tm are not mentioned so the problem must be that Spill 3 is very different from Source 1.

It is difficult to say something about distorted peaks. The distortion may come from a compound present in the oil or from a contamination. Eg the peak before Ts visible in eg So1 and 2 is a compound present in the oils of the Tricolor and the Prestige, but it reduces in concentration relative to 30ab when the oil is released on water.

Most of the time however the distortion is from a compound present in the oil and therefore typical for the oil.

In the CEN_TR we intend that you select those peaks that can be integrated reliable based on duplicate analyses and S/N ratios. The comparison is done to test whether both samples have the same source. If they do not have the same source, patterns are different and then it is difficult to integrate in the same way.

Steve:

The additional document you refer to, was provided as feedback on the ratios we had difficulty determining due to our instrument sensitivity, or peak interferences/distortions. Your comments on the use of distorted peaks are noted. Our laboratory policy presently only uses fully separated peaks for single peak ratios. This may be a good topic for further discussion.

Note

During the workshop the subject of distorted peaks was mentioned but didn't lead to a discussion.

2.3 BE_MUMM

Contact:
Patrick Roose
BMM-Meetdienst
3e & 23e Linieregimentsplein
B-8400 Oostende
Belgium

Organization

The institute uses three abbreviations depending on the language. See http://www.mumm.ac.be/
In English: The Management Unit of the North Sea Mathematical Models and the Scheldt estuary, abbreviated to MUMM, is a department of the Royal Belgian Institute of Natural Sciences (RBINS), a federal scientific establishment that comes under the Federal Science Policy (previously known as OSTC).

Sample handling and Original Conclusions

No report was received:
Patrick informed us that 3 of his 6 colleagues are at home due to pregnancy.
Accidentally, all 6 samples were injected undiluted at a concentration of 100 mg/ml and and an injection volume of 3 ul without the cleanup, that is normally performed on black colored samples like HFO.
Patrick indicated that a conclusion based on these analyses is not possible and that the samples will be re-analyses after cleanup –and after cleaning of the instrument.
This was however not possible before the workshop.

We have asked Patrick for the chromatograms of the series without cleanup to show the effect. These chromatograms can be found in the directory **BE_MUMM_Roose/analysis without cleanup**

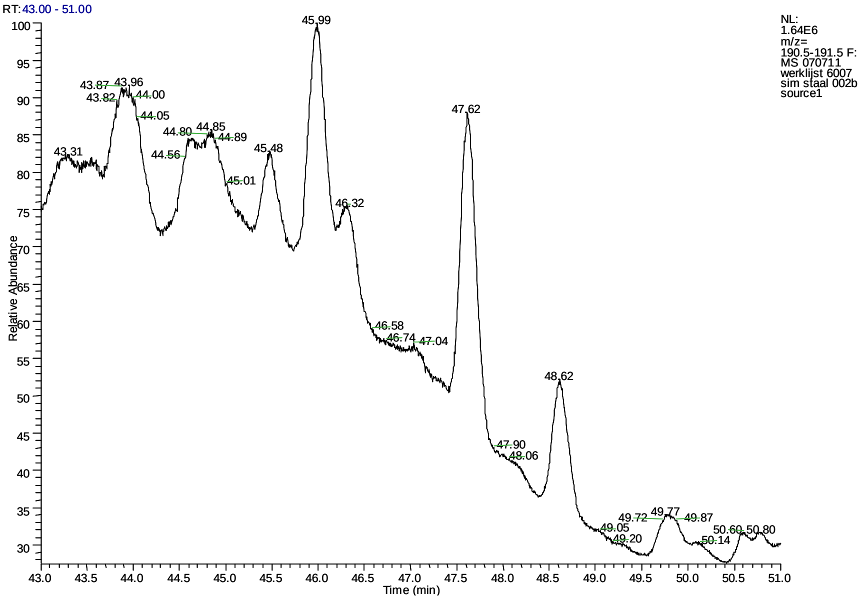


Fig 4
For deterrence, a very bad looking mass-chromatogram is given (Source 1 m/z 191, hopanes)

2.4 BR_Petrobas

Contacts:
Fabiana Galotta and Maria de Fatima Guadalupe Meniconi
Environmental Assessment & Monitoring Division
Research and Development Center - CENPES
PETROBRAS S.A.
Av. Um, Quadra 7, Cidade Universitaria - Ilha do Fundão
Rio de Janeiro - R.J. - BRAZIL
ZIP: 21949-900

Organization

The founding of Petrobras www2.petrobras.com.br/ingles/index.asp was authorized in October 1953, by Law 2004, with the objective of executing, on behalf of the Federal Government, the activities of the oil sector in Brazil.

The Environmental Assessment & Monitoring Department and the Geochemistry Division from PETROBRAS Research and Development Center (CENPES), carry out environmental analyses from all around Brazil, giving support to the Company in forensic litigations issues. This Division analyzed the samples from the RIZA Round Robin Oil Spill Identification.

Sample handling

Aliquots of the samples Source 1, Source 2, Spill 3, Spill 4, Spill 5 and Spill 6 (400 µL each) were submitted for fractioning in silica gel/alumina column. Samples were fractioned into aliphatic and aromatic fractions. The aliphatic fraction was analyzed for determination of saturated biomarkers like hopanes by GC-MS. The aromatic fraction was analysed by GC-MS for determination of polycyclic aromatic hydrocarbons (PAH) and aromatic biomarkers like triaromatic steranes.

The methodology used for **PAH** determination followed EPA-8270D method with some modifications. Quantification of the samples was not performed. All diagnostic ratios were calculated based on area counts.

Analyses for **Biomarkers** were carried out using the same equipment and instrument conditions. Data were acquired in full scan mode.

Our cleanup procedure is described as following:

Sílica/Alumina Column Chromatography

A gravity-flow silica/alumina column is used for removing undesirable polar compounds from the sample.

A silica/alumina column is prepared by adding a small plug of glass wool to a chromatography column (30 cm length with 1.3 cm of internal diameter) and tamping it down with a glass rod. Then it was added 11 g of activated silica (160°C) and followed by 1 g of deactivated alumina (2% with water by mass).

A labeled 250-mL bottle is placed under the column. The sample extract (1 mL) is slowly added into the column, followed by 55 mL of hexane in order to obtain the F1 fraction containing the aliphatic hydrocarbons.

After this, another labeled 250-mL bottle is placed under the column and 50 mL of hexane:dichloromethane (1:1) solution is added into the column. This is the F2 fraction, containing the aromatic hydrocarbons (PAH).

F1 fraction is then concentrated in rotary evaporation and under gentile N2 flux until 1 mL. F2 fraction is then concentrated in rotary evaporation and under gentile N2 flux until 2 mL.

Original Conclusions

	Spill 3	Spill 4	Spill 5	Spill 6
Source 1	non match	non match	positive match	positive match
Source 2	non match	probable match	non match	non match

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X	X				
+3								
+2						X		
+1								
0								
-1								
-2								
-3								
-4	X	X			X		X	X

Comments/Remarks

A correct match is found between samples 1, 5 and 6.
In her report, Fabiana clearly works out the differences between sample 2 and spill 4:

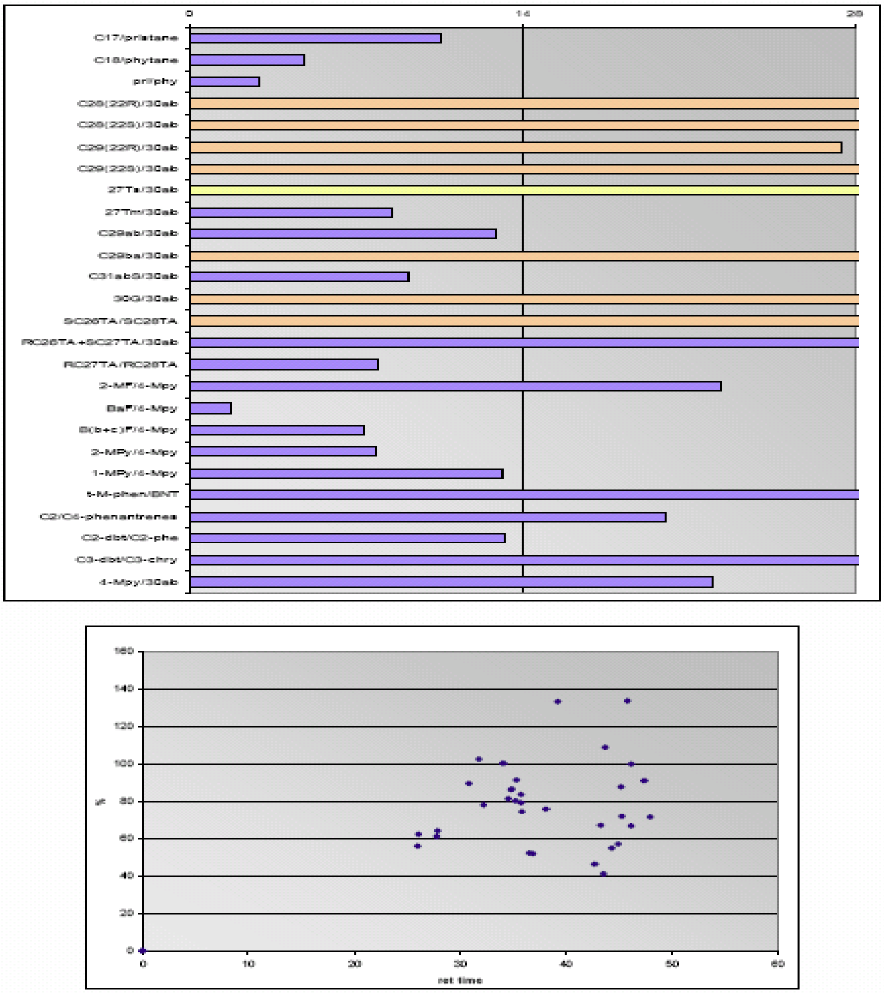


Figure 7 - Spill 4 vs. Source 2 - Diagnostic Ratios Comparison and PW-Plot

Fig 5
Ratio table and PW plot of 2-4a of BR_Petrobas

But she does not explain how she came to the conclusion of a probable match between samples 2 and 4 at level +2 despite those differences, except that:

"Some diagnostic ratios were not considered for comparison test because of the following reasons: (i) peaks of compounds involved presented a signal to noise ratio < 5 (orange bars) or (ii) these peaks were influenced by weathering (yellow bars)."

Low sensitivity and much noise in her mass-chromatograms was detected, which led to an e-mail discussion:

Paul:
I am not sure whether it is possible to analyse biomarkers with an ion trap. All other participants use a quadrupole instrument for the biomarkers. Some years ago we received a report of LASEM (Fr). They also used then an ion trap and had the same problems.

An ion trap regulates the number of ions that are allowed to enter the trap to prevent chemical ionization and bad mass resolution. When analyzing low concentration of compounds in a bulk of other compounds, the entrance to the

trap will be reduced and the compounds with a low concentration will be barely or not visible. This may be more relevant for bunker oil compared to crude oil.
I don't know whether this applies for you because you first separate the samples in two fractions.
It would be interesting to know whether you had good sensitivity before in analyzing bunker oil samples on the ion trap

Fabiana:
I understand your concern about the entrance of low concentration compounds into the trap. We do not think that is our problem. After our cleanup procedure, we do not have a bulk of other compounds anymore. We run saturated fraction and aromatic fraction separately. Before April the instrument had reached 0,002 µg/mL (1µL splitless) for PAH. We are used to analyse PAH with ion trap. Besides, a colleague, who works with ion trap as well, has been analysing biomarkers without trouble.

At the workshop Fabiana indicated that she prefers to use full scan spectra instead of SIM chromatograms for comparison. She misses information when following the CEN guideline.
Susan Sugarman of US_OSPR mentioned the same in her report.
The discussion did not lead to a conclusion that the CEN/TR method should be changed.

2.5 CA_EC_ALET

Contact:
René Losier
Environment Canada
Environmental Science Centre
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Moncton N.B., E1A 3E9

Organization

Environment Canada's mandate is to preserve and enhance the quality of the natural environment; conserve Canada's renewable resources; conserve and protect Canada's water resources; forecast weather and environmental change; enforce rules relating to boundary waters; and coordinate environmental policies and programs for the federal government.

The Department employs about 6000 people and has an annual budget of over half a billion dollars. Approximately 60 percent of its workforce and 80 percent of its budget is devoted to science and technology activities.

Environment Canada's national headquarters are located in Gatineau, Quebec. It has offices in some 100 communities across the country.

The Environmental Science Center is a part of the Atlantic region of Environmental Canada. No specific website for ESC could be found.

Sample handling

Samples were prepared by solvent exchange to hexane for initial Gas Chromatography (GC)-Flame Ionization Detection (FID) analysis to establish the oil type(s) and to determine if the samples were sufficiently similar to require further analysis.

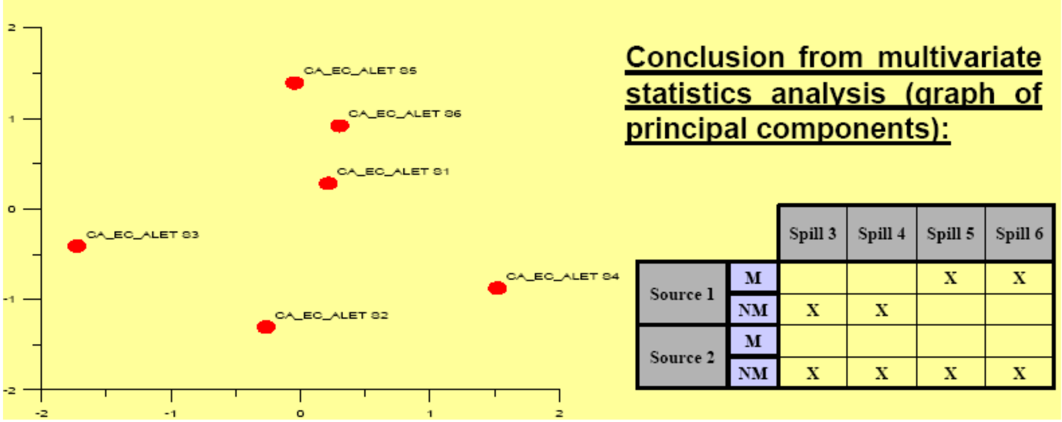
Samples that require further comparison, were prepared for GC-FID analysis, then centrifuged to remove asphaltenes and separated into aliphatic (F1) and aromatic (F2) fractions on a silica gel column as per Wang et al(4; no reference provided). The two fractions were subsequently analyzed by Gas Chromatography-Mass Spectrometry. The GC-MS analysis allows the oil samples to be separated into their constituent parts.

Original Conclusions

In summary, spill #3 is no match to source #1 and source #2. Spill #4 is no match to source #1 but the comparison is inconclusive with source #2. Spill #5 and #6 are a match to source #1 but are no match to source #2

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3								
+2			X	X				
+1								
0								
-1						X		
-2								
-3	X	X			X		X	X
-4								

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M				
	NM	X	X	X	X

Comments/Remarks

A correct match is found between samples 1, 5 and 6.
All conclusions are comprehensibly explained.
It would be interesting to know why René didn't use the extreme values of the SKL table but stays in the range of +2 to –3.

A discrepancy was found in the mass-chromatograms of samples 1, 5 and 6:

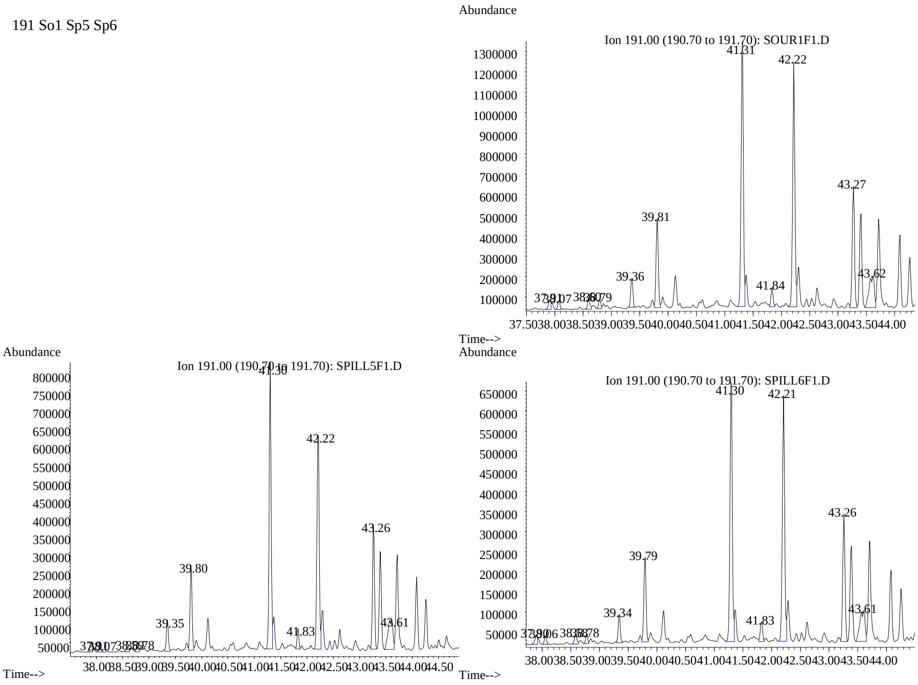


Fig 6
m/z 191 ion chromatograms of So1 and Sp 5 and 6 of Ca_EC_ALET

Part of an email discussion with René

Paul
ppt file: You conclude a match between So1 and Sp5 and Sp 6.
When looking at a first glance to the m/z 191 ion chromatograms Sp5 looks different caused by the peaks 29ab and 30ab(See attachment).
The difference is reflected in the height values but not in the area values you reported.
It might be related to the scan speed. I compared our methods:
You use a dwell of 100 for 7 m/z values (700). In my method I use a dwell of 30 for 11 m/z values (330) and Gerhard a dwell of 50 for 8 m/z values (400).

Rene
Answers to question you have for us in the report and question that we have.

1)Why we did not use +4 and -4?
We did not use +4 because the sample that were matching were weathered and for those one who were not a match we did not used -4 since they were the same type of fuel. So we agreed with you that the probability table needs more guidance to come to a more equal conclusion.

2)As for the discrepancy found in mass-chromatograms of samples 1, 5, and 6, we will try your suggestion about the dwell time, the method was developed on a old instrument, and when we transferred to the 5973 from Agilent, we never changed the dwell time.

3)We notice in section 3.1, that you are able to differentiate between crude and heavy fuel oils

Quote "As most heavy fuel oils are residues of a cracking process in the refinery, the patterns of the methyl-phenanthrenes are different compared to crude oils. Additionally the presence of methyl-anthracene and the absence of retene are indications for HFO."
Is this the only indication you are using to differentiate between the two? We were not able to differentiate between the two when they were weathered.
So, we look at old crude and HFO sample we had, and it is simple to differentiate between the two now when you use the differences in the methyl-phenanthrenes patterns.

Also, do you have a way to differenciate between bilge oil and other type of fuel? Sometime we are able to said it is probably a bilge by using characteristic of the profile, but never with certainty.

4)We do agreed with you in section 3.5 that we should cleanup HFO because of the deterioration of the column. That a reason why we fractionate the samples.

Paul
ad 3
Methyl-anthracene and the absence of retene are the most suitable indicators.

A bilge is a mixture of gas oil and lubrication oil. Typical for lubricating oil is the absence of the aromatic steranes.
As gas oil almost doesn't contain aromatic steranes it is a very good indication whether it is a pure gas oil or a mixture with some lub oil.

ad 4
In the guideline it is advised to clean these type of samples.
At the meeting we concluded that it must be more stringent.
A working group has been established to check the text in the guideline because we think that the use of only hexane will give a problem. Attention will also be given on fractionation.

2.6 CA_ESTD

Contact:
Chun Yang,
Emergencies Science and Technology Division
Environmental Technology Centre
Science and Technology Branch Environment Canada
335 River Road Ottawa, ON K1A 0H3

Organization

The Environmental Technology Centre (ETC) http://www.etc-cte.ec.gc.ca provides specialized scientific support and undertakes research and development for Environmental Protection programs. The Centre focuses on four main areas: technologies for measuring air pollutants in ambient air and from mobile and stationary sources; analysis of a wide variety of organic and inorganic compounds in diverse samples; assessments and clean-up of contaminated sites; and prevention of and response to pollution emergencies such as oil and chemical spills.

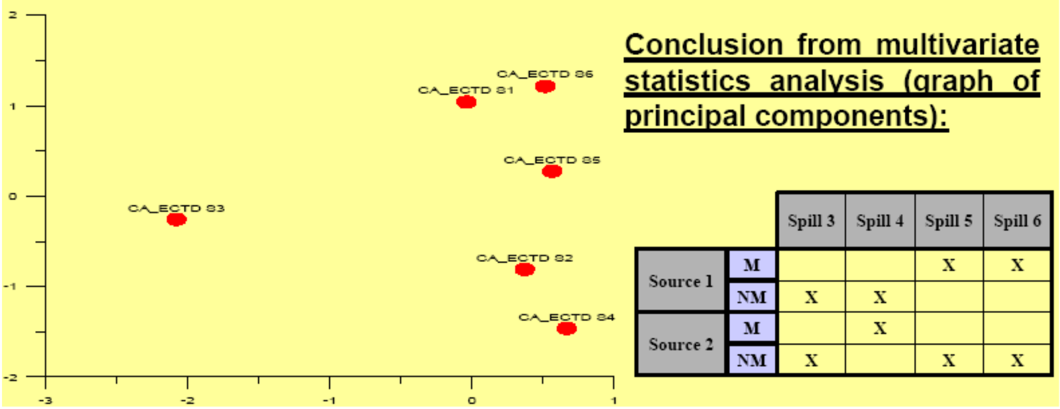
Sample handling

100 µL of each sample solution, spiked with 100 µL of internal standard solution (20 µg/mL of 5a-androstane, 10 µg/mL of d14-terphenyl, and 10 µg/mL of ßß-hopane), and then add n-hexane to made up to 1.0 mL for direct GC/MS analysis.

Original Conclusions

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3			X			X		
+2				X				
+1								
0								
-1								
-2								
-3					X			
-4	X	X					X	X

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks
A correct match is found between samples 1, 5 and 6.
All conclusions are explained in detail.
Chun Yang evaluates the results in steps by first a visual comparison of the chromatograms based on four groups:

1) Comparison of TPH
2) Comparison of PAHs
3) Comparison of biomarker terpanes m/z 191
4) Comparison of m/z 216, m/z 231 and m/z 234
For each group conclusions are described.

Finally 30 diagnostic ratios were calculated from the height and area of target compounds at selected ions 85, 191, 218, 231, 216, 234, 206, 226 and 270.
As the abundance of C28(22R), C28(22S), C29(22R), C29(22R), C29ba, C30G, B(b+c)F, and SC26TA in almost all samples are very low to obtain accurate data, eight ratios relevant to these compounds should not be considered as diagnostic criteria.

Chun finds a level +2 match between source 1 and spill 6. But his data even show a match between these samples more clearly:

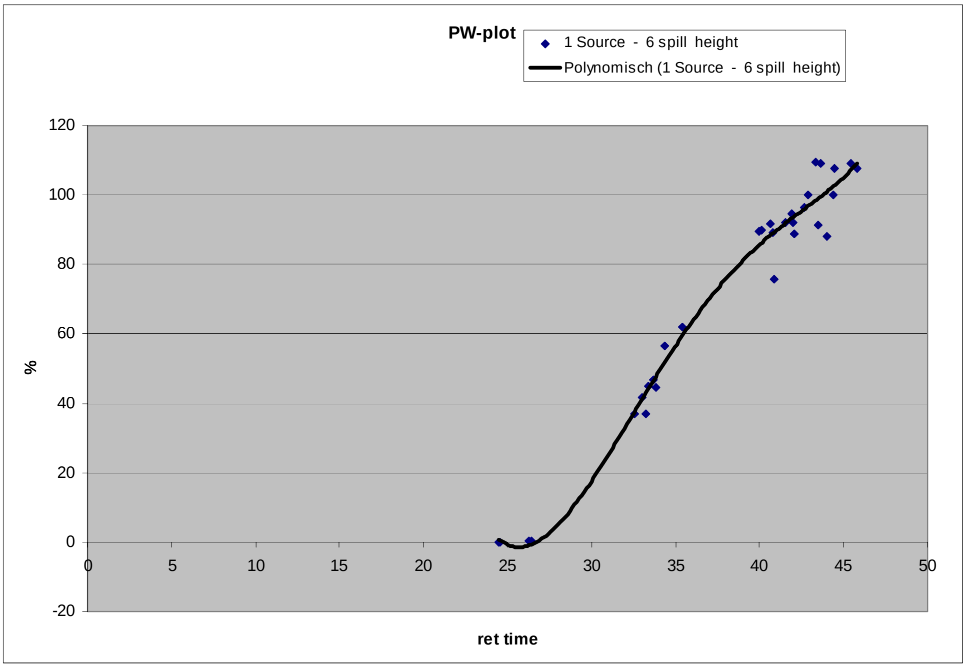


Fig 7
PW-plot of CA_ESTD:
Source 1 and Spill 6 based on height

An S-shaped curve is clearly visible, and only one or two ratios (calculated from very small peaks, such as the triterpenes) seem to be a little bit more outside that curve, if at all. Thus, the reproducibility of Chun's data is very good, and the best-fit curve (simply produced here by means of Excel) must be regarded as a proof that all the differences in the ratios between source 1 and spill 6 are caused by evaporation of compounds in spill 6.

On the other hand, and having in mind this very good reproducibility, the comparison between samples 2 and 4 shows only a cloud of points, and a best-fit curve cannot be found:

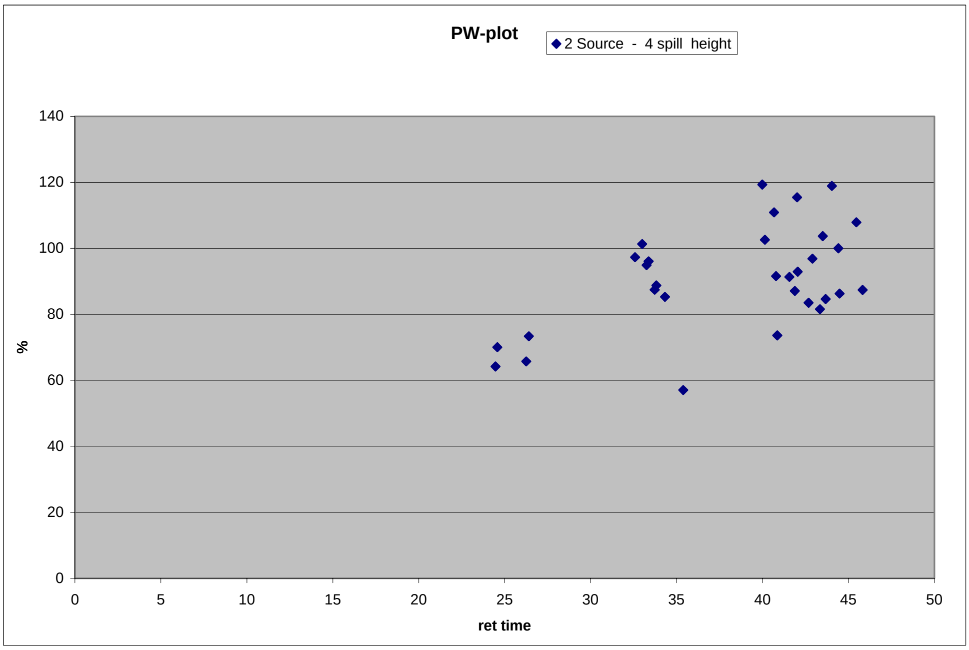


Fig 8
PW-plot of CA_ESTD:
Source 2 and Spill 4 based on height

Thus, the measured differences in the ratios between samples 2 and 4 are “true” differences, which cannot be caused by weathering of compounds in spill 4 (weathering of spill 4 was even not an issue as this sample still contained high amounts of very low boiling compounds).

2.7 CA_PESC_EC

Contact:
Dayue Shang
Pacific Environmental Science Centre
N. Vancouver, BC, V7H 1B1
Canada

Organization
The Pacific Environmental Science Centre (PESC) is Environment Canada's premier science centre in Western Canada. Its state-of-the-art facilities are being used to test the quality of water, soil, sediments and biota, and to administer cooperative research and sampling programs for its users.

PESC provides the core laboratory and field operations capability required to sustain the Department's regional programs in ecosystem science, environmental protection, emergency response, shellfish water quality and environmental quality monitoring.

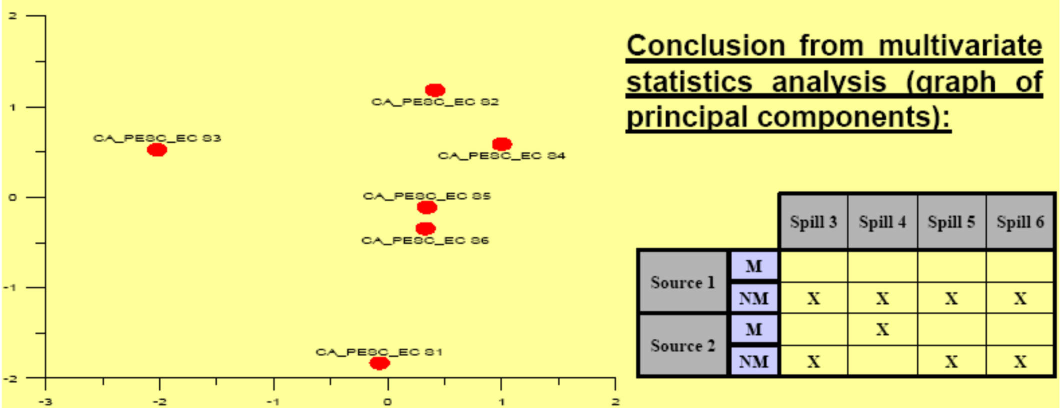
The Environmental Science Center is a part of the Pacific region of Environmental Canada. No specific website for PESC could be found.

Sample handling
All samples were classified as either heavy crude or bunker oil.
Following the oil type identification, all samples were separated into aliphatic (F1) and aromatic (F2) fractions on a silica gel column. The two fractions were subsequently analyzed by GC/MS. In other words, each sample was analyzed twice, first for F1 and then F2, each with a specific method. Data were processed according to our SOP.
Note: ion signal 216 and 234 was not required in our SOP and thus not collected.

Original Conclusions

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3								
+2			X	X				
+1						X		
0								
-1								
-2								
-3	X	X			X		X	X
-4								

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M				
	NM	X	X	X	X
Source 2	M		X		
	NM	X		X	X

Comments/Remarks
A correct match is found between samples 1, 5 and 6 but with relatively low certainty.
The report is very short and does not describe the evaluation of the analytical results.

Part of an email discussion with Dayue Shang:

Paul
I see that you separate the samples into two fractions and analyze them separately.
In the CEN guideline a DCM extract is analyzed directly or after a cleanup on silica with GCFID and GCMS.
Do you see advantages for oil spill identification in using your method compared to the CEN guideline ?

Dayue Shang
To answer your question to our method with two fractions and two injections, I was following an established Environment Canada SOP which specifies that two fractions should be collected after a silica column clean up and fractioning, and each fraction is injected once with different GC/MS programs. Fraction No. 1 contains most saturated compounds and fraction No. 2 the aromatics. From my limited experience in this area and a quick comparison study, I did find that the two fraction approach provided cleaner pre-injection samples and consistent results. The disadvantage is obvious: more sample preparation steps and instrument time.

2.8 CN_NCSEMC

Contact:s
Zhou Qing and Sun Peiyan
The North China Sea Environmental Monitoring Center of State Oceanic Administration
Fushun Road 22, Qingdao ,China,
Postcode:266033

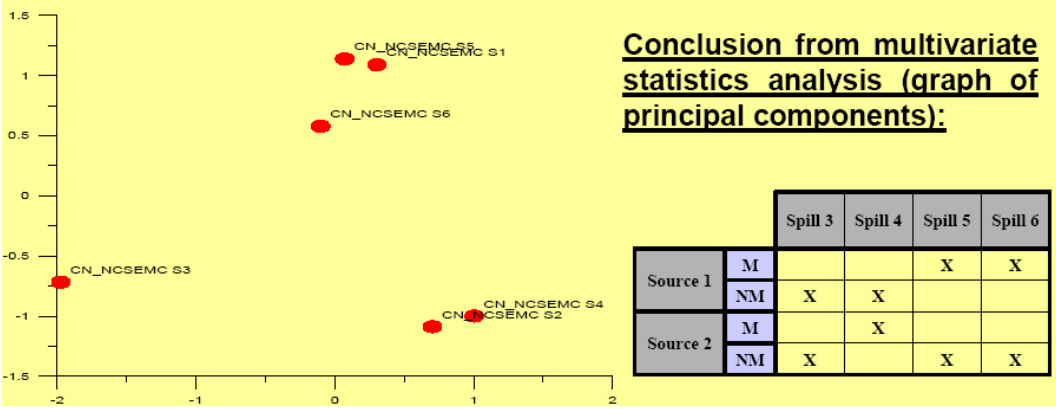
Organization
NCSEMC was set up in 1988, based on the combination of the marine group of North China Sea Branch and Yellow Sea Monitoring Center of State Oceanic Administration. In Sept. 2003, Authentication and Inspection Center of North Branch, CMS was authorized to NCSEMC.

NCSEMC is located in the beautiful coastal city -- Qingdao. It is leaded by both the North China Sea Branch of State Oceanic Administration and North Branch of China Marine Surveillance. The main work of NCSEMC are marine environmental monitoring, investigation and assessment, technique authentication of marine damage etc. The sea aera to be managed is from the southern part of Yalu River estuary to the northern part of Xiuzhen River. The responsibilities of NCSEMC are to provide technique support for the integrated managements implemented in North Sea by State Oceanic Administration, and offer technique guarantee for the administration management and marine inspection implemented in Yellow Sea and Bohai.

Sample handling
100µL oil sample was mixed with internal standards (100µL C24D50 for alkanes, 50µL 5a-androstane for biomarkers, and 100µL D14-terphenyl for PAHs) and 650µL solvent.
Note: In our lab, we usually calculate the concentration results for comparison, so we added IS into the samples for quantitative calculation, but the concentration results were not used in this case.

Original Conclusions
Source 1 and source 2: non-match , match level: -4.
Spill 3: non-match to source samples (source 1 and source 2),
match level: -4.
Spill 4: non-match to source 1, match level: -4;
Spill 4: probably match to source 2; match level:+2.
Spill 5: probably match to source 1, match level: +3;
non-match to source 2, match level: -4.
Spill 6: non-match to source 1, match level: -2;
non-match to source 2, match level: -4.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

Report:

The report follows the CEN guideline and is extensive. All analytical data are presented.

A correct match between samples 1 and 5 is found but not between samples 1 and 6.

The conclusion of a probable match between samples 2 and 4 at match level +2 is in contrast to the presented data and in contrast to the finding that:

Spill 4 is similar to great extent with Source 2 but there are obvious differences in PAHs and sesquiterpanes, the differences of sesquiterpanes may be explained by the instability of light compounds, but the differences of PAHs cannot be explained by weathering.

2.4 of the NCSEMC report

Relative respons factors (RRF) are shown for the alkanes, biomarkers and PAH's of the standard of the series for quality assurance. The results of the standards during the series looks good.

It would be interesting to know which criteria are used to evaluate the results.

4.1 of the NCSEMC report

Totally 32 diagnostic ratios were calculated for further comparison, including 21 biomarker ratios and 10 PAHs ratios. Ratios of the acyclic isoprenoids were not adopted because of their low abundance. Optional ratios of sesquiterpanes were not adopted because of their low molecular weight, either. Table 4.1~4.3 show the diagnostic ratios (based on the formula (A / B)) for all the duplicate samples. Some compounds, such as C28ab, diahopane (30D) and oleanane (30O), show very low concentration in the samples, so the differences of their ratios between duplicate samples are quite high. Therefore, the ratios 28ab, 30D, 30O, and TA26 are not qualified for further comparison.

5.1 of the NCSEMC report

Spill 6 shows a high degree of similarities with Source 1 in biomarkers(m/z 191 and 217), however, some differences were observed in PAHs distribution patterns, and it cannot be explained by weathering.

But according to the PW-plots of the spreadsheet those differences clearly can be explained by weathering of the compounds in spill 6: These show a very good reproducibility, and all aromatic ratios (between 30 and 40 minutes) are on a very straight ascending line.

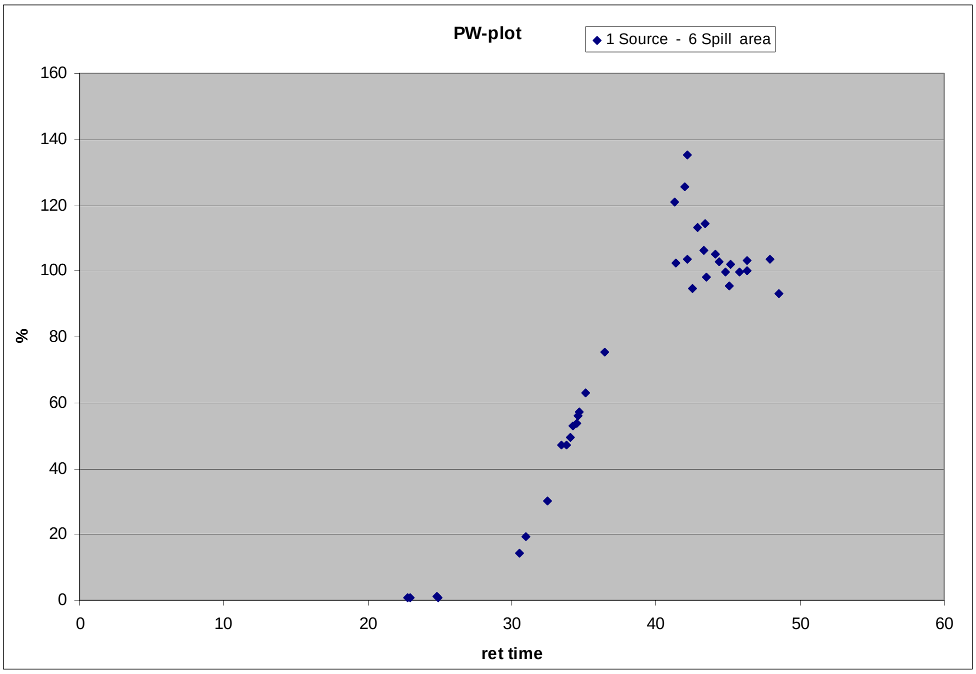


Fig 9
PW plot of NCSEMC:
So1 and Sp6 based on area.
The three point above 120% are resp C28(22R) 135%, C29 (22R) 126% and C29 (22S).

6. of the NCSEMC report

Evaluation of the methodology

- In CEN guideline, no quantitative calculation is required, however, as far as we are concerned, quantitative results are very useful in some cases, especially in dealing with some weathered samples. If there's some difficulty in quantitative calculation of concentration, the relative quantitative results(relative to internal standards) could also provide help.
- There's not an acceptable quantitative method to figure out the precise match level between samples, so the results have some subjectivity. Although this kind of multi-level results have high accuracy in scientific research, it may be thought not very valuable by judges in actual identification cases.
- There are 3 ratios in CEN guideline: DR-C28, DR-C29 and DR-C28+C29 and the third ratio is the sum of the other two. We think it's no use calculating DR-C28+C29 again.

Point 6 has been discussed at the workshop. In general it was concluded that quantification is not needed. The addition of one or several internal standards and the calculation of absolute values can even lead to a higher variance of the results. In case of fractionation it is necessary as a means to check the separation and the final injection concentration. The last remark will be a part of section 3.8.

2.9 DE_BSH

Contact:
Dr. G. Dahlmann
BSH
Bernhard Nocht Str 78
20359 Hamburg
Germany

Organization

The Bundesamt für Seeschifffahrt und Hydrographie (Federal Maritime and Hydrographic Agency) www.bsh.de is a higher federal authority in Germany coming under the jurisdiction of the Federal Ministry of Transport, Building and Urban Development

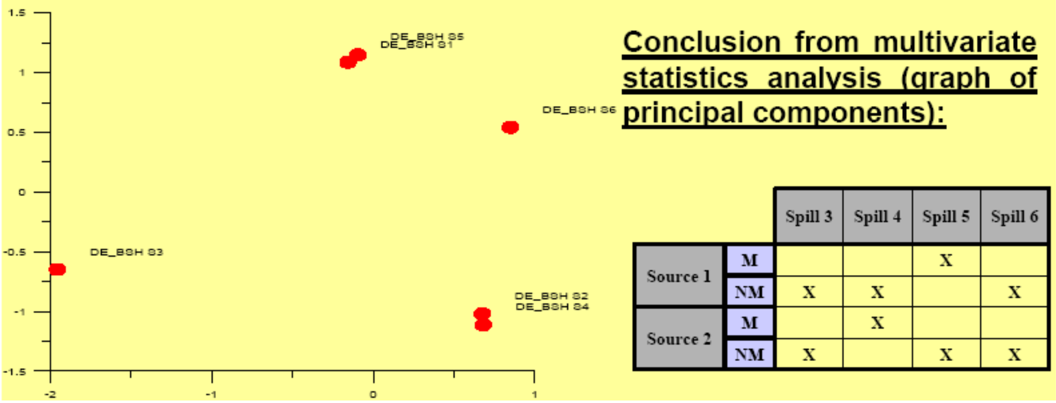
Sample handling

0,5 ml of the samples were dissolved into 5 ml of a Hexan/DCM solution (90:10). A clean-up was conducted by means of small silica-gel columns, which led to a final concentration of about 5mg/ml.

Original Conclusions

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X	X				
+3								
+2								
+1								
0								
-1								
-2								
-3								
-4	X	X			X	X	X	X

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	
	NM	X	X		X
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

The BSH-report describes the results of the sample comparison by means of the COSI-system, developed in the BSH.
For result evaluation, the joint BSH-RIZA database is used.

It is remarkably to see the result of S2 and S4 in the PCA plot based on the ratios selected for RR2007, while Gerhard has concluded a non-match based on his complete results.

2.10 DK_NERI

Contacts

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National Environmental Research Institute
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DK-4000 Roskilde, DENMARK

Organization

NERI http://www.dmu.dk/International/ is an independent research institute under the Danish Ministry of the Environment. NERI undertakes scientific consultancy work, monitoring of nature and the environment as well as applied and strategic research. NERI's task is to establish a scientific foundation for environmental policy decisions.

Sample handling

Original Conclusions

Comments/Remarks

No results and report has been received

At the meeting Asger explained that NERI has implemented a new instrument for the analysis and that the samples have been analysed about one week for the meeting.
Asger showed the results of his analysis in which they used a 0.18 mm column with a length of 40 m. The separation is very good. It might be that the column reduces faster in performance and is more sensitive for dirty samples because of the lower amount of phase. But for clean and cleaned samples it should work well.
Asger will keep us informed about his experiences.

Gerhard noted that he uses a 0.10 mm column with a short length in combination of hydrogen as carrier gas to perform the GC-FID analyzes in a short time. He has used it no for several years without problems.

2.11 EE_EERC

Contact:
Krista Mötz
Estonian Environmental Research Centre
Marja 4D
10617 Tallinn
Estonia

Organization

The Estonian Environmental Research Centre (EERC) www.klab.ee is specialized in chemical analyses in the field of environment protection. We also provide a comprehensive range of analyses for drinking water, foodstuff, fuel etc

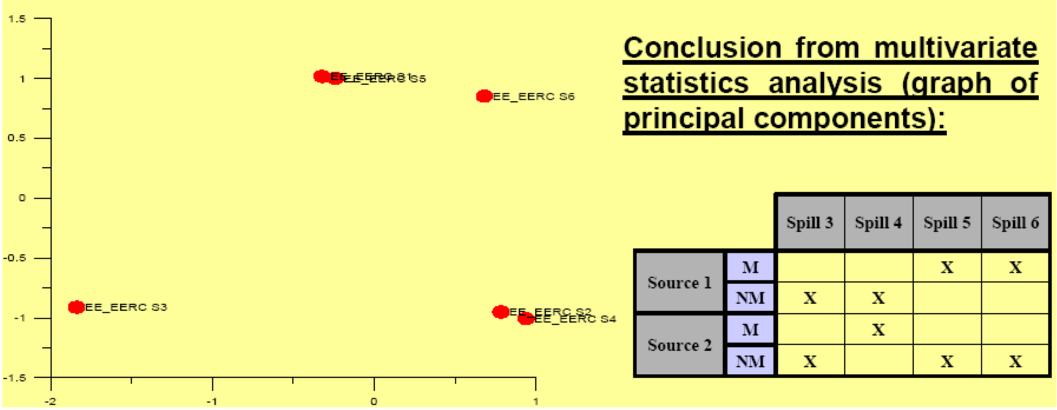
Sample handling

No detailed information about the sample handling is given in the report. The results are based on the Nordtest method (Nordtest Technical Report 502 part 3)

Original Conclusions

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X					
+3						X		
+2								
+1								
0								
-1								
-2				X			X	
-3								X
-4	X	X			X			

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

A correct match is found between samples 1 and 5 but not between samples 1 and 6.

The PW plot of sheet 1-5a shows that almost all points of the biomarkers are very close to 100%, indicating a good chromatography and integration.

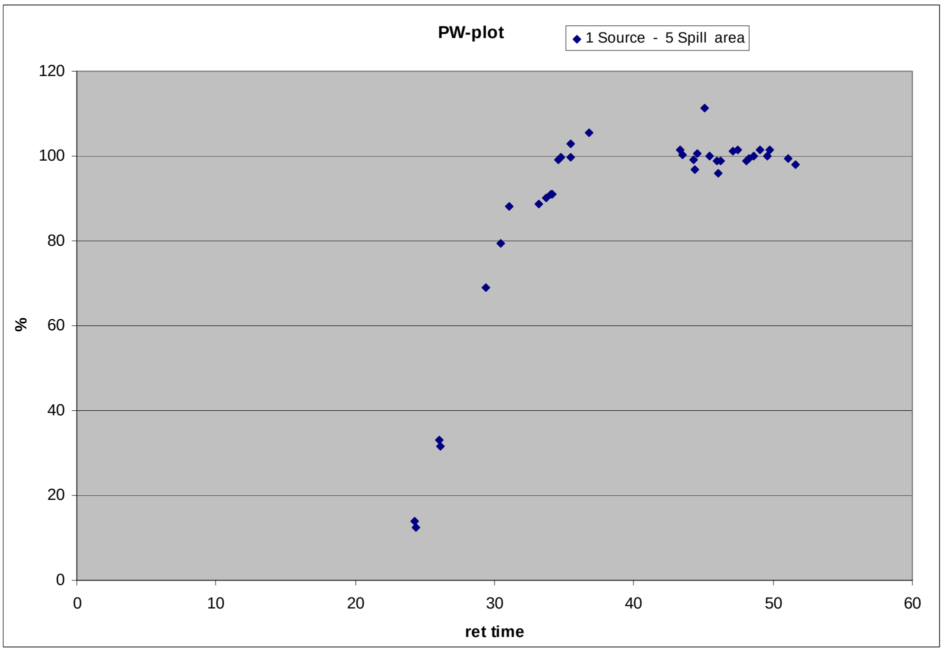


Fig 10
PW plot of EE_EERC:
Source 1 with Spill 5 based on area

A level of –2 is assigned for the combination So1 – Sp 6. The spreadsheet results show no differences for the biomarkers. The PW plot shows weathering up to a retention time of 40 min and does not show any differences for the biomarkers. The aromatics are on a straight ascending line, which strongly indicates that differences in these ratios are caused by weathering of the aromatics in spill sample 6.

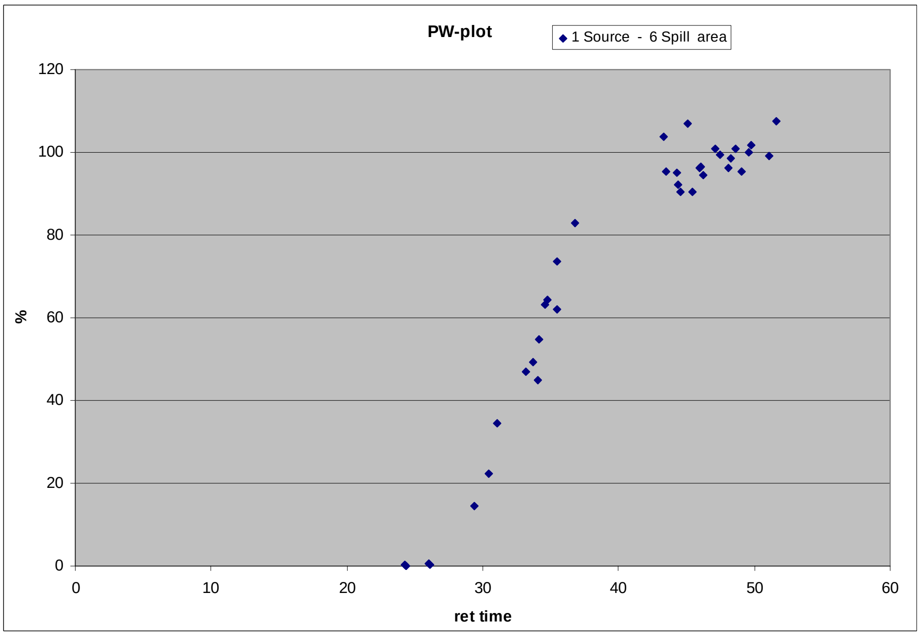


Fig 11
PW plot of EE_EERC
Source 1 with Spill 6 based on area

A level +3 was assigned for the comparison of sample 2 with sample 4. But also here the PW-plots definitely show the contrary: Having in mind also the very good reproducibility shown in the diagrams above, only an arbitrary cluster of points can be seen, and a best-fit (or evaporation-) curve cannot be found.

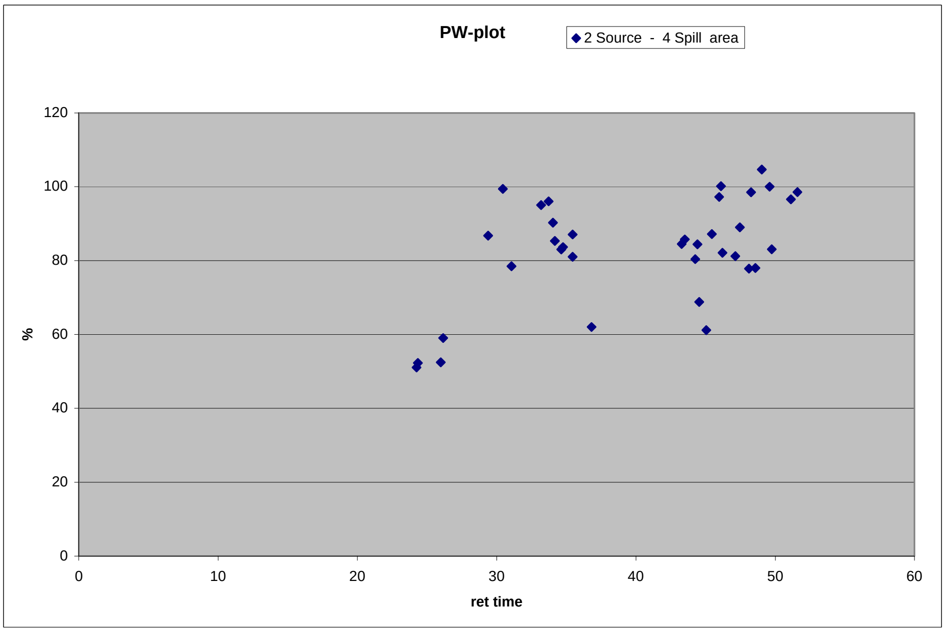


Fig 12
PW plot of EE_EERC
Source 2 with Spill 4 based on area

2.12 ES_CEDEX

Contact:
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SPAIN

Organization

The Centro de Estudios y Experimentación de Obras Públicas (CEDEX) www.cedex.es was created in 1957 as an autonomous organisation, that at present is organically ascribed to the Ministry of Fomento and functionally to the Ministries of Fomento and Environment of Spain, in the sphere of their respective competences. Its goals and functions are collected in the Statute of CEDEX, approved by the Royal Decree 1136/2002 of 31 October.

Sample handling

Samples were analysed by gas chromatography GC/FID and GC/MS applying the analytical conditions described in the excel file, where the analytical results for the inter-laboratory comparison were submitted.

Original Conclusions

The 6 samples were identified like HFO, from the general fingerprinting GC/FID with high content of aromatic hydrocarbons and the characteristic cluster of aromatics from cracking residues (mass 192; M-phenanthrenes, M-anthracene) and mass 234 (C4-phenanthrenes, M-benzo-naphto-thiophenes) without retene presence.

SPILL/SPILL COMPARISON

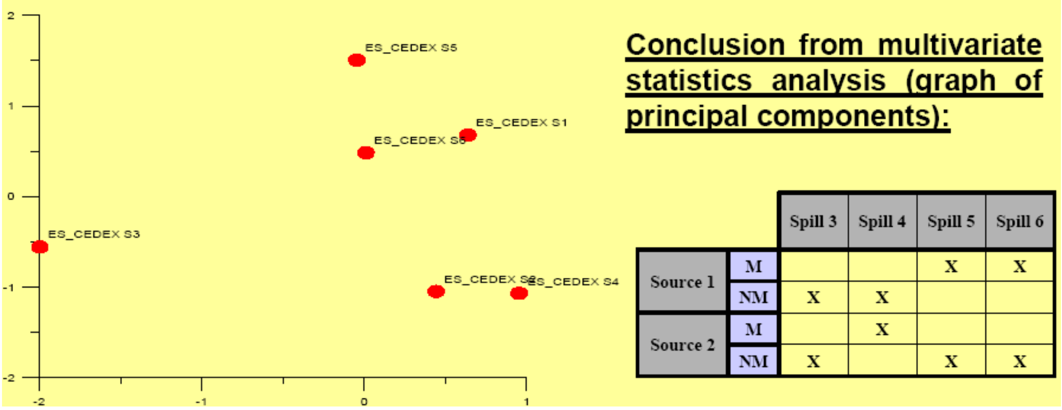
Spill 3/Spill 4	NON-MATCH
Spill 3/Spill 5	NON-MATCH
Spill 3/Spill 6	NON-MATCH
Spill 4/Spill 5	NON-MATCH
Spill 4/Spill 6	NON-MATCH
Spill 5/Spill 6	POSITIVE MATCH

SOURCE/SPILL COMPARISON

Source 1/Spill 3	NON-MATCH
Source 1/Spill 4	NON-MATCH
Source 1/Spill 5	POSITIVE MATCH
Source 1/Spill 6	POSITIVE MATCH

Source 2/Spill 3	NON-MATCH
Source 2/Spill 4	POSITIVE MATCH
Source 2/Spill 5	NON-MATCH
Source 2/Spill 6	NON-MATCH

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

A correct match is found between samples 1, 5 and 6.

In the report it is indicated that the integration of pristane is difficult because of the low resolution with C17:

We had some problems with the measure of the compounds C17, pristane, related with the mass 85 profile, due to low resolution. However, the measures of the peaks were carried out in the best possible way.

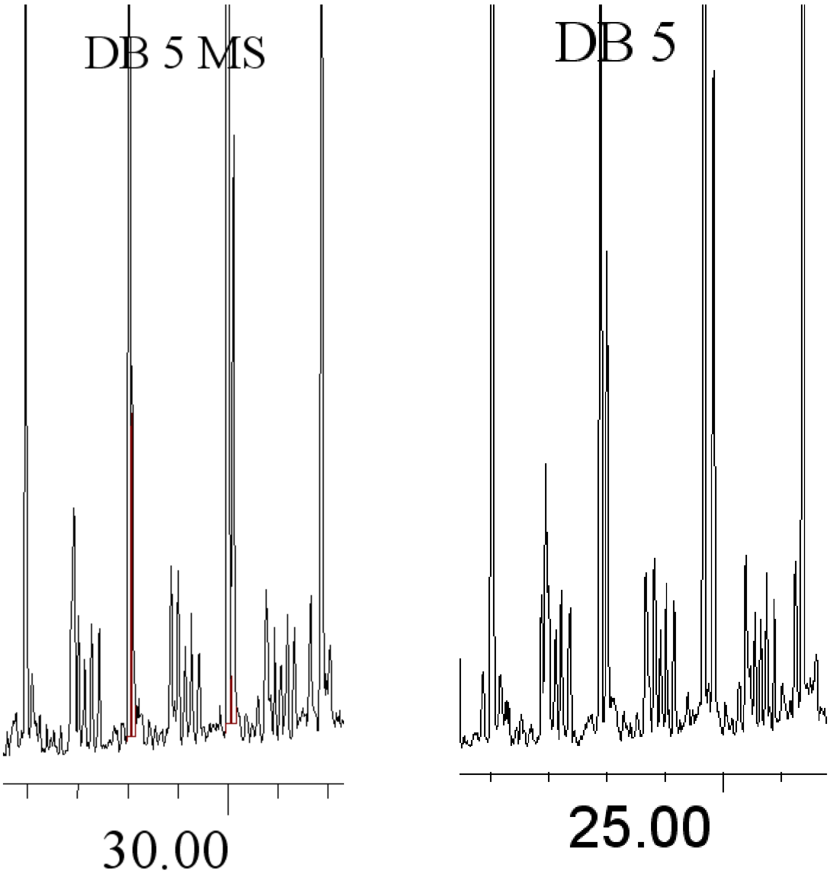


Fig 13
Difference between the separation of C17 and pristane on a DB5MS column (results CEDEX) and a DB5 column (results RIZA).

This low resolution is a typical problem for the DB5 MS column and is less for the DB 5 column. A reason for Gerhard Dahlmann to use the DB5 column to build the COSI database.

Compared to the results of the other labs the area/height values are very high due to very low height values. Also the variance in the area/height values is high, probably caused by the low number of digits in the height values. Therefore only the results of the spreadsheet based on area have been assessed.

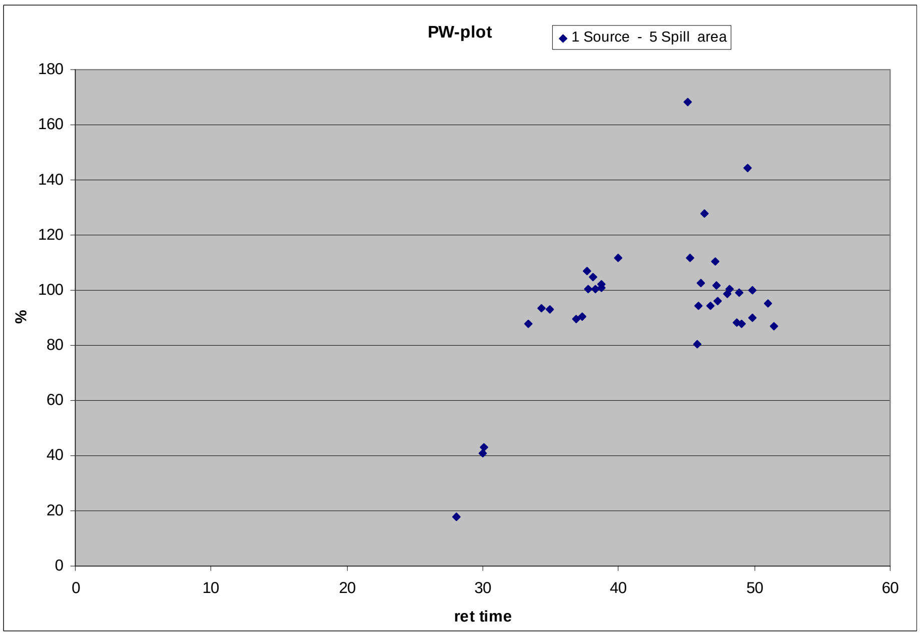


Fig 14
The PW plot 1_5a of CEDEX

The PW plot of 1_5a (Fig 14) however shows also a high variance.

CEDEX remarks:
Serious repeatability problems were detected in ratios implying small peaks: C28(22R)/30ab, C29(22R)/30ab, C29(22s)/30ab and C29ba/30ab, in addition to the mentioned ones previously, and they were not considered or considered with caution.

That is correct but also for the higher peaks a higher variance is visible. Looking at the integration lines of C29ab, C29ba and C30 ab however revealed that also the way of integration plays an important role.

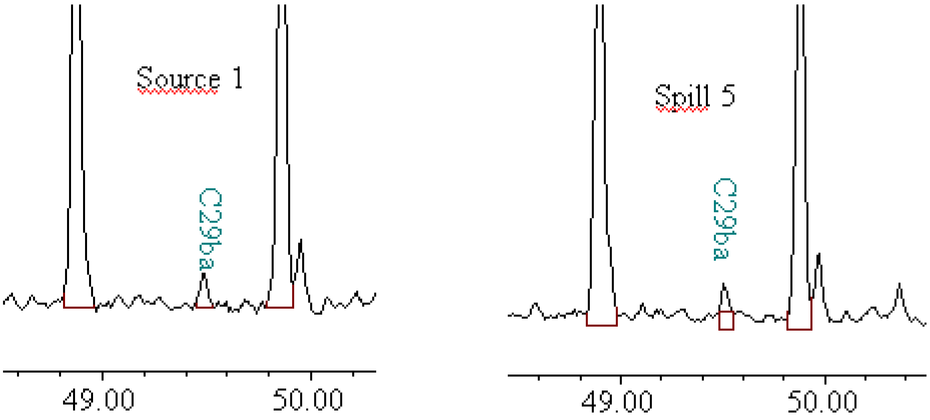


Fig 15
Parts of the m/z 191 ion chromatograms of CEDEX

At the meeting it became clear that CEDEX had to work with an old instrument for the analysis. In a few month a new instrument will be implemented which should improve the analyses.

2.13 ES_CSIC

Contact:s
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Department of Environmental Chemistry
(CSIC)
Barcelona, Spain

Laura de la Torre Gutiérrez
Dirección de Operaciones - Área de Medio Ambiente
SASEMAR (Sociedad de Salvamento y Seguridad Marítima)
Fruela 3
28011 Madrid
SPAIN

Organization
CSIC
The CSIC (www.csic.es) is an autonomous public research body belonging to the Ministry of Education and Science, to which it reports through the State Secretariat for Universities and Research. It has its own legal identity, assets and cashflow, and is independently managed.

Its aim is to promote and carry out scientific and technical research to serve Spain's science and technology policy, with the overall goal of contributing to the country's economic, social and cultural development.

SASEMAR
In November 1992 the Spanish Marine Safety Agency (SASEMAR) was created by law 27/92, under the overall co-ordination of the DGMM to provide the maritime SAR, marine pollution combat at sea and the maritime traffic control services, among others related with the mentioned ones.
Combating pollution at sea service is provided by SASEMAR by co-ordination of air-sea own resources and any other means from different administrations. SASEMAR has 10 Regional MRCC's centres around the coast and aditional Local Centers at the important ports.

Information from Laura:
I am writing you to clarify SASEMAR's position in the Bonn OSINET. For the moment we are coordinating the Spanish participation in the Net mainly forthe following reasons:
- SASEMAR is responsible for taking the samples.
- SASEMAR and the Spanish Maritime Administration that represents are the end users of the results.
- To establish at a national level a methodology for oils spill identification.

Sample handling
A cleanup without fractionation has been performed before analysis.

Original Conclusions

The comparison of the samples led to the following conclusions:

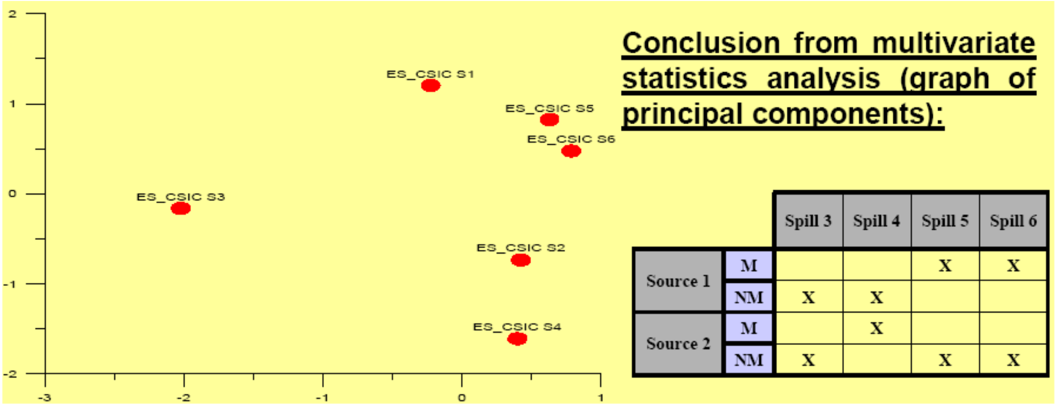
- Samples 5 and 6 exhibit a positive match with sample source 1. The findings show that differences in chromatographic patterns and diagnostic ratios of the samples are lower than the analytical variance of the method and in the case of particular ratios clearly explained by the influence of weathering processes. Consistently, the chromatographic patterns and diagnostic ratios of sample source 2 show differences beyond the analytical variance of the method and external factors like weathering, contamination or heterogeneity.

- Sample 4 does not mach with sample source 1 but exhibits some common features with sample 2. The findings strongly indicate probable match, because the present differences in concentration between biomarkers and aromatic compounds can be caused by a mixture of cutter stock with HFO.

- Sample 3 does not-match and probably not-match with samples 1 and 2, respectively.

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X	X				
+3						X		
+2								
+1								
0								
-1								
-2								
-3					X			
-4	X	X					X	X

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

A correct match is found between samples 1, 5 and 6.

The samples were injected with a concentration of 1 ug/ul and an injection volume of 2 ul. Also the samples were analyzed in scan mode from m/z 50 to 350

It is quite common for the Agilent systems (many of the labs work with them) to inject 10 ug/ul with an injection volume of 1 ul for this type of samples. Also samples are analyzed in SIM mode to increase sensitivity.

It results in a difference of 5 for the injection and ,(lets guess 300 mass units/ 15 mass units = 20) 20 for the scan mode.
It might be that the Thermo-Finnigan Trace GC-MS is much more sensitive than the Agilent systems, but from the chromatograms it be learn that the S/N ratios are much lower than of most of the other participants.

This is reflected in the variance of the data especially for the lower peaks. Eg gammacerane is barely visible.

The ratios are very well comparable with the others although a DB1 column has been used, while most participants use a DB5 of DB5MS.

The PW plots in the spreadsheet file show in general a higher variation then usual, but especially in the concentration of the PAH's relative to the biomarkers.

In the assessment of the case CSIC has been concluded a reasonable match between Source 2 and Spill 4 and explained it by mixing problems of cutter stock and HFO. During the workshop special attention has been paid on the composition and content of cutterstock in HFO. This issue is discussed in section 3.1 and 3.2

At the workshop Joan has given a presentation (**Oil biodegradation.PDF**) about the fate of the oil of the Prestige. Oil samples were collected during 2003 on the North-West coast of Spain and the composition and change of aromatic compounds and biomarkers were studied. As a result it can be concluded that even the biomarkers are sensitive for degradation on a longer period of time. The presentation of Joan and three papers about the fate of the Prestige oil can be found in the directory of ES_CSIC

2.14 FI_NBI

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Niina Viitala and Petra Pollari
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Crime laboratory
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FINLAND

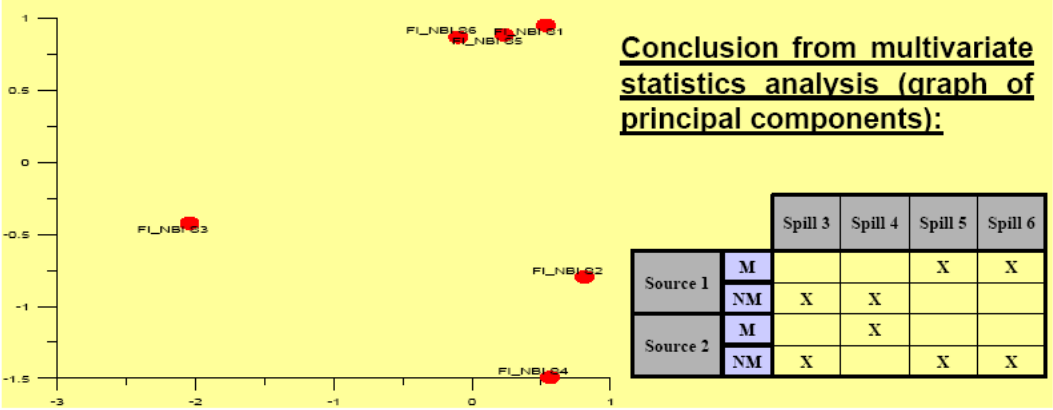
Organization
The National Bureau of Investigation http://www.poliisi.fi/nbi is one of the national units of the Finnish Police. The NBI is specialized in investigating and preventing serious, organized and international crime. At the national level, the NBI is responsible for criminal intelligence and identification of new types of crime. The NBI also develops techniques for criminal investigation and provides training in the mentioned subjects.

Sample handling
1 ul of the samples as received, have been injected in split mode with a ratio of 1:30.

Original Conclusions
Sample 3 can not be proved to origin from source 1 or 2.
Sample 4 is possibly from source 2.
Sample 5 may originate from source 1, but because of strong weathering of sample 5, it cannot be proved with certainty.
Because of strong weathering of Sample 6, it cannot be proved to originate from source 1 or 2.

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3								
+2						X		
+1			X					
0	X			X	X			
-1								
-2								
-3		X					X	X
-4								

PCA- plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

The NBI report is very short and shows only the conclusions and comments on the spreadsheet and the SKL table.

The written conclusions are according to the results of others. The SKL table however is different compared to the other results. The highest value is given for the comparison of Source 2 with Spill 4

The samples were injected at a concentration of 100 mg/ml in split mode with a ratio of 1:30. Comparable with an injection of 3.3 mg/ml with an injection volume of 1 ul. The resulting chromatograms look good.

All others have used the splitless mode. NFI reported as only lab that the amount of sample provided for the Round Robin was to small.

A splitless injection is very useful in cases in which only a small amount of sample is available. At the RIZA lab sometimes samples without a layer of oil are received. After extraction and concentration it is possible to get a good chromatogram for interpretation. In split mode this would not be possible.

The spreadsheet file shows a reasonable variation of the area/height ratios. The PW plot of 1_5a however shows a lot of variation.

Comment NFI about the SKL conclusions:

it would be good for court proceedings to have a standard scale. The SKL-scale seems to have too many options, whereas the CEN method has too few. The best method would probably be the compromise of these two.

Comments of NBI on CEN/TR 15522-2

1. Page 46 Table C.1 Ion 134 retention time scale is different then in page 50 Figure D.2
2. Page 82 HFO Figure H17 and H19, the same Figure in both, why? Is the point in Figures H17, 18 to show, that HFO don’t differ so much with ions 192 and 234, although the FID is so different?
3. Page 92, Figure H30, wrong fig number H.26, it should be H29?
4. Page 95 under H6.2.2 (see Annex1, Table A2) > wrong number?

5. Page 105 Table I5, delete DR-27dia (was discussed already)

The comments were shortly mentioned at the workshop. The comments are correct and will be implemented in the next version of CEN/TR 15522-2.

2.15 FR_CEDRE

Contact:
Julien GUYOMARCH
CEDRE
Service Recherche & Développement
715 rue Alain Colas / CS 41836
29218 BREST Cedex 2
FRANCE

Organization

Cedre (http://www.le-cedre.fr/) is a governamental institute started in 1978 within measures taken after the wreckage of the “Amoco Cadiz”, to improve the preparedness against accidental water pollution and to strengthen the national response organization. Its expertise encompasses both marine and inland waters.

Sample handling

1 ul of each sample was injected at a concentration 10 mg/ml.
It is unknown, whether a cleanup has been performed.

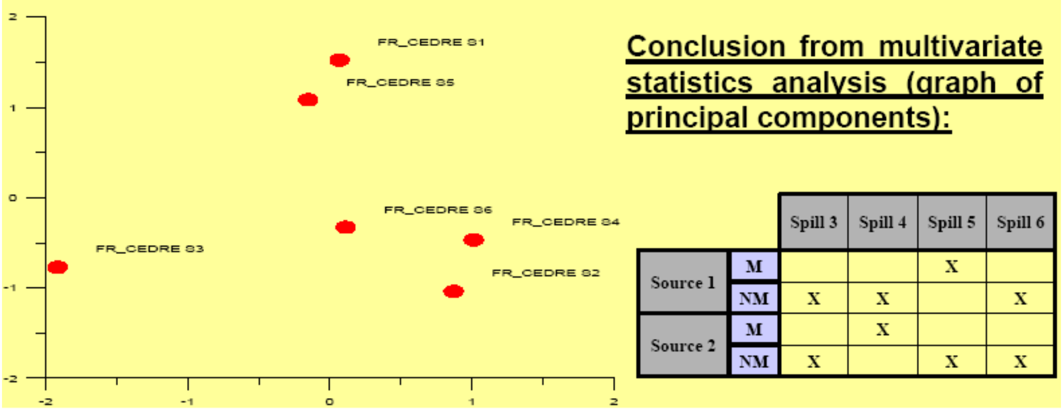
Original Conclusions

The conclusions of this oil spill identification are that the **Spill 5** matches with **Source 1** (level +3) and **Spill 4** with **Source 2** (level +2). As regards the other spill samples (**spill 3**, **4** and **6**), differences are very significant, thus excluding any relationship with the source samples.

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3			✓					
+2						✓		
+1								
0								
-1								
-2								
-3								
-4	✓	✓		✓	✓		✓	✓

Finally, taking into account the methylphenanthrenes/anthracenes distributions, it appears that the six oil samples could be heavy fuel oils.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	
	NM	X	X		X
Source 2	M		X		
	NM	X		X	X

Comments/Remarks
A correct match is found between samples 1 and 5 but not between samples 1 and 6.
All conclusions are explained in detail.

The report follows the CEN/TR in comparing the results and Cedre has used additionally cross plots of some diagnostic ratios:

In order to establish correlations between samples, figures 2 and 3 were drawn by using respectively Hopanes and PAHs Diagnostic Ratios. Moreover, the variability considered by the CEN methodology was illustrated on figures for samples which were apparently close to each other. The boxes correspond to respectively ±7 % (blue) and ±14 % (violet) of the average value: samples not included in the same box cannot be correlated. On the other hand, samples outside the box can be considered as different (figures 2 and 3 represent only the “matching” boxes).

The cross plots work well for the biomarker ratios in Fig 2 of the Cedre report but less for Fig 3 of the report, because the ratios are influenced by weathering (Spill 6).

The ion-chromatograms show good patterns for the biomarkers, but the peaks of the PAH’s are broad. See e.g. m/z 216.

The PW-plots of Juliens data for the comparison of samples 1 and 5 and 1 and 6 don’t look so different:

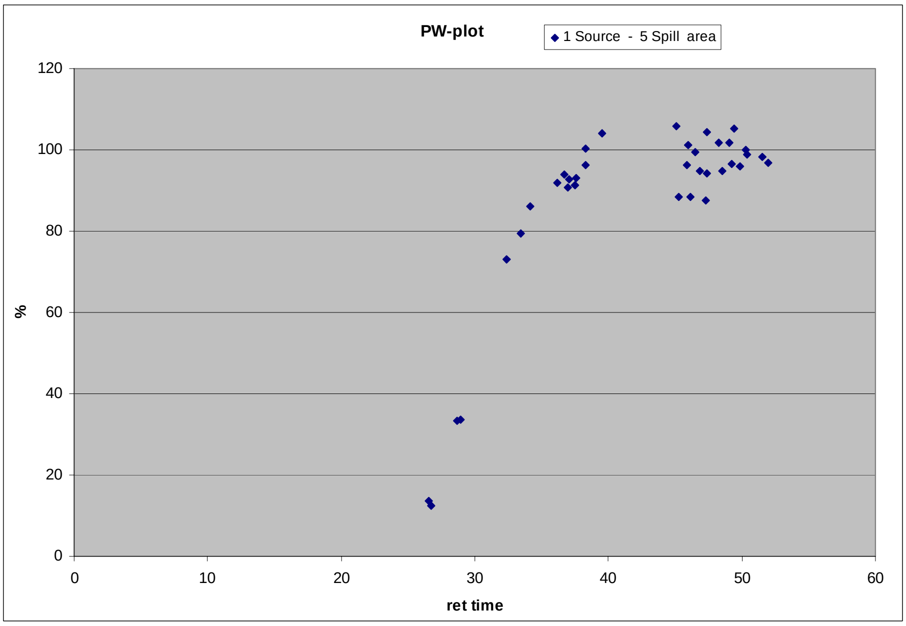


Fig 16
PW plot of FR_Cedre
Source 1 with Spill 5 based on area

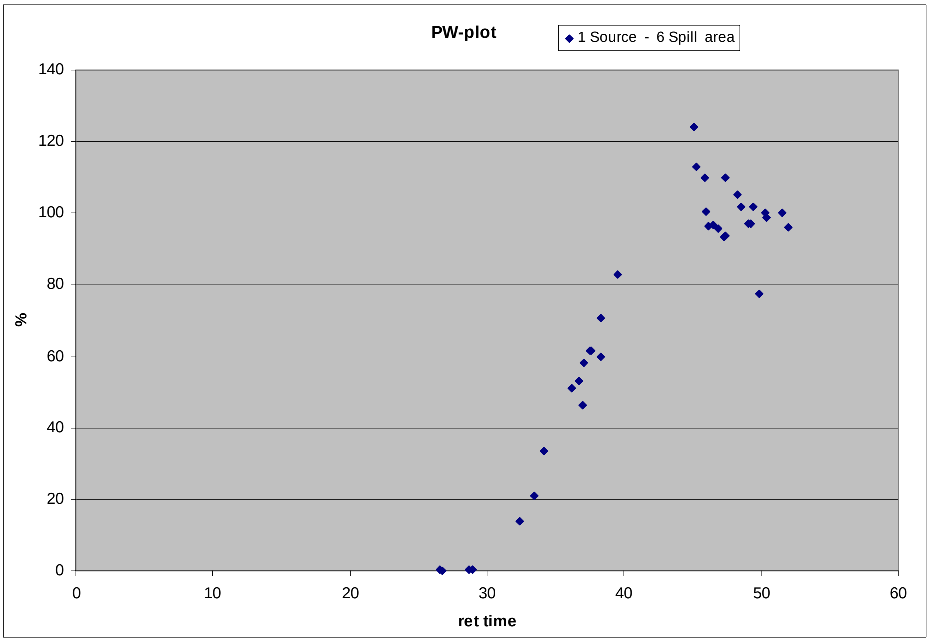


Fig 17
PW plot of FR_Cedre
Source 1 with Spill 6 based on area

There are merely two obvious outliers, when sample 1 is compared with sample 6, and these belong to two very small peaks.
Again here differences are very obvious, when samples 2 and 4 are compared:

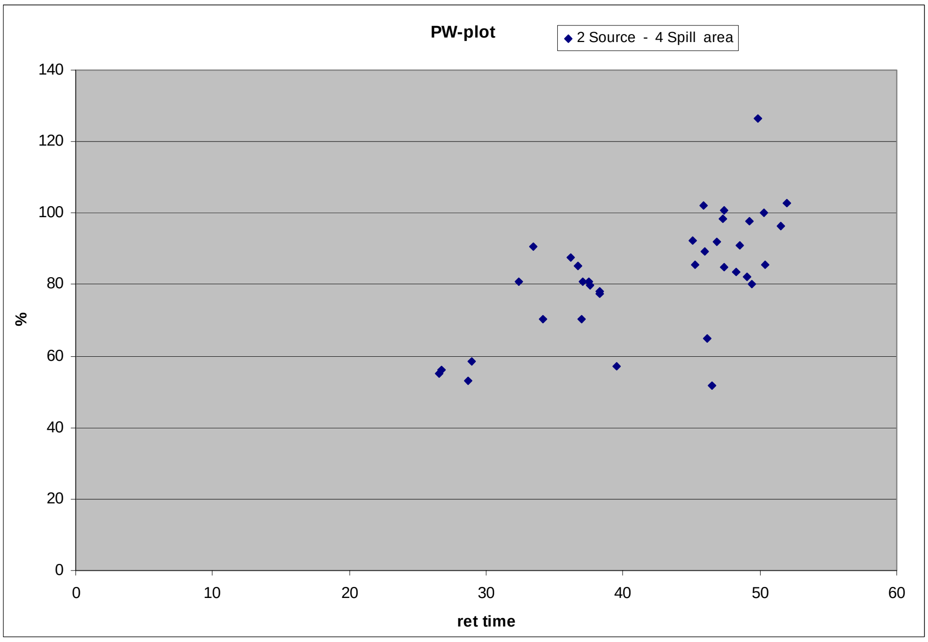


Fig 18
PW plot of Fr_Cedre
Source 2 with Spill 4 based on area

2.16 LV_LEGMA

Contact:
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Environmental Laboratory
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Latvia

Note:
In the spreadsheet files the old name LVA can be found.

Organization

The state agency of "Latvian Environment, Geology, and Meteorology Agency " (LEGMA) (www.lvgma.gov.lv) is an institution subordinated to the LV Ministry of Environment, which started its work on the 1st of January, 2005. The agency was created by combining the Latvian Hydrometeorology Agency, the Latvian Environment Agency, and the Latvian Geology Service.

Sample handling

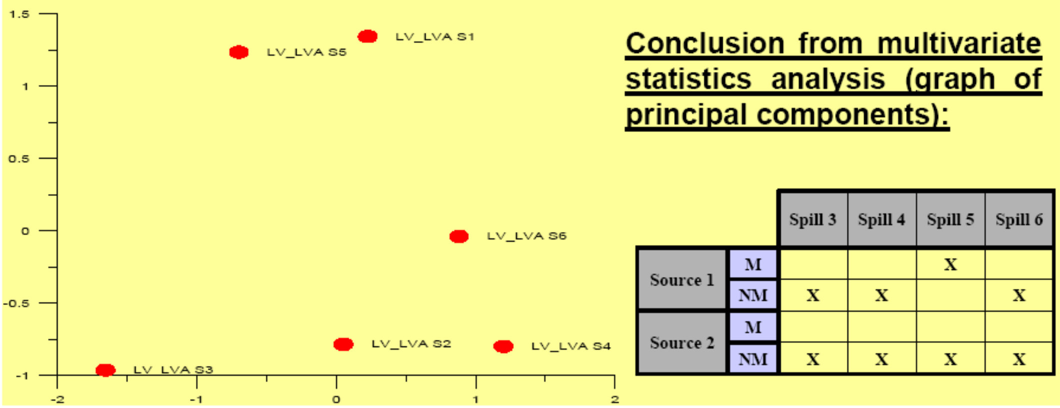
The RR2007 samples extract solvent were changed to hexane and cleaned with silicagel and analyzed with GC-FID and GC-MS.

Original Conclusions

Source1	Spill3	non match
Source1	Spill4	non match
Source1	**Spill5**	**Spill 5 is weathered source 1**
Source1	Spill6	non match
Source2	Spill3	non match
Source2	Spill4	probably match
Source2	Spill5	non match
Source2	Spill6	non match

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X					
+3								
+2								
+1						X		
0								
-1				X				X
-2	X	X						
-3					X		X	
-4								

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	
	NM	X	X		X
Source 2	M				
	NM	X	X	X	X

Comments/Remarks

A correct match is found between samples 1 and 5 but not between samples 1 and 6.
All conclusions are explained in detail.

The report is clear and shows and discusses the comparison of each combination of source and spill sample. The conclusions are according to the results of others. The conclusions in the SKL table are however much more unsure than concluded by others.

The report shows PW plots for the alkanes, but for the calculation of the **deviation %** obviously the values of the spill sample were used as 100% value instead of the values of the source sample. See Fig. 19 as an example.

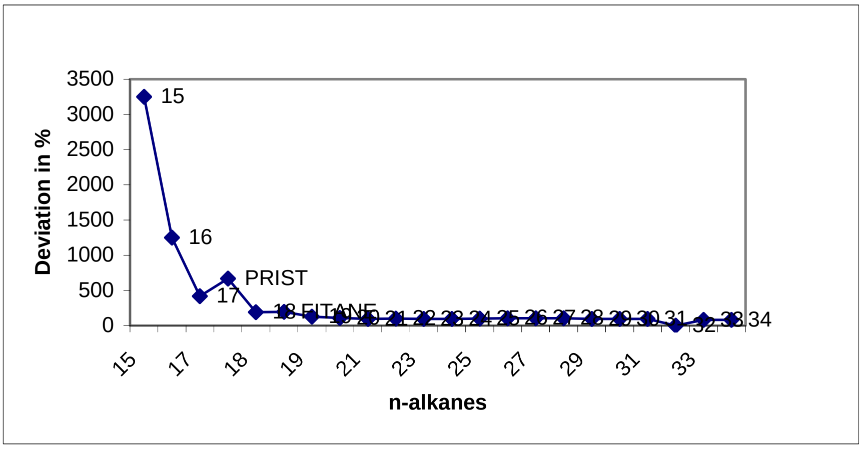


Fig 19
Fig.9 Deviation in % for the n-alkanes between the Source1 and Spill5 normalised relative to the mean of C24-30

For the comparison of the isoprenoid ratios based on the FID results LEGMA has used the folowing calculation to compensate for evaporation. As the difference between Source 1 and Spill 5 is totally based on evaporation the formula works well.

	mean	mean	mean	Abs.dif	r95% based on RSD 5%	Flag
	Source1	spill5				
C17/pristane	3.4	3.7	3.55	0.3	0.49	
C18/phytane	2.7	2.72	2.71	0.02	0.38	
C17/C18	0.98	0.48				
Pri/phy	0.79	0.36	0.575	0.43	0.08	1

Table3 Comparing the pristine/phytane ratios of the mean values of source I and Spill 5

GC/FID chromatograms overlay for Source1 and Spill5 (fig7) shows identical UCM.
Weathering check shows similar pattern.
Spill5 looks like weathered Source1, but only evaporation (evaporation seems artificial) had take place.

Corrected values for pristine/phytane ratios (if weather evaporation has influenced this ratio)
(pr/ph)spill= (pr/ph)susp.source x (C17/C18)spill/C17/C18)susp.source= 0.38

This leads to

Pri/phy	0.38	0.36	0.37	0.05		

GC/FID results show a match for Source1 and Spill 5

It is strange however that for the comparison of the GCMS results (Table 4 of the LEGMA report) the ratio C17/pristane shows a relative difference of 39%

LEGMA concludes:
GC/MS results show that Spill5 is weathered Source1. Only differences are .ratios -C17/pristine and pristine/phytane as the weathering result.

This is correct for the pristane/phytane ratio but not for C17/pristane.

As found in the results of others, Rita's results of samples 1 and 6 actually don't differ so much, and a best-fit curve can easily be found (showing that the differences are actually caused by weathering.

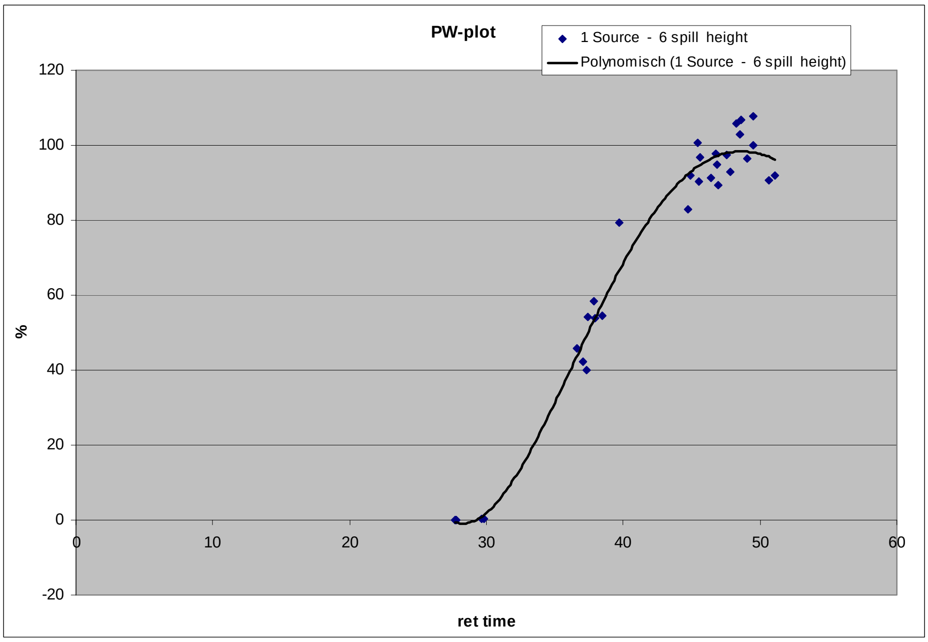


Fig 20
PW plot of LV_LEGMA
Source 1 with Spill 6 based on height

Also here, this is not the case, when her values of samples 2 and 4 are compared.

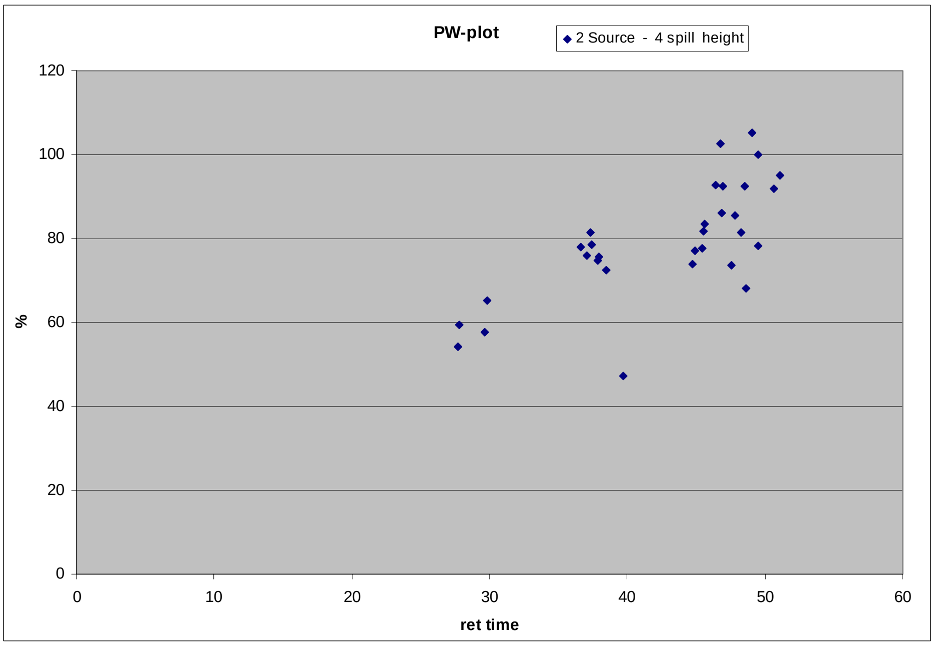


Fig 21
PW plot of LV_LEGMA
Source 2 with Spill 4 based on height

2.17 NL_NFI

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The Netherlands

Organization

The Netherlands Forensic Institute www.forensischinstituut.nl analyses oil samples in cases of arson (e.g. gasoline and kerosene) and environmental contaminations.

Sample handling

Samples were diluted in petroleum ether (1 g/l en 10 g/l) and transferred to a gc-vial.
The RR-samples were analyzed in duplicate with GC-MS. In full scan mode, at a concentration of 1 g/l dissolved in petroleum ether for screening and at 1 and 10 g/l for SIM analysis of PAH's and terpanes. The method uses 14 specifically formulated PAH ratios and 7 terpane ratios, which are separated in two graphs based on stability and weathering behavior according to Venosa et al.

Original Conclusions

The question to compare the two source samples with the four spill samples can be split into a several one-on-one comparisons and accessory a hypothesis and an alternative hypothesis. For example:
Hypothesis 1: The oil from source 1 is the same oil as the oil from spill 3.
Hypothesis 2: The oil from source 1 is the not the same oil as the oil from spill 3.

The range of conclusions:
The results of the examination are
- somewhat probable
- probable
- more probable
- highly probable

if hypothesis 1 is true than if hypothesis 2 is true.

This is a best effort translation of the last proposition within the NFI on how to report with likelihood gradations.

Hypothesis 1: The oil from source 1 is the same oil as the oil from spill 3.
Hypothesis 2: The oil from source 1 is the not the same oil as the oil from spill 3.

The results of the examination are highly probable if hypothesis 2 is true than if hypothesis 1 is true.

Hypothesis 3: The oil from source 1 is the same oil as the oil from spill 4.

Hypothesis 4: The oil from source 1 is the not the same oil as the oil from spill 4.

The results of the examination are highly probable if hypothesis 4 is true than if hypothesis 3 is true.

Hypothesis 5: The oil from source 1 is the same oil as the oil from spill 5.
Hypothesis 6: The oil from source 1 is the not the same oil as the oil from spill 5.

The results of the examination are more probable if hypothesis 5 is true than if hypothesis 6 is true.

Hypothesis 7: The oil from source 1 is the same oil as the oil from spill 6.
Hypothesis 8: The oil from source 1 is the not the same oil as the oil from spill 6.

The results of the examination are highly probable if hypothesis 8 is true than if hypothesis 7 is true.

Hypothesis 9: The oil from source2 is the same oil as the oil from spill 3.
Hypothesis 10: The oil from source2 is the not the same oil as the oil from spill 3.

The results of the examination are highly probable if hypothesis 10 is true than if hypothesis 9 is true.

Hypothesis 11: The oil from source2 is the same oil as the oil from spill 4.
Hypothesis 12: The oil from source2 is the not the same oil as the oil from spill 4.

The results of the examination are highly probable if hypothesis 12 is true than if hypothesis 11 is true.

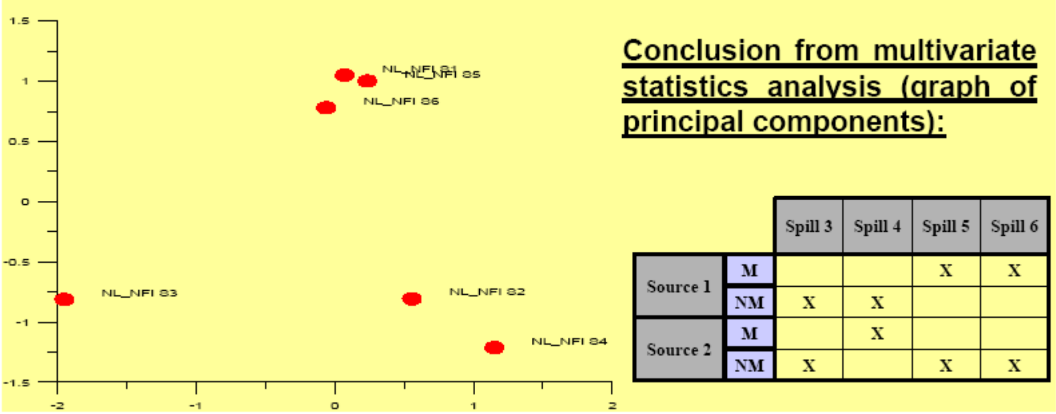
Hypothesis 13: The oil from source2 is the same oil as the oil from spill 5.
Hypothesis 14: The oil from source2 is the not the same oil as the oil from spill 5.

The results of the examination are highly probable if hypothesis 14 is true than if hypothesis 13 is true.

Hypothesis 15: The oil from source2 is the same oil as the oil from spill 6.
Hypothesis 16: The oil from source2 is the not the same oil as the oil from spill 6.

The results of the examination are highly probable if hypothesis 16 is true than if hypothesis 15 is true.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

A correct match is found between samples 1 and 5 but not between samples 1 and 6.
All conclusions are explained in detail.

The report is clear and shows and discusses the comparison of each combination of source and spill sample.

The way of describing the conclusions is very comparable with the method of SKL. Rene explained the NFI method also in the email send together with the results:

It's interesting to read the reactions in the discussion. It's a bit like what went on in the NFI the last couple of years (and is still going on). It's always difficult to formulate your conclusion if the results are qualitative and not quantitative. A problem is also the interpretation of the verbale scale. I've included an article "Evett et al 2000 evidence interpretation" on this subject. An other article I include is "Pro and Cons of Bayesian Reasoning in Forensic Science" which I think will be interesting to read.
I also want to point to a fundamental difference: “The Forensic Scientist only reports on the probability of the evidence given the hypothesis but never on the probability of the hypothesis given the evidence.” This is the reason why the hypothesis in our report is formulated as it is.
It's difficult to fill in the table because there's no hypothesis and the explanatory text below each level makes it clear that one reports on the probability of the hypothesis which is something one should not do.
Nevertheless I've filled in the table and used the following hypothesis to fill the dots:
source 1 is the same as spill 3
source 1 is the same as spill 4
source 1 is the same as spill 5
Etc.

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3			X					
+2								
+1								
0								
-1								
-2								
-3								
-4	X	X		X	X	X	X	X

Concerning the spreadsheet and chromatograms:
The integration of gammacerane between samples 1, 5 and 6 is not consequent, which is e.g. visible in the PW plot of 1-5a (See Fig 32 section 3.3)

2.18 NL_RIZA

Contact:
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Organization

RIZA is a part of Rijkswaterstaat (the Directorate-General for Public Works and Water Management) and responsible for the inland water. RIKZ has the same function, but is responsible for the North Sea. Since 1 October 2007 both institutes have been combined and is now called in Dutch: Waterdienst.
The English translation is the RWS_Centre for Water Management. The website www.waterdienst.nl is at the moment only in Dutch available.

Sample handling

Samples were diluted with DCM to a concentration of 10 mg/ml. Sample were analyzed with GC-FID (Chromatograms available on the in the RR2007 RIZA directory in **FID std sample bl RR2007.ppt**) and GCMS (SIM mode)

Original Conclusions

CEN TR 15522-2 defines 4 possible conclusions.
Using this method results in the following conclusions.

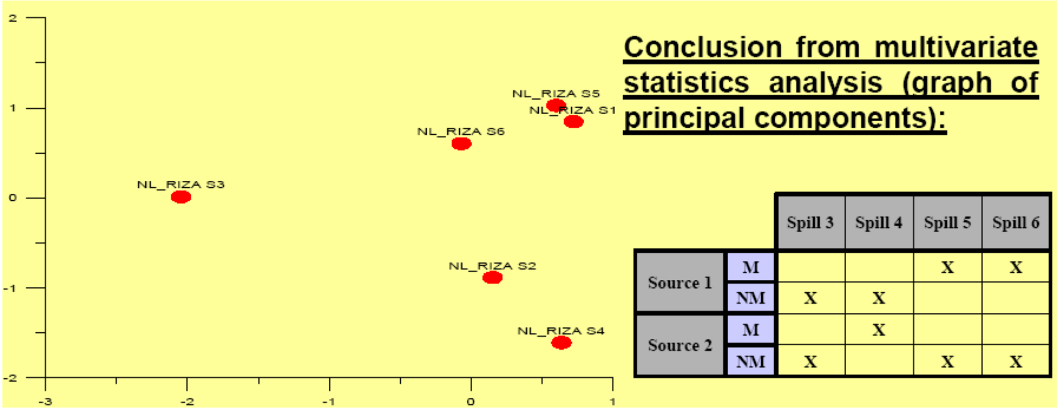
Source 1				Source 2			
Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
non-match	non-match	match	match	non-match	non-match	non-match	non-match

Using the table of the Swedish forensic institute results in:

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X					
+3				X				
+2								
+1								
0								
-1								
-2								
-3								
-4	X	X			X	X	X	X

All PAH's of sample 6 are weathered and therefore only the biomarker information can be used for comparison. Therefore the level +3 has been used in the table.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

At RIZA normally all samples are injected directly, except when polar compounds or a lot of high boiling compounds are expected.
In case of the RR2007 it was decided to inject the samples directly after dilution. The result is visible in Fig. 22 for the two alkane standards analysed around the samples by GCFID

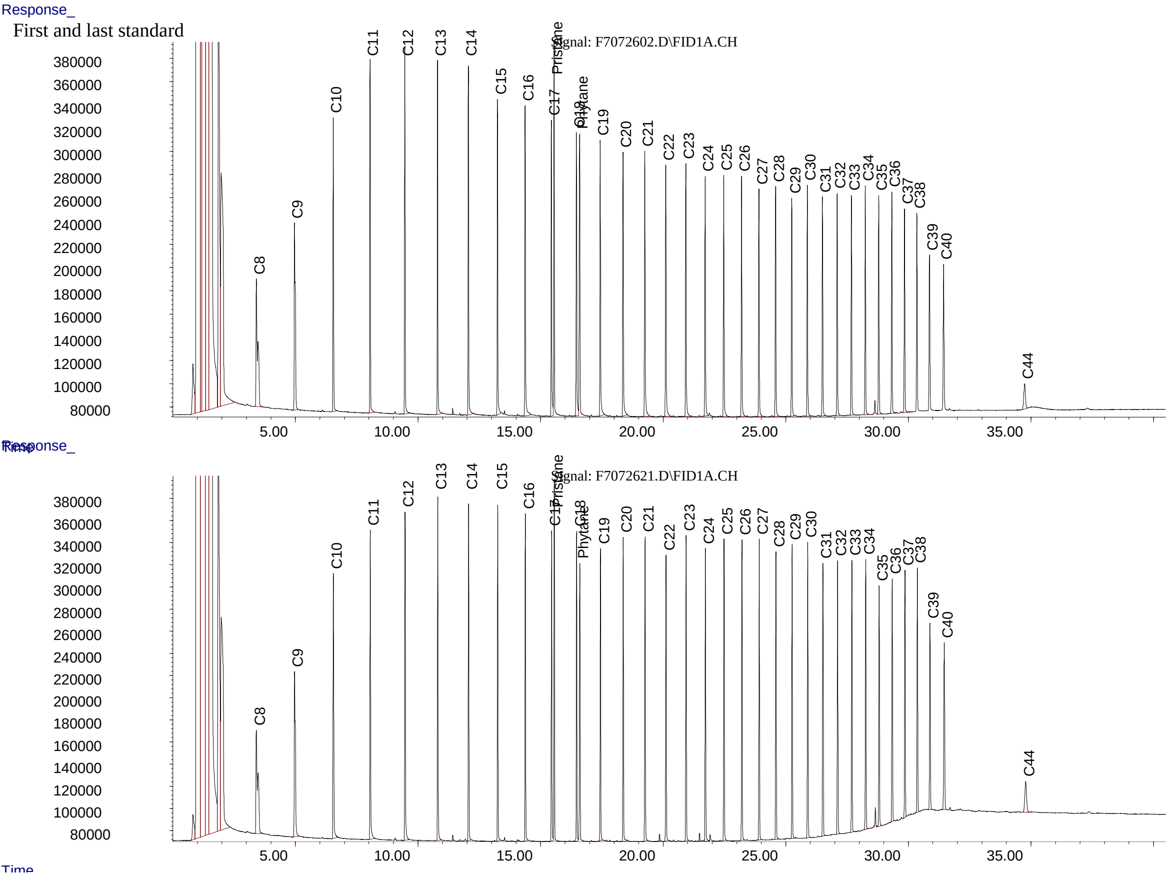


Fig 22
First (above) and last alkane standard of the sequence for the analysis of the RR2007 samples.

As an effect the last standard shows an elevated baseline and the compounds after about C19 elute with a smaller peak width. It seems almost an advantage, but the results are not reproducible and after more of these series the column performance becomes worse. Cutting

about 0.5 m of the column on the injection side of the column solved the problem.
In CEN/TR 15522-2 section 5.4.1 it is advised to clean samples containing a high amount of high boiling compounds.
It is advised to additionally prescribe that all suspected bunker or fuel oil samples should be cleaned, because it can influence the final conclusions.

Besides the report, spreadsheet and chromatograms in the NL_RIZA directory also spreadsheet files for the comparison of the GCFID and GCMS results can be found.
Compared to the EXCEL template of RR2007, much more compounds and ratios are used. As a result the PW plots based on the GCMS data give more weathering information. To separate the biomarker and PAH ratios different colors are used. As an example the comparison of 1-5 based on area is shown in Fig 23 and 1-6 in Fig 24

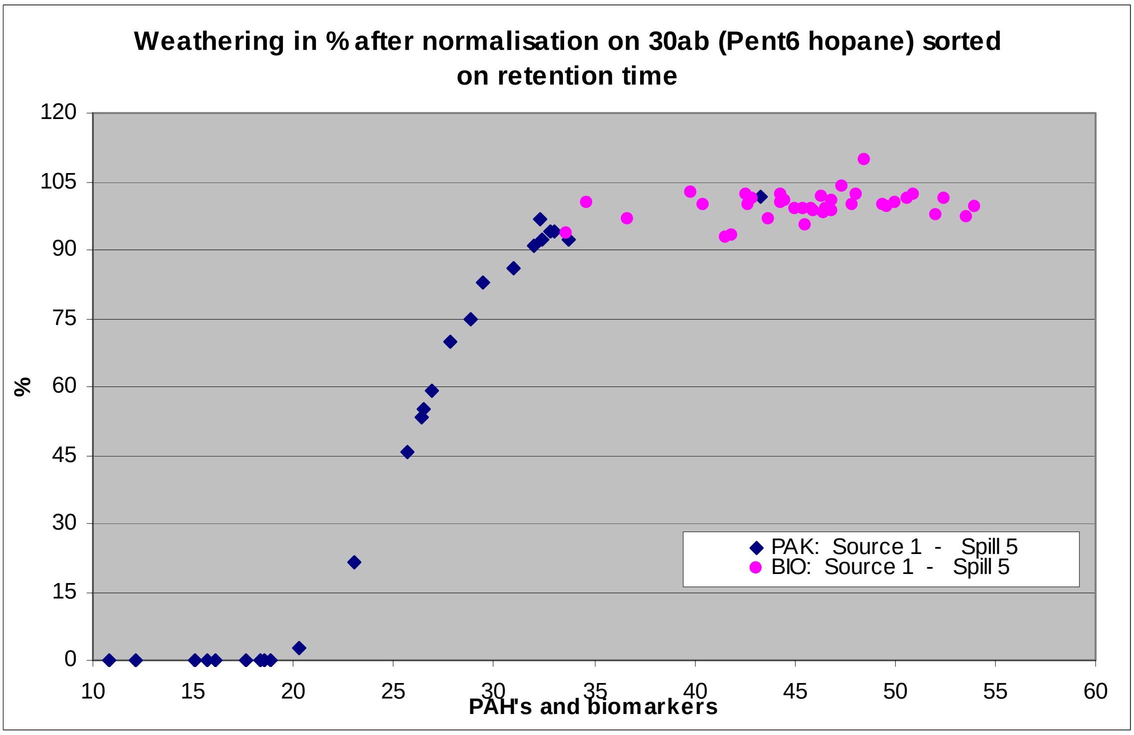


Fig 23
PW plot of the samples 1 and 5 based on area for a part of the compounds mentioned in the CEN/TR

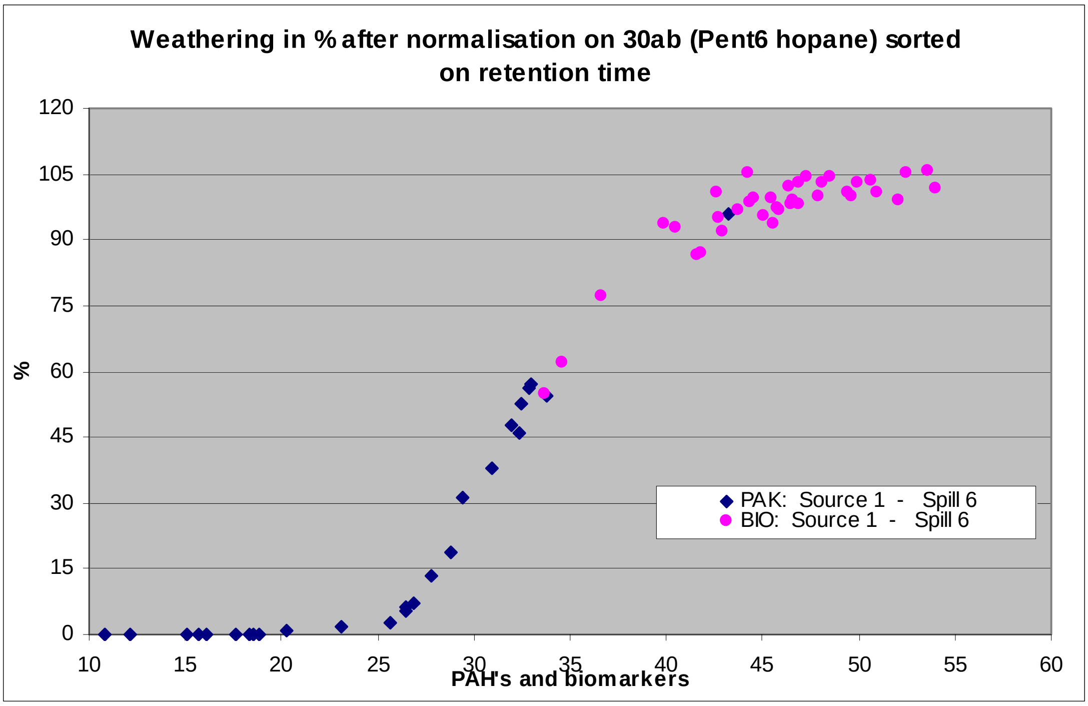


Fig 24
PW plot of the samples 1 and 6 based on area for a part of the compounds mentioned in the CEN/TR

2.19 NO_Sintef

Contact:s
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Norway

Organization
Sintef http://www.sintef.no/ is a large Norwegian engineering institute and is among others active in the petroleum industry and petroleum research. Sintef analyzes all oil spill samples for the Norwegian government.

Sample handling
All samples were diluted in dichloromethane(DCM) to give a concentration of approximately 10 mg/ml. The samples were analyzed in duplicates as described in the CEN guideline.

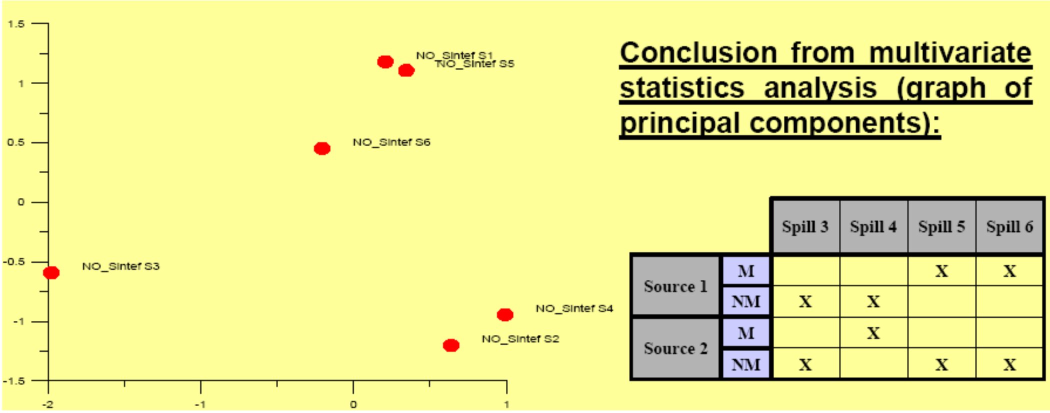
Original Conclusions
The following conclusion can be drawn from the oil comparison case study:

- The GC/FID results that the spill samples 5 and 6 were very highly exposed to weathering, hence, the sesquiterpanes can not be included in the diagnostic ratios. The ratio of the acyclic isoprenoids (area of nC17 – nC18) is also excluded as diagnostic ratio. The chromatograms of source sample 2 and spill sample 4 is visually very similar.
- The GC/MS analysis showed that the biomarkers revealed that the two source samples differ from each other. Source sample 1 is found to be positive match to spill samples 5 and 6, non-match to spill samples 3 and 4. Source 2 and spill sample 4 is found to be probably match, whereas source sample 2 is non-match to spill samples 3,5, and 6.

Source sample 1 and source sample 2: Non-match
Source sample 1: Non-match to the spill samples 3 and 4
Source sample 1: Positive match to the spill samples 5 and 6
Source sample 2: Non-match to the spill samples 3,5 and 6
Source sample 2: Probably match to spill sample 4

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4			X	X				
+3						X		
+2								
+1								
0								
-1								
-2								
-3								
-4	X	X			X		X	X

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	X
	NM	X	X		
Source 2	M		X		
	NM	X		X	X

Comments/Remarks

A correct match is found between samples 1, 5 and 6.

Following the CEN/TR (a part of) the samples should be analyzed in duplicate. Sintef has done that.

The duplicate chromatograms have to be compared. After integration the calculated ratios of the duplicates can be use to test whether:

- The variance is lower than 5%.
- Ratios should be eliminated from the final comparison.

In the Sintef report this test is not shown and discussed.

The pattern of m/z 216 shows a very good separation compared to others, probably because of the 60 m column that has been used.

Per:

The source sample 2 and spill sample 4 is reported a probably match even though there are found diagnostic ratios which are higher than the critical difference of 14%. This conclusion is based on

1.)Visual similarities of the source Sample 2 and spill sample 4

2.)The tricyclic hopanes have not been sufficiently evaluated due to their (low) robustness.

3.)Due to possible inhomogeneities in the bunker fuel

4.)SINTEF has in recent projects revealed that the tricyclics have been reported with a higher level of the critical difference than 14% even the samples by certainty came from the same source.

2.20 SE_SKL

Contact:s
Magnus Källberg and Helen Turreson
National Laboratory of Forensic Science
Chemistry and Technology
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Sweden

Organization
SKL is the only forensic laboratory in Sweden and thus all kinds of investigations are performed, mainly to assist the police. The total number of persons employed is about 240. SKL has four departments:

biology+morphology
documents+IT
drugs
chemistry+technique+weapon.

One group of nine persons is dealing with investigations related to fire, oil and environment. A big part of this is the analyses of oil samples in cases of fire-raising (e.g. gasoline and kerosene) and environmental contaminations.

SKL does not (yet) have a home page on the Internet in English, they only have information in Swedish: www.skl.polisen.se.

Sample handling
For this year's Round Robin we have been using two different methods.

For the first part of the RR2007 we applied the CEN/TR 15522-2 published in November 2006 to our newest Agilent GC-MS. The results of this part of RR2007 are reported together with instrument data in the two data files named rr2007_SE.xls (Excel file) and Swedish chromatograms RR2007.ppt (Power Point file). These two files were sent to Paul Kienhuis by email on 2007-July-17. It was easy to follow the instructions for filling in the two data files and the results were immediately presented in separate sheets in the Excel file following the raw data sheet. For making faster data analysis maybe a decision on whether to use height or area could be useful.

We did not use the results from this first investigation to make the conclusions (see page 11) in this report about the eventual identity of the oil samples from the water and the possible sources.

For the second part of the RR2007 we used the standard procedure for oil investigation at the Swedish National Laboratory of Forensic Science for comparison of the four water samples (Spill 3 to Spill 6) and the two possible source samples (Source 1 and Source 2).

The procedure is also available on CD in the SE_SKL directory

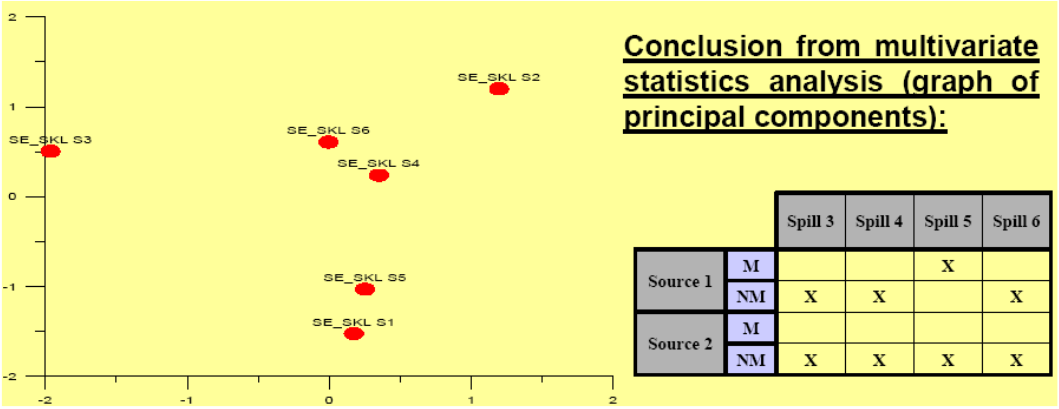
The standard procedure is basically the “Nordtest method NT CHEM 001 Edition 2” which may be found also in the Internet: www.nordicinnovation.net/nordtestfiler/chem001.pdf

After a first preliminary GC-FID run we eventually dilute or concentrate the extracts so they all will have approximately the same concentration. Most of our samples that are collected from the water are taken with a Teflon cloth, so the concentration can vary a lot.

Original Conclusions

Level	Source 1				Source 2			
	Spill 3	Spill 4	Spill 5	Spill 6	Spill 3	Spill 4	Spill 5	Spill 6
+4								
+3								
+2			X					
+1				X				
0								
-1								
-2								
-3						X		
-4	X	X			X		X	X

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M			X	
	NM	X	X		X
Source 2	M				
	NM	X	X	X	X

Comments/Remarks
The report looks good, the data show a low variance and the conclusions are according to the results of others and for spill samples 5 and 6 according to the preparation of the samples.

SKL analyses the samples three times with different masses instead of using sim sections. This is not done for the results reported in the spreadsheet file.
It would be interesting to know why SKL has concluded a +2 instead a +4 for the combination Source 1 – Spill 5. In the report a match has been concluded.

2.21 US_OSPR

Contact:

Susan Sugarman and David Hostetter
California Department of Fish and Game
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Petroleum Chemistry Lab
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USA

Organization

The Office of Spill Prevention and Response (OSPR), the pollution division of the Department of Fish and Game, is the lead State agency in charge of California's oil spill prevention, preparedness, response, and natural resource restoration. The 1989 Exxon-Valdez oil spill in Alaska prompted many government agencies to review their ability to respond to major oil spills. The 1990 American Trader spill off Orange County increased the pressure on California's legislature to ensure this state's capabilities. As a result, the OSPR was established by the Lempert-Keene-Seastrand Oil Spill Prevention and Response Act (The Act). The Act passed in September of 1990, followed by the federal Oil Pollution Act (OPA-90) in October. The Act gives the OSPR administrator substantial authority to direct all oil spill prevention, response and clean-up activities, natural resource damage assessment (NRDA) and restoration, as well as the authority to conduct studies and incorporate the findings into spill prevention and response programs throughout California.

Sample handling

These samples were analyzed "as received" with no sample preparation performed other than dilution. Instructions for the OSIRR 2007, were to compare the spill samples with the source samples using our normal analytical method and send a report.

Our normal analytical method includes specific sample preparation methods which are selected by the type of investigation, number and type of samples received and the expected time the results are needed. For example, during a response to a spill, time to perform multiple analyses used to characterize or fingerprint samples is a critical element during the response. A "whole sample" is often analyzed to provide information to be used immediately by field personnel during the spill response. Collected samples are extracted into methylene chloride and diluted to obtain a concentration of 25. mg/ml followed by analysis by our gas chromatography/mass spectrometry (gc/ms) method PHP51. This is followed later by a more comprehensive sample preparation which includes extraction into methylene chloride, a clean-up step, followed by fractionating the whole extract into 2 fractions; an aliphatic fraction and aromatic fraction, which are subsequently analyzed by gc/ms method PHP51a for aliphatics and PHP51b for aromatics.

Samples were analyzed with GCMS in scan mode from 40-500 m/z.

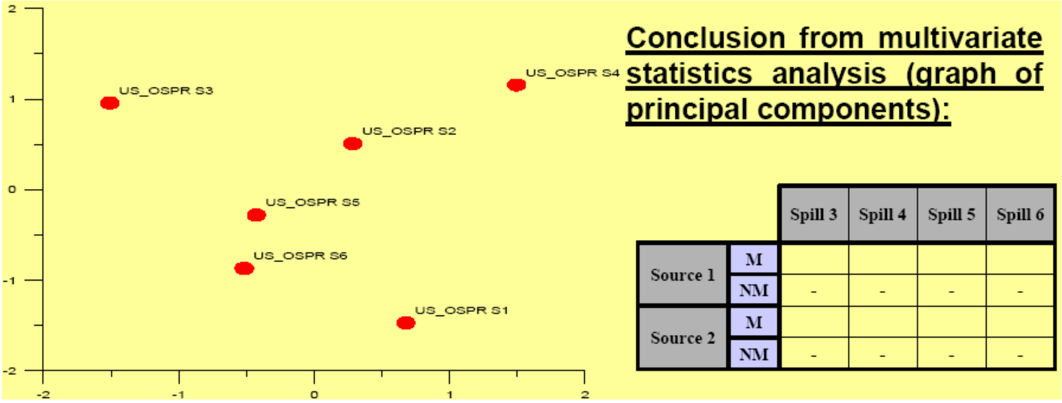
Original Conclusions

OSPR has send in photos of the sample envelop, the enclosed letter and in pdf format a custody report and a sample information and analysis report.
The sample information and analysis report describes the findings and conclusions for each sample. The results for source 1 and 2 are shown:

LAB NUMBER: 1 SAMPLER: Bonn-OSINET
DATE: MATRIX: 100mg/ml DCM solvent
TIME: CONTAINER: glass vial
LOCATION:
LABEL INFO: 1 - Source 1, round robin 2007, Oil comparison RIZA (NL)
SAMPLE ANALYSIS: Sample S-0 17-07-1 was analyzed by GCMS for petroleum hydrocarbon characterization and fingerprint comparison to samples S-017-07-3,4, 5, and 6 using PCL method PH5 1. This method incorporates quality control and quality assurance procedures to assure stable and consistent analytical system response for valid fingerprint comparison.
PETROLEUM HYDROCARBON CONFIRMATION: Petroleum hydrocarbons were confirmed.
PETROLEUM HYDROCARBON FINGERPRINT COMPARISON: Sample S-0 17-07- 1 is, in my opinion, consistent with sample S-0 17-07-5 (Spill 5) and S-0 17-07-6 (Spill 6) and a common source. Sample S-0 17-07-1 is, in my opinion, not consistent with sample S-0 17-07- 2 (Source 2), S-017-07-3 (Spill 3) or S-017-07-4 (Spill 4). This sample will be entered in the Petroleum Hydrocarbon Library for further study and comparison.

LAB NUMBER: 2 SAMPLER: Bonn-OSINET
DATE: MATRIX: 100mg/ml DCM solvent
TIME: CONTAINER: glass vial
LOCATION:
LABEL INFO: 2-Source 2, round robin 2007, Oil comparison RIZA (NL)
SAMPLE ANALYSIS: Sample S-017-07-2 was analyzed by GCMS for petroleum hydrocarbon characterization and fingerprint comparison to samples S-017-07- 1,3,4,5, and 6 using PCL method PH5 1. This method incorporates quality control and quality assurance procedures to assure stable and consistent analytical system response for valid fingerprint comparison.
PETROLEUM HYDROCARBON CONFIRMATION: Petroleum hydrocarbons were confirmed.
PETROLEUM HYDROCARBON FINGERPRINT COMPARISON: Sample S-017-07-2 is, in my opinion, consistent with sample S-017-07-4 (Spill4) and a common source. Sample SO 17-07-2 is, in my opinion, not consistent with sample S-O 17-07-1 (Source I), S-O 17-07-3(Spill3), S-017-07-5 (Spill 5) or S-017-07-6 (Spill 6). This sample will be entered in the Petroleum Hydrocarbon Library for further study and comparison.

PCA plot



Conclusion from multivariate statistics analysis (graph of principal components):

		Spill 3	Spill 4	Spill 5	Spill 6
Source 1	M				
	NM	-	-	-	-
Source 2	M				
	NM	-	-	-	-

Comments/Remarks

Susan and David have made an interesting evaluation report with their findings of the samples spreadsheet file and ratio comparison.
Some parts of the text

The percentage weathering plot, while interesting, did not provide assistance to David or I in ascertaining weathering or homogeneity. We do not have experience using this type of plot, so while it may be useful to others, we did not find it particularly helpful. The PCL fingerprint method is a scan method, not a sim method. It is likely that more precision than our data provided could be produced with a sim method and would be required to provide a more useful plot.

The spreadsheet file of US_OSPR contains a area/height table on the results sheet that shows that the variation is much higher than for labs like SE_SKL, NL_NFI. As a result the PW-plot of e.g. 1-5a shows a lot of scattering making it less useful to estimate weathering. The higher variation is probably caused by the full scan method and is visible in the chromatograms.

It is our hope that the BONN group will benefit from the data generated in your ongoing effort to develop a searchable database for petroleum fingerprint matching and that the CDFG-OSPR-PCL will also be able to benefit from this collaborative effort through the sharing of results.

BSH and RIZA work together on a database called COSI, developed and constantly improved by Gerhard Dahlmann. It is one of the options to build a database for oil spill identification. More information can be found on
http://www.bsh.de/de/Meeresdaten/Umweltschutz/Oelidentifizierung/Oeldatenbank.ppt

Selected Ion Selected Peaks Ratio Comparisons Versus Selected Ion Total Response Comparisons — Any method that involves the selection of selected ion peaks to calculate ratios that can prove useful for discriminating between source samples will always be weaker than a method that takes into account the total selected ion response within the selected time window for each compared oil sample. When an extracted ion chromatogram is examined visually, the complete response within the selected time window is being observed. There is a great potential, in a non-visual method using pre-selected constituents in an oil sample to measure, ratio and compare, to miss significant differences between two oil samples.

The ratio calculation is a means to reduce the personal interpretation of the chromatograms. It is however a step in the process to come to a conclusion according to CEN/TR. At the end of each comparison all information including all ion chromatograms must be checked.

3. Interlaboratory results

3.1 Nomenclature and blending

3.1.1. Oil type

The participants were asked to identify the samples on type of oil
The results are listed in Table 1

Participant	Source 1	Source 2	Spill 3	Spill 4	Spill 5	Spill 6
AU_EC_CES	HFO	HFO	HFO	HFO	weathered HFO	weathered HFO
AU_NSWDECC	HFO	HFO	HFO	HFO	weathered HFO or crude oil	weathered HFO or crude oil
BR_Petrobas	HFO	HFO with lub oil	HFO	HFO with lub oil	HFO	HFO
CA_EC_ALET	HFO, weathered HFO or weathered crude	HFO, weathered HFO or weathered crude	HFO, weathered HFO or weathered crude	HFO, weathered HFO or weathered crude	weathered HFO, weathered bunker or weathered crude	weathered HFO, weathered bunker or weathered crude
CA_ESTD	HFO	HFO	HFO	HFO	HFO	HFO
CA_PESC_EC	heavy crude or bunker oil	heavy crude or bunker oil	weathred crude oil	weathred crude oil	weathered heavy crude or bunker oil	weathered heavy crude or bunker oil
CN_NCSEMC	refined oil	refined oil	refined oil	refined oil	refined oil	refined oil
DE_BSH	HFO	HFO	HFO	HFO	HFO	HFO
EE_EERC	HFO	HFO	HFO	HFO	HFO	HFO
ES_CEDEX	HFO	HFO	HFO	HFO	HFO	HFO
ES_CSIC	HFO	HFO	HFO	HFO	HFO	HFO
FI_NBI	HFO	HFO	HFO	HFO	HFO	HFO
FR_CEDRE	HFO	HFO	HFO	HFO	HFO	HFO
LV_LVA	no indication	no indication	no indication	no indication	no indication	no indication
NL_NFI	HFO	HFO	HFO	HFO	?	?
NL_RIZA	HFO	HFO	HFO	HFO	HFO	HFO
NO_Sintef						
SE_SKL	HFO	HFO and possibly also lub. oil	HFO	HFO and possibly also lub. oil	HFO	HFO
US_OSPR	no indication	no indication	no indication	no indication	no indication	no indication

Table 1
Sample identification of the participants

Most of the participants concluded that the samples contain heavy fuel oil(HFO). Source 1 and 2 come from the fuel tanks of the Vicky and the Tricolor so this conclusion is correct for these two samples. Spill 5 and 6

are artificial weathered from Source 1 and therefore are also heavy fuel oil samples. The origin of Spill 3 and 4 is unknown, but the properties point also to HFO (see CEN/TR annex H4 for a lot of analytical information about HFO).
Several participants didn't make a difference between heavy fuel oil and crude oil. As most heavy fuel oils contain residues of a cracking process in the refinery, the patterns of the methyl-phenanthrenes are different compared to crude oils. Additionally the presence of methyl-anthracene and the absence of retene are indications for HFO.

Steve Fuller of AU_NSWDECC has indicated HFO for the samples 1 to 4 and weathered HFO or crude oil for the samples 5 and 6. But even after the heavy evaporation of sample 6(relative reduction of the two first eluting compounds) the methyl-phenathrenes pattern is typical for HFO (Fig 25).

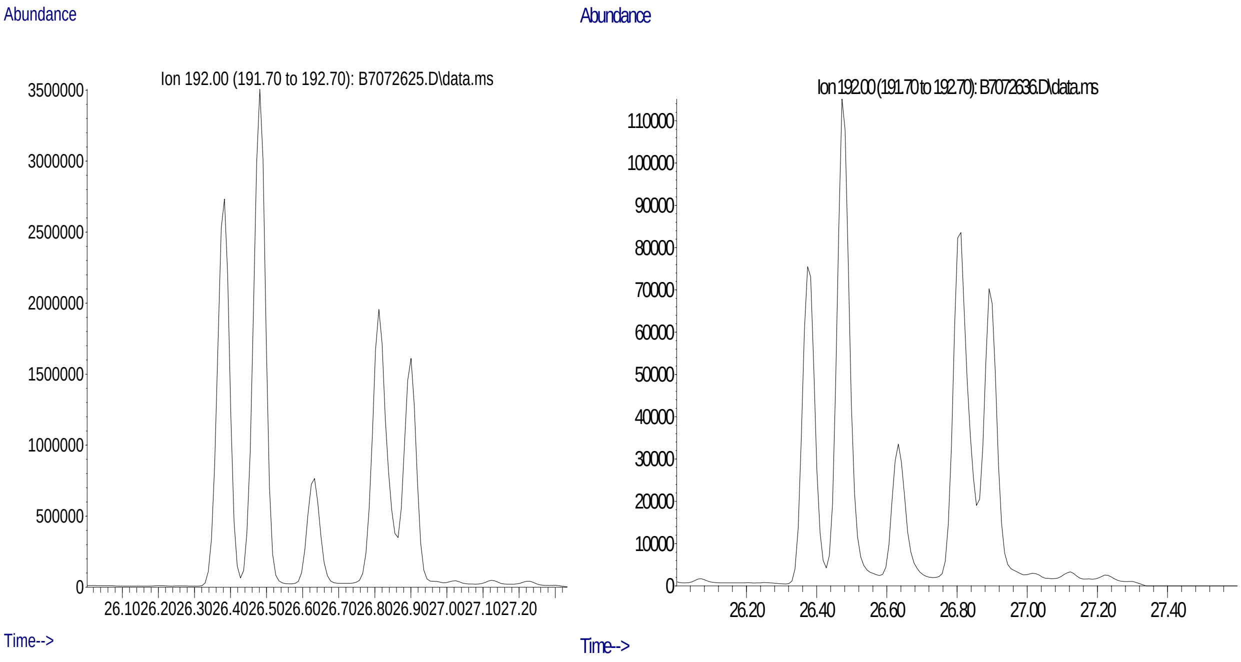


Fig 25
M/z 192 chromatograms of source sample 1 (left) and spill sample 6 (right)

Rene Losier (CA_EC_ALET) indicated weathered HFO, weathered bunker or weathered crude oil for samples 5 and 6. Below some information of wikipedia about the meaning of bunker oil, fuel oil and heavy fuel oil:

http://en.wikipedia.org/wiki/Fuel_oil
Bunker fuel is technically any type of fuel oil used aboard ships. It gets its name from the containers (known as Bunker Tanks) on ships and in ports that it is stored in, called bunkers. Bunker A is No. 2 fuel oil, bunker B is No. 4 or No. 5 and bunker C is No. 6. Since No. 6 is the most common, "bunker fuel" is often used as a synonym for No. 6. No. 5 fuel oil is also called navy special

fuel oil or just navy special, No. 6 or 5 are also called furnace fuel oil (FFO); the high viscosity requires heating, usually by a reticulated low pressure steam system, before the oil can be pumped from a bunker tank. In the context of shipping, the labeling of bunkers as previously described is rarely used in modern practice.

Fuel oil in the United States is classified into six classes, according to its boiling temperature, composition and purpose. No. 5 fuel oil and No. 6 fuel oil are called residual fuel oils (RFO) or heavy fuel oils. As far more No. 6 than No. 5 is produced, the terms heavy fuel oil and residual fuel oil are sometimes used as synonyms for No. 6. They are what remains of the crude oil after gasoline and the distillate fuel oils are extracted through distillation. No. 5 fuel oil is a mixture of No. 6 (about 75-80%) with No. 2. No. 6 may also contain a small amount of No. 2 to get it to meet specifications. Residual fuel oils are sometimes called light when they have been mixed with distillate fuel oil, while distillate fuel oils are called heavy when they have been mixed with residual fuel oil. Heavy gas oil, for example, is a distillate that contains residual fuel oil. The ready availability of very heavy grades of fuel oil is often due to the success of catalytic cracking of fuel to release more valuable fractions and leave heavy residue.

At the meeting it was concluded that the name Heavy Fuel Oil should be used to describe this product. It is applicable for both the use on board of ships as for other purposes like energy plants.

3.1.2. Blending

CSIC indicated the possibility, that a difference in the concentration of cutter stock in spill 4 compared to source 2 has caused the lower differences in biomarker patterns and higher differences in aromatic patterns between the two samples. Sintef was the opinion that the differences could be caused by possible in-homogeneities in the bunker fuel.

Concawe (http://www.concawe.be , product dossier no. 98/109 : HEAVY FUEL OILS) gives information about the composition and toxicity of HFO):

2.2. HEAVY FUEL OIL BLENDING COMPONENTS.
Heavy fuel oils can be blended from a wide range of refinery components, the most important of which are:
Long residue: the residue from the atmospheric distillation of crude oil. As mentioned earlier, historically this was a major fuel oil blending component, but it is now mainly used as a feedstock for the vacuum distillation unit or for a thermal or catalytic cracking unit.
Short residue: the residue from the vacuum distillation of crude oil.
Thermal cracker or visbreaker residue: the residue from thermal cracking processes designed to increase the yield of distillate components from atmospheric and vacuum residues.
Cat cracker slurry oil (clarified oil): a heavy fraction from a catalytic cracking operation, a process for the conversion of heavy hydrocarbon fractions into highquality gasoline components.

Thermally cracked or visbreaker gas oil: a middle distillate fraction from thermal cracker or visbreaker units.
Cat cracker cycle oil: a middle distillate fraction from the catalytic cracking unit.
Kerosine: a lighter middle distillate fraction from the atmospheric column.
Gas oil: a heavier middle distillate fraction from the atmospheric column.
Vacuum gas oil: a heavy gas oil fraction from the vacuum column.

http://en.wikipedia.org/wiki/Visbreaker gives information about a visbreaker:

A visbreaker is a processing unit in oil refinery whose purpose is to reduce the quantity of residual oil produced in the distillation of crude oil and to increase the yield of more valuable middle distillates (heating oil and diesel) by the refinery. A visbreaker thermally cracks large hydrocarbon molecules in the oil by heating in a furnace to reduce its viscosity and to produce small quantities of light hydrocarbons (LPG and gasoline). The process name of "visbreaker" refers to the fact that the process reduces (i.e., breaks) the viscosity of the residual oil. The process is non-catalytic.

The Chevron paper “Everything you need to know about Marine Fuels” gives information about marine fuels. It is a very interesting paper describing the production, use and specifications of marine fuels. It is added to the literature provided with RR2007, but can also be found on the internet.
The paper describes that IFO-380 is made by the refinery and suggests that lower IFO grades are blended outside the refinery:

IFO-380
This grade is usually manufactured at the refinery and contains visbroken residue, HCO and LC(G)O. These three components influence the characteristics of the visbroken IF-380.
IFOs < 380 mm2/s
These grades are generally blended starting from 380 mm2/s IFOs (at 50°C), by using a suitable cutter stock (marine diesel, gasoil, LC(G)O, or a mixture of these). The blend composition has to be construed in such a way that the product stability is safeguarded, while at the same time direct or indirect density limits are fulfilled.

The paper indicates that cutter stock is a general name for light products used to blend with heavier products of the refinery.

Blending is a careful process in order to keep the asphaltenes in solution. Asphaltenes are defined as residual fuel components that are insoluble in heptane but soluble in toluene)

RIZA has received samples of a product that is described as “cutter stock/ blend material” for comparison last year. The GC-FID chromatogram and ion chromatograms of the sample can be found in the powerpoint file with the RR2007 chromatograms of RIZA.
In general: The amount of biomarkers and alkanes is very low. Alkanes are present up to C30.

In section 3.2 Fig 29 the alkane patterns of Source 2 and Spill 4 are compared, showing differences of the higher alkanes, that cannot be caused by mixing differences of the cutter stock RIZA received.
But it is very well possible that a cutter stock with a different composition is used for blending Source 2. The Chevron paper shows that different streams of different parts of the refinery are used for the blending of fuel oil, which means that also the composition will be different.
In general it can be concluded that solvents with a low viscosity, high aromatic content and low biomarker content are used to blend heavy products from the refinery into a stable fuel oil.
If the blending is not done thoroughly, concentration differences can exist in the fuel oil, leading to different chromatograms from samples from the same tank.

Blending to lower grades than IFO-380 is often done directly on board of bunker ships. The right amounts of IFO-380 and e.g. LCO are taken on board and mixed on board by pumping the mixture around before bringing it to the ships for bunkering. As this technique is difficult, it may easily happen here that the resulting lower grade HFO is not fully homogeneous.

It can be concluded that the suggestion of CSIC and Sintef that the differences are caused by a different amount of cutter stock is reasonable. E.g. the Tricolor had 8 fuel tanks on board filled with oil from two different bunkering locations. It is possible that the tanks filled at one bunker location contain slightly different oil mixtures.

3.1.3. Consequences of inhomogeneous distributions.

In oil spill identification the information above is not useful, when comparing two samples. Two samples must be identical or not.

At the workshop in Trondheim, possible explanations for the differences between source 2 and spill 4 were controversially discussed, including the possibility of inhomogeneous distributions (different amounts of cutter stocks, mixing of oil from different compartments of the ship during the salvage operation). At the end, there was agreement that nobody would swear at court that the samples originated from the same source.

Inhomogeneous distributions are in fact a sampling issue. Often one sample of one of the tanks is taken and one sample of the water. It would have been much better when all tanks of the Tricolor were sampled, even when four of them were filled at one time. Then the variation in the oil can be studied and the chance to find a matching sample increased. In CEN /TR 15522-1 is described that samples of each tank should be taken, but in practice it is often not done.

An other aspect is the fact that it is know that the Tricolor and the Vicky have spoiled oil. Also the amount of oil is know.

So if oil is found on the coast and issues like the amount of oil and backtracking are correct but the samples do not fully match, it should be considered whether an inhomogeneous distribution in the samples can be the cause for the differences.

3.2 Sample evaluation

All 6 samples contained typical Heavy Fuel Oils, which contain high aromatics in the mid-boiling region (crude oil residues were blended with cutter-stocks from the cracking-units of the refineries to achieve the proper viscosity).
Those typical clusters of the alkylated naphthalenes and phenantrenes of samples 1, 2, 3 and 4 could easily be found already in the gas-chromatograms -but rarely in samples 5 and 6 because here the mid boiling region was highly effected by evaporation. Here, GC/MS was needed to identify the product:

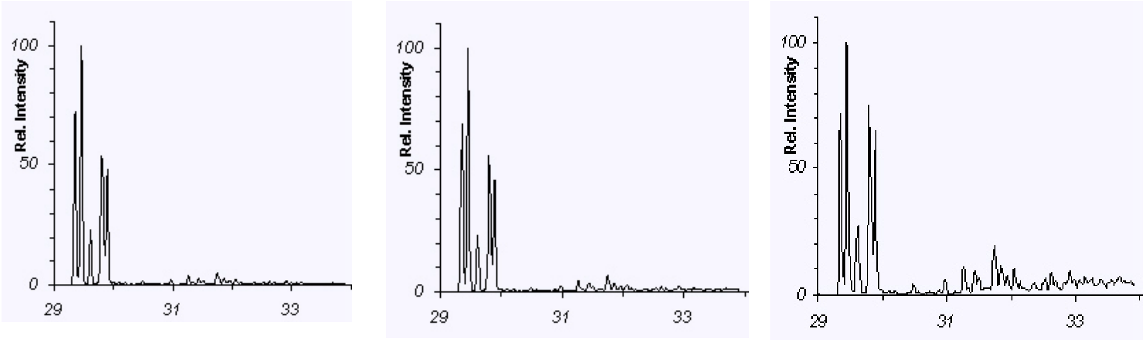


Fig 26
m/z 192, samples 1, 5 and 6

Thus, also samples 5 and 6 showed the typical M-phenantrene cluster of a corresponding HFO with a higher first doublet and a very high M-anthracene in the middle of the M-phenantrene doublets. This can never be found in a crude oil. Those aromatics originate from high temperature production (correspondingly, retene (m/z 234) could not be found in the samples, as aromatics with longer side chains are not produced in high temperature production).
But Fig. 26 also shows successive evaporation: the first M-phen-doublet becomes smaller in relation to the second one, and the Di-M-phenantrenes (maximum at about 31.8 minutes) increase relatively.
Successive evaporation of these samples could already be observed in GC-screening:

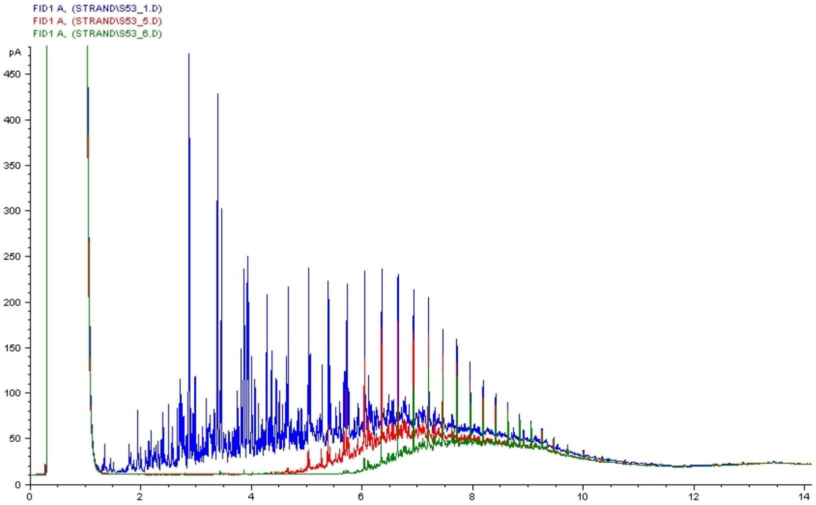


Fig 27
Gas-chromatograms of samples 1, 5 and 6

The unresolved complex mixtures (UCMs) of samples 5 and 6 are identical with sample 1, and identity could also be found, when the higher boiling biomarkers were compared.
There thus seems to be no reason not to conclude a match between sample 1 and 6 with the same level of certainty as between 1 and 5 (+4): although all aromatics (and corresponding ratios) are highly effected by evaporation, and the mere number of matching compound ratios is smaller in sample 6, all mass-chromatograms follow the general evaporation rule from left to right (as in m/z 192 (Fig. 26), similar patterns are observed in m/z 216, 234, 240 etc.). Thus, evaporation even supports here the conclusion of a "full match" between sample 1 and 6 –especially also because here a "linking sample" (sample 5) exists.
Of course, the kind of producing weathered samples could not really be realistic here.

No other signs of weathering than evaporation were found in samples 5 and 6. But about 60% evaporation in sample 5 and even about 70% evaporation in sample 6 must be regarded as very high, and would mean a relatively long time of exposure of the oil to environmental conditions. Normally during such a long time, bacterial degradation would have taken place as well as dissolution of the more solvable aromatics. Due to all experience, the more solvable M-anthracene, for example, would have decreased drastically in a "real" sample.

In addition, the remaining higher boiling biomarkers in sample 5 and 6 (compounds, which were not effected by evaporation) showed similar peak intensities as those in sample 1. If in an actual case a similar amount of oil of these 3 samples would have been weighted (as it is normally done), the intensities of those biomarker-peaks of samples 5 and 6 would have increased correspondingly to about the three- to fourfold compared to the original oil of sample 1.

As in case of the comparison of samples 1 and 6, the range of conclusions reached actually from +3 to –4, when samples 2 and 4 were compared.
Very big differences of samples 2 and 4 could have been found already in GC-screening:

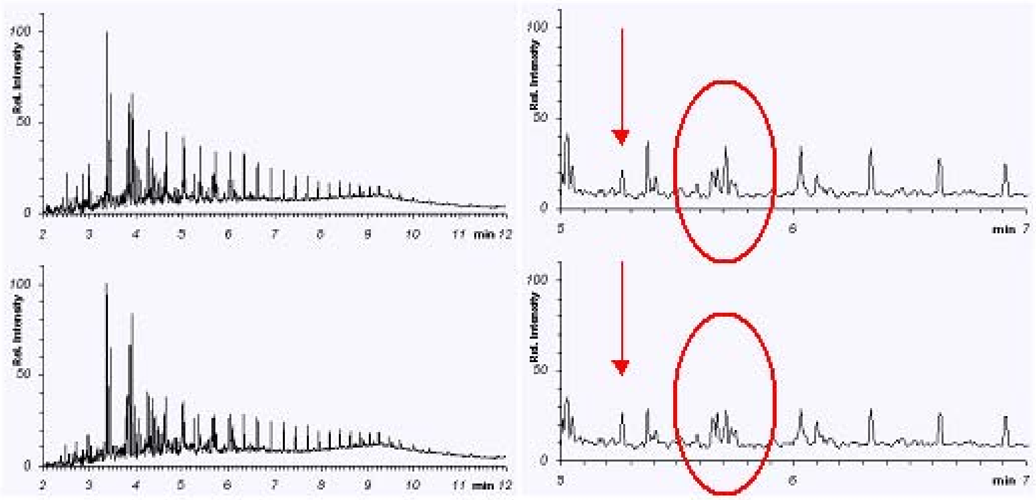


Fig. 28:
Gas-chromatograms of samples 2 (above) and 4 (sections on the right

Spill sample 4 seems to be only very slightly effected by evaporation (if at all), and the much higher amount of aromatics is obvious (phenantrene (arrow on the right side) and M-phenantrenes (circle) in relation to n-C18 and n-C19). This difference could hardly be explained, especially because sample 4 is (actually) a spill sample (By the way: such a fresh oil spill was rarely ever observed).
In addition, the n-alkan-distribution of samples 2 and 4 was different:

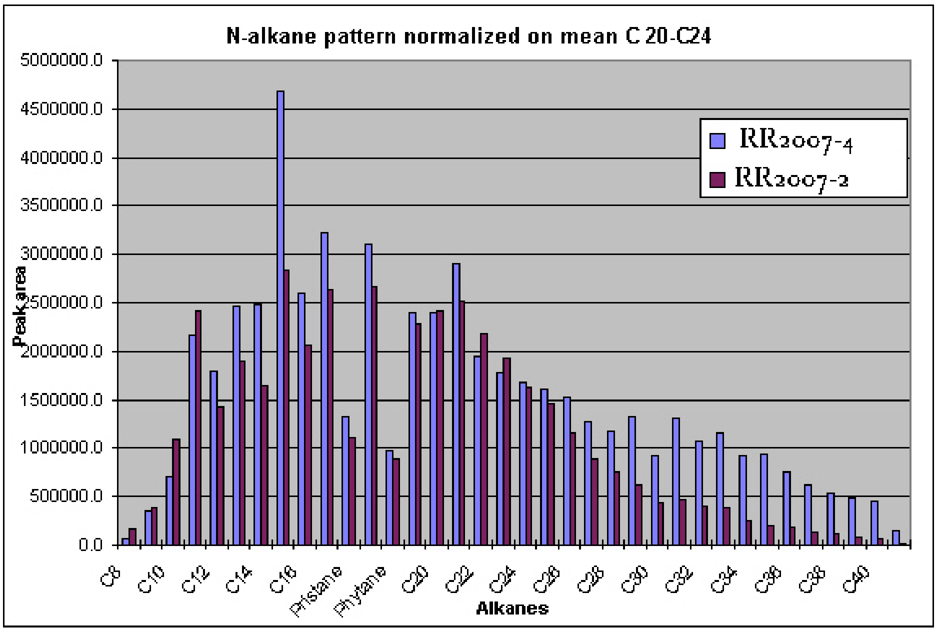
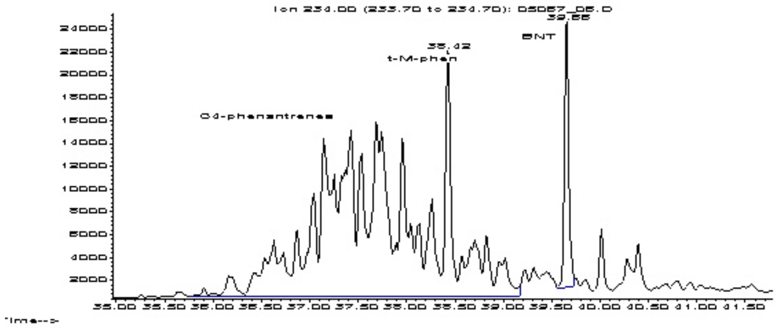


Fig. 29:
PW-plot samples 2 and 4 (RIZA,Nl,)

Conclusion by RIZA: The patterns are similar but the lower and higher alkanes are clearly different.

These results were confirmed by differences in the mass-chromatograms:



FigA **Mass chromatogram of mass 234 for source2**

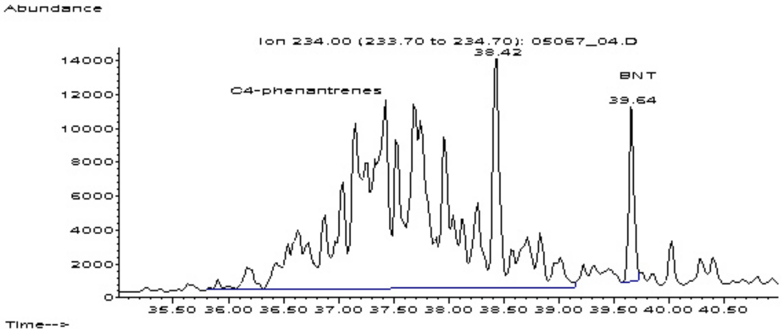


Fig. 30
Comparison of m/z 234 between samples 2 and 4 (LVGMA, Lv, showing an about 40% difference in BNT in relation to t-M-phenantrenes)

Thus, only a "non-match" can be the conclusion, when samples 2 and 4 are compared.

Of course, as the biomarkers of these two samples are at least very similar, it could be discussed that both HFOs could have been produced from a very similar or even the same crude oil. But there is no indication about the actual source of spill sample 4, when only samples 1 and 2 are at hand for comparison.

3.3 The PW plot

In the Nordtest method NT CHEM 001 (available on the CD in the directory of SE_SKL) a weathering check by means of a percentage weathering (PW) plot is described and discussed.
The PW-plot for the alkanes, analyzed by GC-FID, is discussed in section G.7 of CEN/TR 15522-2.
In an email to Susan Sugarman (US_OSPR) Gerhard has written about the PW-plot in the RR2007 spreadsheet:

We just want to test, whether such a plot may be of additional help for coming to a conclusion (i.e. for finding out, whether differences are caused by weathering).
In contrast to the Chem001-report, compound ratios of different compound groups are plotted in the excel spreadsheet into one plot.
There might be some scatter in the points, and nothing is said about the analytical error.
But in contrast to the evaluation of weathering for every single compound individually -all you know is merely that the value is lower in the spill sample- there is a sorting here in retention time, and thus roughly the boiling point. So you get roughly the information, whether it is true that compounds with lower boiling point are more effected (are more reduced) then higher boiling compounds.

So, when you look at the PW-plots you have to decide, whether there is a curve (despite the scatter of the points) or not.

Each compound (Nx) of the spill sample is presented as a percentage of the area or height of the same compound in the source sample. To compensate for concentration differences a stable compound (e.g. hopane 30ab) or the average value a series of compounds (e.g. alkanes C20 to C24 for gas oil) are used for normalization:

……

Formula to calculated each % of the PW-plots of RR2007.

% = area Nx(spill) / area Nx (source) * 100 * area 30ab (spill)/area 30ab (source).

The % values can be plotted in a graph sorted on retention time (as done in the RR2007 excel spreadsheet file) or (as mentioned in NT CHEM 001) relative to the retention times of the alkanes for comparison between laboratories with different GC temperature programs.

The PW-plot has been added to the spreadsheet of RR2007, because we have seen in previous round robins, but also in the reports of laboratories involved in the Tricolor case, that laboratories have problems to correctly assess the effects of weathering on the analytical results.
The PW plot can also be used to estimate the precision of the analytical system and integration in case it is known that the samples originate from the same source. Due to experience gained at RIZA the % of the stable compounds is generally be between 85 and 115%.

In the evaluation of the results of RR2007 this precision check was very handy to quickly get an impression of the precision of the results of each participant by looking at the PW-plots of 1-5 and 1-6.
See e.g. the PW plots shown in this report at section 2.11 and 2.12 and the PW plots shown below in Fig 31 and Fig 32:

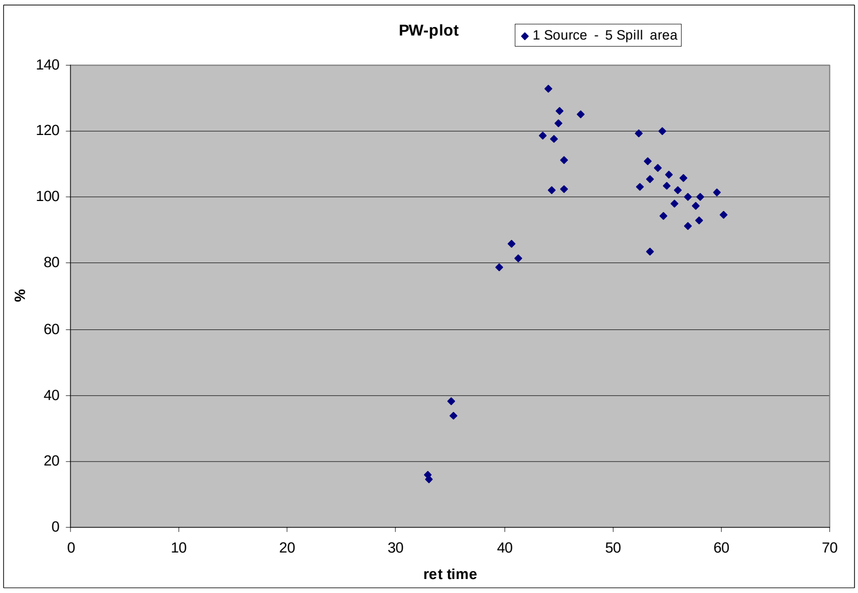


Fig. 31
PW-plot of 1-5a based on full scan analyses showing a higher variance

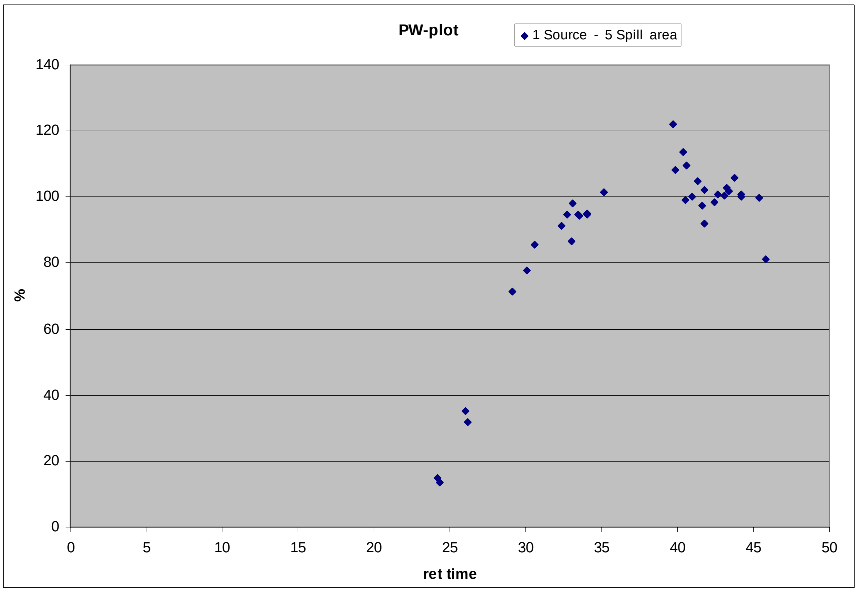


Fig.32
PW-plot of 1-5a of based on SIM analyses showing a lower variance with two exceptions representing ratios calculated from very small peaks.

The PW plot of Fig 32 shows that compounds with a retention time less than 31 min are influenced by weathering.

At RIZA even more compounds than mentioned in the CEN/TR to calculated the diagnostic ratios are integrated. To improve the “readability” of the graph, PAH’s and biomarkers have a different color.

When a sample is analyzed in duplicate all results should theoretically be 100%. Differences are caused by the variance of the analytical system and by the variance in integration. The highest value of 116% shown in Fig 33 represents C28(22R). For the rest all ratios are between 85 to 115%.

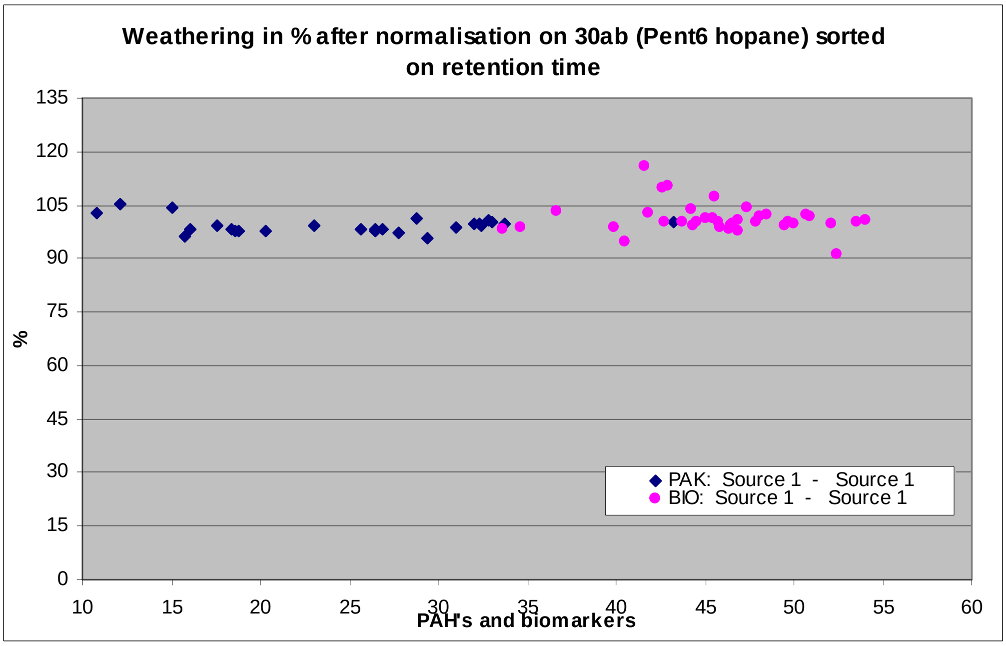


Fig 33
Pw plot of a duplicate analysis of source 1 analyzed by NL-RIZA.

RIZA PW plots of 1-5a and 1-6a are shown in section 2.18.

It can be concluded that the PW plots of the GCMS results are very useful to find out whether observed differences in ratios are caused by weathering or not.

3.4 Conclusions and conclusion definitions

In principle, oil samples are either identical or they are not (or they match or do not match).
But oil spill cases vary widely in possible explanations for why a clear determination cannot be made: the spilled oil may be excessively weathered and/or contaminated. Another complicating factor may be a very little amount of oil in the sample. In addition, some sources are highly inhomogeneous, and a sample of such a spill may not reflect the composition of the product remaining in such a source.

In CEN/TR 15522-2 four conclusion definitions are used:
positive match, probably match, inconclusive and non-match.
The positive match, inconclusive and non-match are easily to under stand conclusions for a layman in oil spill identifications and easily to assign by the oil identification expert.
The probably match is a non-match situation for ratio comparison. Especially this conclusion needs additional text to explain the reason why it is chosen. Even then it is often questionable, what the value of the conclusion is.

Another approach to give conclusions is the probability table commonly used by forensic institutes. Rene de Bruyn (NL-NFI) has paid attention to this approach in his report and added two papers as annex. The papers can be found on the CD in the NL_NFI directory.

In RR2007 we have asked the participants to use both the CEN/TR conclusions and the table applied by the forensic institute SE_SKL. The table is explained in the letter **conclusion definitions** (email dated 12-6-07). The results of all participants are shown in Table 2 and summarized in Table 3.

Participant	So1_Sp3	So1_Sp4	So1_Sp5	So1_Sp6	So2_Sp3	So2_Sp4	So2_Sp5	So2_Sp6
AU_EC_CES	NM	NM	M	PbM	NM	NM	NM	NM
AU_NSWDECC	NM	NM	PbM	NM	NM	NM	NM	NM
BR_Petrobas	NM -4	NM -4	M +4	M +4	NM -4	PbM +2	NM -4	NM -4
CA_EC_ALET	NM -3	NM -3	M +2	M +2	NM -3	Inc -1	NM -3	NM -3
CA_ESTD	NM -4	NM -4	PbM +3	PbM +2	NM -3	PbM +3	NM -4	NM -4
CA_PESC_EC	-3	-3	+2	+2	-3	+1	-3	-3
CN_NCSEMC	NM -4	NM -4	PbM +3	NM -2	NM -4	PbM +2	NM -4	NM -4
DE_BSH	NM -4	NM -4	M +4	M +4	NM -4	NM -4	NM -4	NM -4
EE_EERC	NM -4	NM -4	M +4	NM -2	NM -4	PbM +3	NM -2	NM -3
ES_CEDEX	NM	NM	M	M	NM	M	NM	NM
ES_CSIC	NM -4	NM -4	M +4	M +4	PbNM -3	PbM +3	NM -4	NM -4
FI_NBI	Inc 0	NM -3	PbM	Inc 0	Inc 0	PbM +2	NM -3	NM -3
FR_CEDRE	-4	-4	3	-4	-4	2	-4	-4
LV_LVA	NM -2	NM -2	M +4	NM -1	NM -3	PbM +1	NM -3	NM -1
NL_NFI	-4	-4	3	-4	-4	-4	-4	-4
NL_RIZA	NM -4	NM -4	M +4	M +3	NM -4	NM -4	NM -4	NM -4
NO_Sintef	NM -4	NM -4	M +4	M +4	NM -4	PbM +3	NM -4	NM -4
SE_SKL	-4	-4	+2	+1	-4	-3	-4	-4
US_OSPR	NM	NM	M	M	NM	M	NM	NM

Comparison level assignment according to CEN /TR 15522-2

NM= non match — Inc = inconclusive — M = match

PbNM = possible non-match — PbM = probable match

Comparison level assignment according to SKL (Sweden)

+4 to -4

Table 2
Overview of the results of all participants.

Match	+2 to +4
Probable match	+1 to +3
Inconclusive	0
Probable non-match	-3
Non-match	–1 to -4

Table 3
Summary of Table 2 for the conclusion definitions versus level assignment

It can be concluded that for the SE-SKL method more guidance would be useful. In the letter **conclusion definitions** an approach has been given in annex 4 of the letter. A summary of this approach is listed in Table 4:

Level	
+4	Positive match. The findings show with certainty that …….
+3	Probable match. The findings strongly indicate that ……
+2	Probable match. The findings indicate that ……
+1	Probable match. The findings point to some extent towards that ……
0	Inconclusive
-1	Probable non-match. The findings point to some extent towards that…..was not….
-2	Probable non-match The findings indicate that …..was not….
-3	Probable non-match The findings strongly indicate that….was not …
-4	Non-match The findings show with certainty that … was not…

Table 4
Combination of the probability level indication and the CEN/TR conclusion definitions.

The conclusion definitions have been discussed several times during the workshop, but it was not possible to come to a conclusion

Working group 5 will work further on this issue

3.5 Sample handling before injection.

Most labs have analyzed the samples as received. After dilution with DCM or another appropriate solvent in general 1 µl at a concentration of 10 mg/ml has been injected.
RIZA noticed for the GC-FID analyzes an increase of the baseline and a different pattern of the last eluting alkanes for the alkanes standard. (see section 2.18 Fig 12).
During the Tricolor case BE_MUMM has analyzed many samples, but always after a cleanup. The RR2007 samples however have been analyzed directly without dilution with an injection volume of 3 µl. As a result the chromatograms were very bad and Patrick Roose decided not to report the results.
Three labs (BR_Petrobas; CA_EC_ALET; CA_PESC_EC,) separated the samples in aliphatic and aromatic fractions and analyzed the samples after adding an internal standard. This procedure is described by Br_Petrobas in section 2.4.
The internal standards are used to calculate the concentration of compound and compound groups in the original oil.
As a result a PW plot should be based on area or height after correction of the end volumes of the fractions or by the area or height values of the internal standards. Else a strange plot will be created with different concentrations for the PAH's and biomarkers. (see Fig 34)

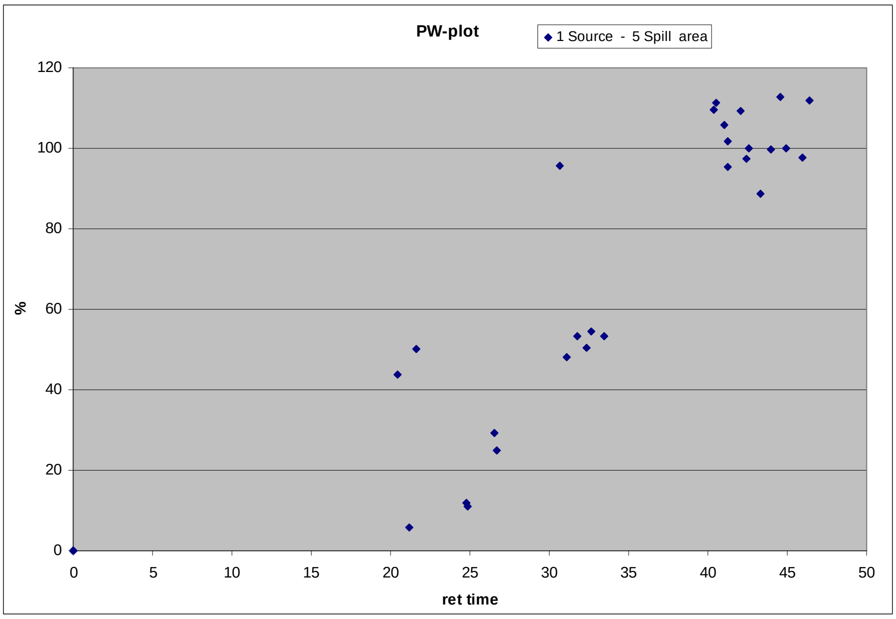


Fig 34
PW plot of CA_PESC_EC based on samples separated in aromatic and aliphatic fractions but normalized on hopane 30ab

This is caused by the normalization on hopane 30 ab in the spreadsheet template provided with RR2007

At the workshop two issues have been discussed in detail:

3.5.1. Cleanup

In CEN/TR 15522-2 section 5.4.1 it is **advised** to cleanup HFO samples to remove the high amount of asphalthenes.
It has been decided that the text in the guideline must be changed in **prescribed** because deterioration of the column can influence the final results.
The cleanup method described in the guideline makes use of a silica column. The oil sample is dissolved in hexane and after bringing an aliquote on the column, eluted with hexane. Due to the experience of several participants hexane is not able to elute the aromatic compounds completely from the silica column. At least a mixture of hexane with 10% of DCM or more should be used.

Working group 1 will study this issue

3.5.2. Fractionation.

Fractionation of the samples in an aliphatic and an aromatic part has the advantage that the chromatograms are cleaner and the compounds more easier to find and integrate. When an ion trap is used for the detection, it is even advised to perform a cleanup in order to reduce the total amount of compounds entering the detector. It reduces quenching of the smaller peaks, like the biomarkers.

The amount of labor is limited, because it can be combined with the cleanup, but the time needed for analysis is doubled.

A disadvantage is the introduction of extra variation in the results.
It is influenced by:

- the type of silica used
- the humidity of the silica
- the total amount of sample on the column
- the flow, amount and composition of the extraction solvent
- the variation in the end volumes after separation. The addition of internal standards can reduce this variation.

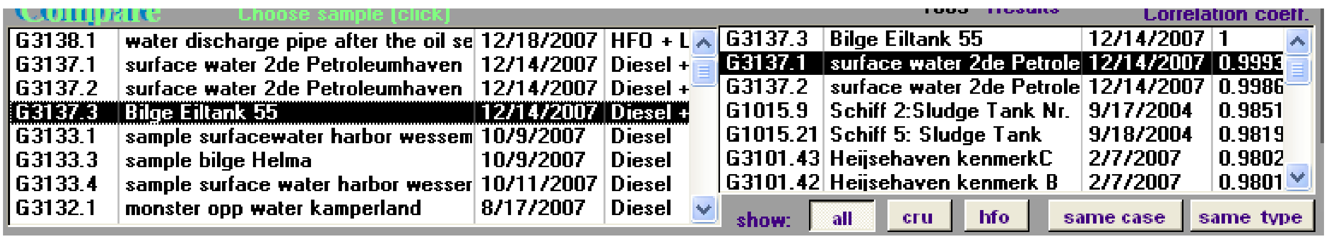
The separation of such a range of different compounds will lead to separation of a part of the compounds over both fractions. This will also be influenced by the issues mentioned above.

Working group 1 will study this issue

3.6 Multivariate statistics.

In CEN/TR 15522-2 (2006) all ratios are compared individually (univariate comparison). Multivariate statistics are shortly mentioned in section 6.4.4.
The advantage of multivariate statistics is the ability to compare a large number of samples on a series of parameters.

When applied on a large number of samples multivariate statistics can be very important, because an impression of the uniqueness of a sample may be achieved.
E.g RIZA and BSH use a common database, that contain now more than 1000 samples. Compound ratios are used to calculate the best fit by means of correlation analysis. In addition, ratios can be compared individually, and a visual comparison of the mass-chromatograms is possible.
An example with 3 samples of case G3137 is given in Fig 35 and 36



G3138.1	water discharge pipe after the oil se	12/18/2007	HFO + L
G3137.1	surface water 2de Petroleumhaven	12/14/2007	Diesel +
G3137.2	surface water 2de Petroleumhaven	12/14/2007	Diesel +
G3137.3	Bilge Eiltank 55	12/14/2007	Diesel +
G3133.1	sample surfacewater harbor wessem	10/9/2007	Diesel
G3133.3	sample bilge Helma	10/9/2007	Diesel
G3133.4	sample surface water harbor wesser	10/11/2007	Diesel
G3132.1	monster opp water kamperland	8/17/2007	Diesel

G3137.3	Bilge Eiltank 55	12/14/2007	1
G3137.1	surface water 2de Petrole	12/14/2007	0.9993
G3137.2	surface water 2de Petrole	12/14/2007	0.9986
G1015.9	Schiff 2:Sludge Tank Nr.	9/17/2004	0.9851
G1015.21	Schiff 5: Sludge Tank	9/18/2004	0.9819
G3101.43	Heijsehaven kenmerkC	2/7/2007	0.9802
G3101.42	Heijsehaven kenmerk B	2/7/2007	0.9801

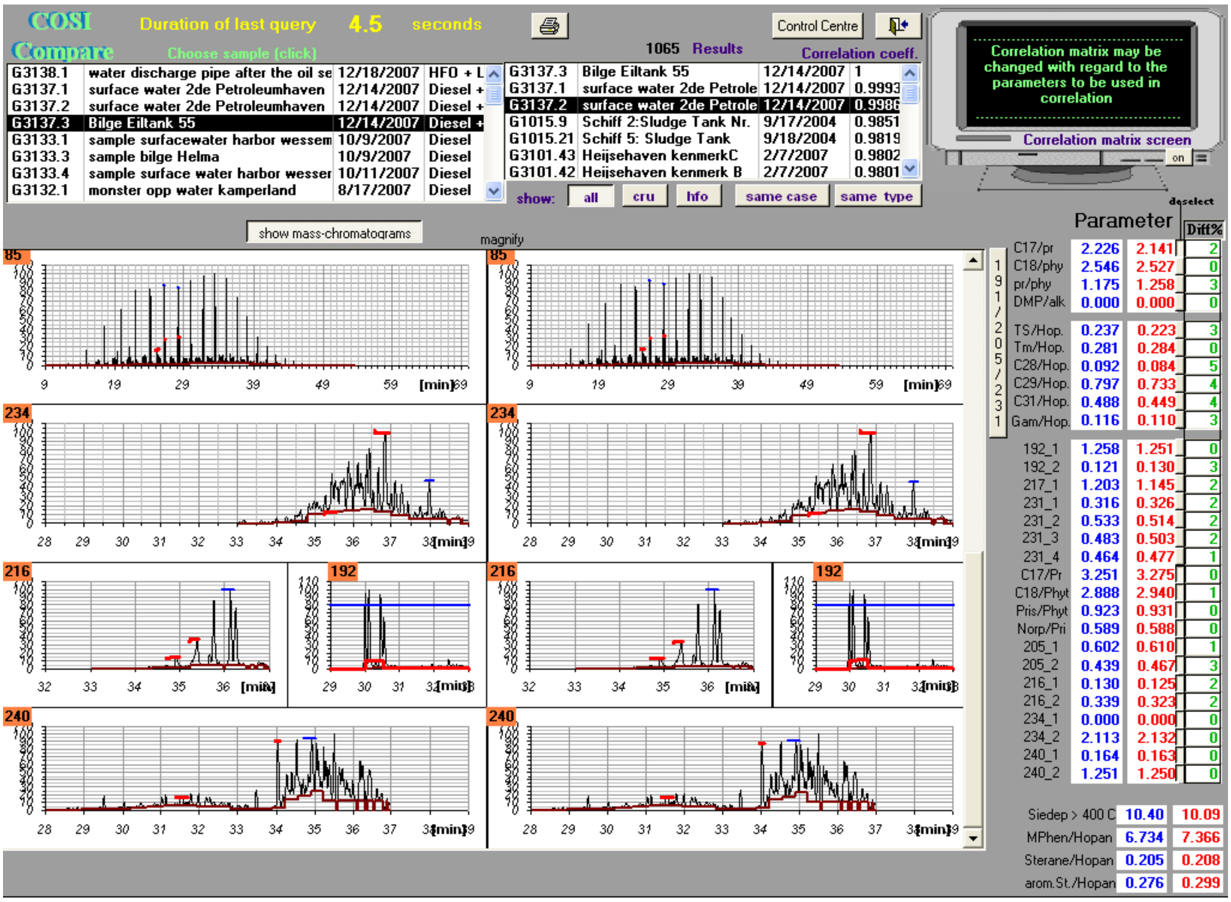
. . . .

Fig 35
A search in the COSI database on sample 3 of case G3137 (left table) results is a best fit for the samples 1 and 2 of case G3137 (right table)

When a sample in the left table of Fig. 35 is selected, the database comes with the best comparing samples in the right table, sorted on the correlation coefficient (most right column of Fig. 35).
Most similar to bilge sample 3 is surface water sample 1 of the same case and next sample 2 of the same case. The third most similar sample is from another case and the correlation coefficient (right column) shows a much larger difference.
The next step is to compare the ratios of the samples 3137_3 and 3137_1 and to check the chromatograms visually. This is shown in Fig 36
The blue and red columns at the right side represent the ratios of sample 3137_3 (blue) and 3137_1. The green column shows the difference between the blue and red values divided by the mean in %. The differences are far below 14%, showing a very high similarity. The same result was found for sample 3137_2.

The next best fit is sample 1015_9. This sample shows several larger differences with sample 3137_3. 13 of the ratios are > 14%.
As a result it can be concluded that:

- bilge sample 3137_3 is very similar to samples 3137_1 and _2.
- the samples of case 3137 are unique compared to all other samples in the database.



G3138.1	water discharge pipe after the oil se	12/18/2007	HFO + L
G3137.1	surface water 2de Petroleumhaven	12/14/2007	Diesel +
G3137.2	surface water 2de Petroleumhaven	12/14/2007	Diesel +
G3137.3	Bilge Eiltank 55	12/14/2007	Diesel +
G3133.1	sample surfacewater harbor wessem	10/9/2007	Diesel
G3133.3	sample bilge Helma	10/9/2007	Diesel
G3133.4	sample surface water harbor wesser	10/11/2007	Diesel
G3132.1	monster opp water kamperland	8/17/2007	Diesel

			Correlation coeff.
G3137.3	Bilge Eiltank 55	12/14/2007	1
G3137.1	surface water 2de Petrole	12/14/2007	0.9993
G3137.2	surface water 2de Petrole	12/14/2007	0.9986
G1015.9	Schiff 2:Sludge Tank Nr.	9/17/2004	0.9851
G1015.21	Schiff 5: Sludge Tank	9/18/2004	0.9819
G3101.43	Heijsehaven kenmerkC	2/7/2007	0.9802
G3101.42	Heijsehaven kenmerk B	2/7/2007	0.9801

Parameter			Diff%
C17/pr	2.226	2.141	2
C18/phy	2.546	2.527	0
pr/phy	1.175	1.258	3
DMP/alk	0.000	0.000	0
TS/Hop.	0.237	0.223	3
Tm/Hop.	0.281	0.284	0
C28/Hop.	0.092	0.084	5
C29/Hop.	0.797	0.733	4
C31/Hop.	0.488	0.449	4
Gam/Hop.	0.116	0.110	3
192_1	1.258	1.251	0
192_2	0.121	0.130	3
217_1	1.203	1.145	2
231_1	0.316	0.326	2
231_2	0.533	0.514	2
231_3	0.483	0.503	2
231_4	0.464	0.477	1
C17/Pr	3.251	3.275	0
C18/Phyt	2.888	2.940	1
Pris/Phyt	0.923	0.931	0
Norp/Pri	0.589	0.588	0
205_1	0.602	0.610	1
205_2	0.439	0.467	3
216_1	0.130	0.125	2
216_2	0.339	0.323	2
234_1	0.000	0.000	0
234_2	2.113	2.132	0
240_1	0.164	0.163	0
240_2	1.251	1.250	0
Siedep > 400 C	10.40	10.09	
MPhen/Hopan	6.734	7.366	
Sterane/Hopan	0.205	0.208	
arom.St./Hopan	0.276	0.299	

Fig 36
Comparison of sample 3 with sample 1. The chromatogram are individually compared while to the right a number of ratios are compared. The low values of the % difference between the ratios indicate a match.

During the workshop Maria Plaza showed some PCA plots of the ES_CEDEX results. The plots were made in the program **Statistica 6.0** On request of the meeting she has taken the effort to make plots of the results of all participants. These are shown in chapter 2.
Maria has also made **match** and **non-match** conclusions based on the results of the PCA-plots. These conclusions are solely based on the PCA test by using the criterion of relative distances:

About the conclusions of the statistical analysis, we have made a geometric representation of the statistical results, but for this conclusions we have not defined a metric in which to base the quantitative criterion. Our conclusions are based on the criteria of relative distances. The establishment of a critical difference would require the definition of an absolute metric based on the standard deviation of the principal components (Multidimensional Normal Distribution).

All plots and some extra comparisons are combined in the file **MultivariateStatistic.pdf** which can be found in the ES_CEDEX directory.

Maria has also made plots based on all individual results (Fig 37) and after averaging all results for each sample (Fig 38).

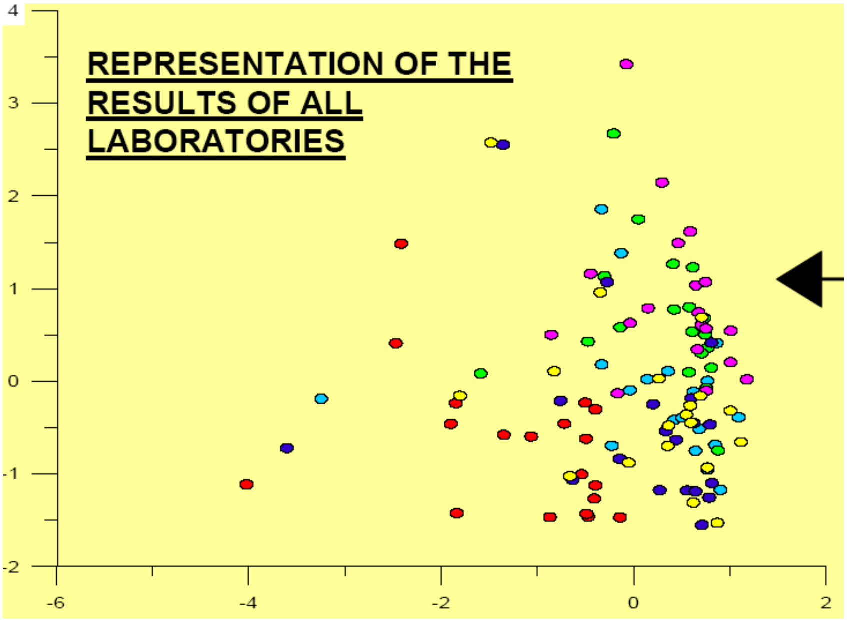


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Fig 37
Representation of the results of all laboratories.
Each colour is associated to one of the 6 samples. We can see that the interlaboratory variability is much bigger than the variability among the samples (represented by their averages)

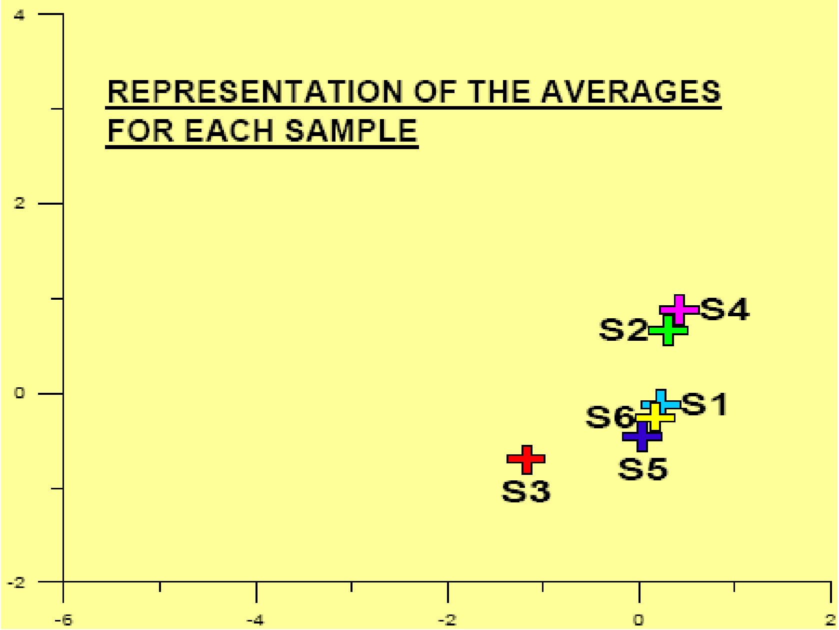

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Fig 38
Representation of the average calculated with the results of all laboratories.
Two different clusters, one of them with samples 1, 5 and 6, and another with samples 2 and 4 can be observe
Sample 3 is clearly different from the other samples.

Conclusions of ES_CEDEX

- All laboratories (18) show that sample 3 is very different from the rest of the samples.
- 11 laboratories show clusters (S1,S5, S6) and (S2,S4).
- 4 more laboratories show cluster (S1,S5) and 1 more laboratory show cluster (S1,S5,S6), but fail to show cluster(S2,S4).
- 2 laboratories show one wrong cluster (S2,S4,S6).
- The rest of the results do not show cluster or they show clusters that appear only in one laboratory.
- The averaged results show clearly clusters (S1,S5, S6) and (S2,S4).
- The interlaboratory variability is much bigger than the variability among the samples (represented by their averages).It is remarkable taking into account that the results are ratios (not absolute values).

Generally, PCA-analysis was conducted here just for demonstration purposes, as the sample set of this Round Robin was not very useful for this technique: sample 5 and especially sample 6 were highly weathered samples. Of course, ratios influenced by weathering have to be excluded before multivariate statistics can be used.
On the other hand, the comparison of sample 2 and 4 revealed high differences (e.g. the relation of aromatics to n-alkanes, see section 3.2), which were not covered by the measured ratios.

Working group 4 will study the implementation of PCA in the guideline.

3.7 Interlaboratory comparisons

Unexpectedly, there was a very great variety of analytical conditions and procedures, including even pre-separation of aromatics and aliphatics and measuring them on different instruments, or using the full-scan mode.

Of course, analytical parameters were not prescribed. But “analytical parameters” were already one of the major points in RR2006 (the results of RR2006 and the minutes of the OSINET06-meeting in Hamburg were sent to all participants). Thus, one of the conclusions of the Hamburg-meeting was that much more clear guidance should be given with regard to the analytical parameters than presently can be found in the CEN-TR. As also discussed already, analysts may well come to the right conclusion by using their own analytical parameters but, of course, bigger differences may appear, when measured data (compound ratios) are compared between the laboratories.

But there are of course some general rules of chromatography, which should be followed, especially when single compounds in a very complex mixture, such as oil, are measured. Sufficient sensitivity must be achieved, the temperature gradient should not be too high (rapid chromatography), and this gradient should not end before the measurements are finished. Peaks become broader and broader under isothermal conditions and the first measurements are thus not comparable with the last ones. Especially the ratios based on peak-heights do of course no longer reflect the “true” relations of peaks, which correspond to the relative concentrations of the compounds.

Participant	column type	ret time hopane	calculated final temp	Final time - ret time hopane	init time	init temp	rate 1	final temp 1	rate 2	final temp 2
AU_EC_CES	HP-5MS	44.00	42.17	-1.83	3	55	6	290	1	290
AU_NSWDECC	DB5 MS	35.52	34.75	-0.77	1	40	8	310	1	310
BR_Petrobas	J&W DB-5-MS-	46.11	45.33	-0.78	2	40	6	300	1	300
CA_EC_ALET	HP-5MS	42.22	45.33	3.11	2	50	6	310	1	310
CA_ESTD	Agilent HP-5MS	44.41	45.33	0.92	2	50	6	310	1	310
CA_PESC_EC	Restek Rtx-5MS	44.90	45.33	0.43	2	50	6	310	1	310
CN_NCSEMC	J&W DB 5 MS	46.30	43.67	-2.63	2	50	6	300	1	300
DE_BSH	Varian CP-Sil 8 CB	47.76	51.91	4.15	1	40	5.5	320	1	320
EE_EERC	HP-5MS	49.59	56.00	6.41	1	50	6	200	4	320
FI_NBI	HP-5MS	44.88	41.00	-3.88	1	60	6	300	1	300
FR_CEDRE	HP 5	50.29	51.00	0.71	1	50	5	300	1	300
LV_LVA	HP5MS	49.49	50.09	0.60	1	40	5.5	310	1	310
NL_NFI	Rxi-5ms	44.16	51.67	7.51	2	50	6	300	20	320
NL_RIZA	J&W DB5	47.92	57.25	9.33	1	50	6	200	4	325
NO_Sintef	J&W DB 5 MS	53.67	46.00	-7.67	1	40	6	310	1	310
SE_SKE	HP5ms	45.51	47.00	1.49	2	40	6	310	1	310
ES_CEDEX	J&W DB 5 MS	49.86	51.91	2.05	1	40	5.5	320	1	320
ES_CSIC	HP 1 MS	41.40	47.00	5.60	1	70	15	100	5	320
US_OSPR	HP5MS	58.10	57.00	-1.10	2	50	5	325	1	325

Table 5
Column type, temperature program and difference between the final time and the retention time of hopane

Table 5 shows the column type and temperature settings of the participants.
The column **Final time - ret time hopane** shows the difference between the calculated final time and the retention time of 30ab hopane
This difference varies between -7.67 min. and 9.33 min. for respectively NO_Sintef which uses as the only participant a 60m column and NL_RIZA which uses a low rate of 4°C and a high end temperature.
A graphical result of the final temp. versus the retention time of gammacerane is shown in Fig 39

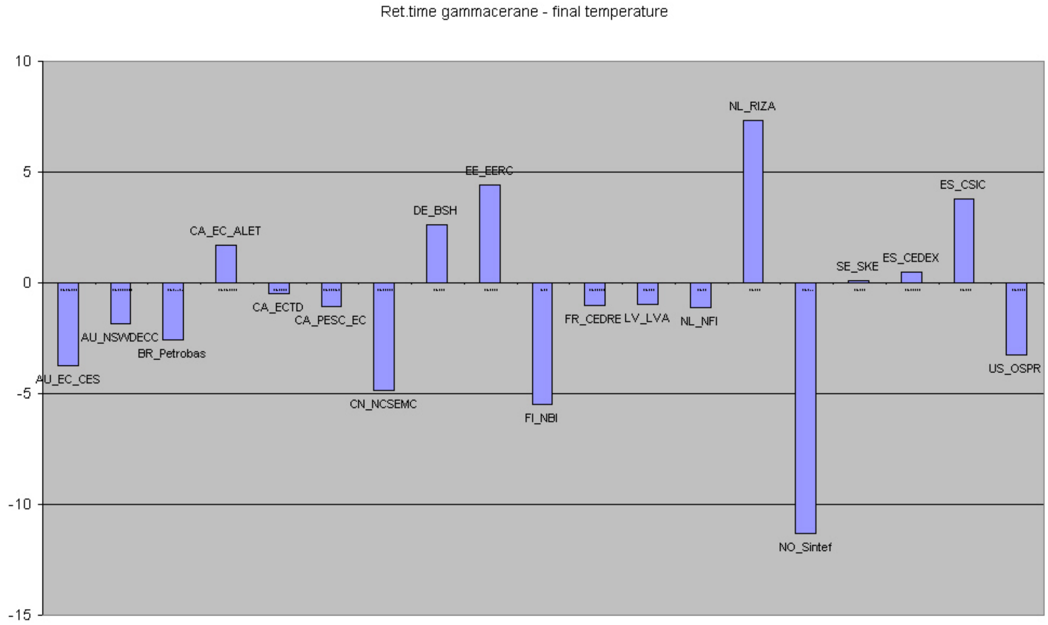

Fig 39
Retention time of gammacerane - final temp. of the temperature prog.

The effect of the temperature program on the area/height ratio can be seen in Fig 40 and Fig 41

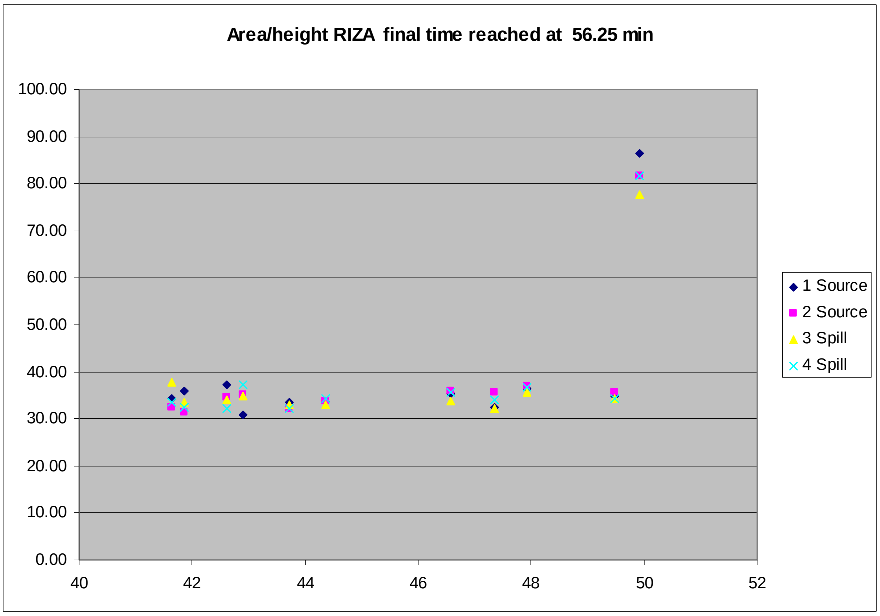

Fig 40
Area/Height ratio for NL-RIZA. The higher value of the last compound is caused by integrating the peak cluster around gammacerane

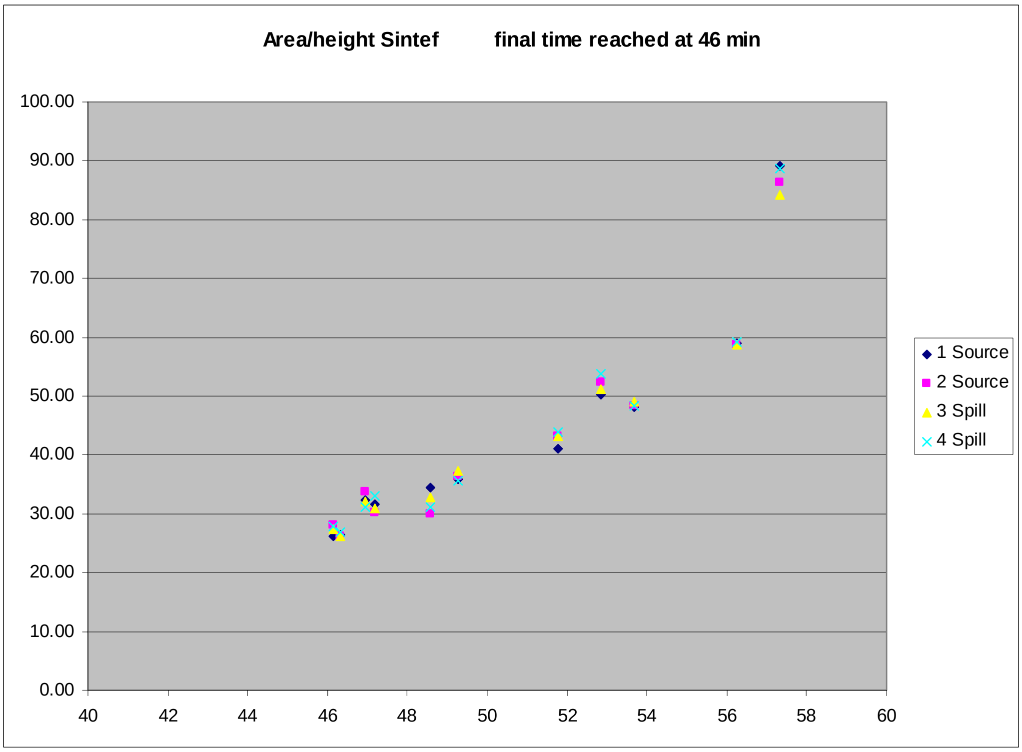

Fig 41
Area/Height ratio for NO_Sintef.

For intra-laboratory comparison of samples the temperature is less important, but for building a database a common temperature program is essential.

Another aspect is the column phase. Table 5 shows that all participants have used a DB-5 column, but most with the more stable DB-5 MS version. Although the phase has the same polarity the encapping of the MS version has an effect on the elution pattern of the compounds. An example and disadvantage of the MS column is the lower separation between C17 and pristane (see section 2.12 Fig 13)

Working group 2 will work on this issue.

3.8 Ratio selecting based on oil type

At the workshop Gerhard has gone through the text of working paper **WP3ratios comment Paul Kienhuis.doc**

Working group 4 will work on this issue.

3.9 Selection of ratios from the dataset.

In order to compare the ratios of the participants some selection is needed to eliminate results based on analyses with a low sensitivity, fractionated samples or results missing some of the masses. A summary can be found in Table 6

participant	average A/H variance		analysis in	reported
	area/height	comments	fractions	ions
NO_Sintef	7.7		no	m/z 85 FID results
NL_NFI	8.7		no	all
SE_SKL	9.3		no	all
NL_RIZA	9.3		no	all
EE_EERC	9.4		no	all
AU_EC_CES	12.6	strange PW plot	no	all
CA_EC_ALET	13.2	29ab/30ab So5	yes	all
FR_CEDRE	13.9		no	all
FI_NBI	13.9		no	all
DE_BSH	15.4		no	all
CN_NCSEMC	16.7		no	all
CA_PESC_EC	16.7		yes	no 216 and 234
CA_ESTD	17.2		no	
ES_CSIC	19.6	low S/N	no	
AU_NSWDECC	20.1	PAH Biomarkers different instrument	no	no 216 234 and sc26TA
LV_LVA	20.6		no	no 270
US_OSPR	29.6	low S/N	no	
BR_Petrobas	31.3	low S/N	yes	no 218
ES_CEDEX	126.4	low height values high variance pw plot on area	no	

Table 6
Summary of the results used to eliminated contributions for an interlaboratory comparison of the ratios.

In the spreadsheet **rr2007_evaluation** on the sheet **area_height selection** present in the RR2007 main directory, the combined results of the relative **maximum value -minimum value** differences for the area/height calculations can be found for all participants. These results have been averaged and are shown in the second column of Table 6 sorted on value.
The high value of 126.4 for CEDEX is partly caused by the low height values, but also for the areas, as can be seen in the variance of the PW plots based on area.
BR_Petrobas and US_OSPR have reported a low sensitivity based on respectively problems with the instrument or full scan analyses.
Other criteria have been the PW plots, fractioning of samples which influences the sterane_PAH_biomarker ratios and the fact that some of the masses have not been analyzed.

Contributions of the ten labs assigned in bold in Table 5 have been used for further evaluation in the spreadsheet file **RR2007selection** that also can be found on the main directory of RR2007.
Table 7 shows the mean and RSD results for Source 1 and 2 of the ratios of the 2007 template.

	Height RSD	So1 mean	Area RSD	So 1 mean	Height RSD	So2 mean	Area RSD	So2 mean
C17/pristane	6.2	400.5	3.8	317.6	10.4	427.0	8.7	323.1
C18/phytane	7.0	285.5	3.6	217.1	10.1	347.7	3.3	254.6
pri/phy	5.5	71.1	5.7	66.7	4.0	85.3	4.7	82.5
C28(22R)/30ab	19.2	5.5	14.3	5.2	18.1	5.4	18.5	5.1
C28(22S)/30ab	27.5	5.9	28.0	5.4	25.6	5.3	27.9	4.9
C29(22R)/30ab	24.8	5.4	17.4	4.5	23.1	4.8	16.9	4.0
C29(22s)/30ab	25.6	5.9	15.4	5.1	22.5	5.2	17.8	4.7
Ts/30ab	16.9	15.6	8.6	13.6	20.0	10.8	22.4	9.6
Tm/30ab	10.9	43.5	6.8	40.1	11.9	46.7	7.0	42.7
C29ab/30ab	6.5	124.6	5.7	118.6	5.1	75.0	6.9	71.5
C29ba/30ab	10.8	9.0	19.9	9.3	10.7	6.9	12.5	7.0
C31s/30ab	9.4	46.6	5.3	48.7	10.2	42.6	6.2	44.3
G/30ab	9.5	12.6	16.9	25.4	15.3	8.7	32.7	16.8
28bb(R+S)/27bb(R+S)	6.2	72.7	6.0	83.2	3.9	70.8	7.4	81.3
29bb(R+S)/27bb(R+S)	8.0	100.0	4.5	113.7	7.4	104.8	4.2	120.2
27bb(R+S)ster	7.4	58.2	4.2	50.9	5.4	57.1	4.2	49.7
28bb(R+S)ster	4.1	36.3	5.5	38.9	4.4	34.6	7.5	36.9
29bb(R+S)/30ab	23.8	17.4	24.0	29.9	22.3	14.8	23.3	25.0
SC26TA/SC28TA	15.9	49.0	15.0	37.4	31.4	81.6	37.1	65.1
RC26TA+SC27TA/30ab	33.9	42.5	32.5	43.6	27.3	42.1	29.1	45.5
RC27TA/RC28TA	8.7	116.7	9.5	117.0	7.9	89.4	9.1	92.7
2-MF/4-Mpy	6.5	18.8	8.1	30.4	7.5	18.6	5.7	29.7
BaF/4-Mpy	7.9	51.3	7.0	66.0	8.5	40.4	5.4	56.0
B(b+c)F/4-Mpy	18.1	28.6	12.0	39.1	19.3	21.3	12.5	28.1
2-MPy/4-Mpy	5.5	96.7	6.6	94.0	3.4	102.1	4.2	99.1
4-Mpy/30ab	36.1	522.5	36.6	457.9	38.0	231.6	37.5	200.9
1-MPy/4-Mpy	5.6	90.9	5.5	87.0	3.9	90.3	3.2	87.5
t-M-phen/BNT	18.3	97.7	15.4	145.6	26.5	107.1	17.7	155.0
C2/C4-phenantrenes			6.8	259.5			12.3	371.6
C2-dbt/C2-phe			5.7	40.1			6.0	36.5
C3-dbt/C3-chry			29.5	157.6			29.7	356.3

Table 7
Mean value and RSD of the ratio results of ten selected labs for source 1 and source 2

In the discussions which compounds or compound groups should be used to calculate ratio's several criteria like:
only large peaks,
ratios between peaks from the same m/z
well separated peaks,
close eluting peaks
based on height or area

have been mentioned in order to reduce the variance of the ratios. To give some answers on this points the information of table 7 is rearranged by sorting on the combined RSD average of source 1 and 2 including area and height RSD results. Also some description of each ratio is added. The result is shown in Table 8

	large	small	double	coelute	diff. m/z	RSD Source 1		RSD Source 2		average
						Height	Area	Height	Area	
28bb(R+S)ster	large		do			4.1	5.5	4.4	7.5	4.7
1-MPy/4-Mpy	large					5.6	5.5	3.9	3.2	5.0
pri/phy	large					5.5	5.7	4.0	4.7	5.1
2-MPy/4-Mpy	large					5.5	6.6	3.4	4.2	5.2
28bb(R+S)/27bb(R+S)	large		do			6.2	6.0	3.9	7.4	5.4
C2-dbt/C2-phe					m/z		5.7		6.0	5.7
27bb(R+S)ster	large		do			7.4	4.2	5.4	4.2	5.7
C29ab/30ab	large			co		6.5	5.7	5.1	6.9	5.8
29bb(R+S)/27bb(R+S)	large		do			8.0	4.5	7.4	4.2	6.7
C2/C4-phenantrenes					m/z		6.8		12.3	6.8
C17/pristane	large					6.2	3.8	10.4	8.7	6.8
C18/phytane	large					7.0	3.6	10.1	3.3	6.9
2-MF/4-Mpy	large					6.5	8.1	7.5	5.7	7.4
BaF/4-Mpy	large					7.9	7.0	8.5	5.4	7.8
C31s/30ab	large					9.4	5.3	10.2	6.2	8.3
RC27TA/RC28TA	large					8.7	9.5	7.9	9.1	8.7
Tm/30ab	large					10.9	6.8	11.9	7.0	9.9
C29ba/30ab		sm				10.8	19.9	10.7	12.5	13.8
G/30ab				co		9.5	16.9	15.3	32.7	13.9
Ts/30ab	large					16.9	8.6	20.0	22.4	15.2
B(b+c)F/4-Mpy						18.1	12.0	19.3	12.5	16.4
C28(22R)/30ab		sm		co		19.2	14.3	18.1	18.5	17.2
t-M-phen/BNT	large			co		18.3	15.4	26.5	17.7	20.1
SC26TA/SC28TA		sm				15.9	15.0	31.4	37.1	20.8
C29(22s)/30ab		sm				25.6	15.4	22.5	17.8	21.1
C29(22R)/30ab		sm				24.8	17.4	23.1	16.9	21.8
29bb(R+S)/30ab					m/z	23.8	24.0	22.3	23.3	23.4
C28(22S)/30ab		sm				27.5	28.0	25.6	27.9	27.0
C3-dbt/C3-chry					m/z		29.5		29.7	29.5
RC26TA+SC27TA/30ab					m/z	33.9	32.5	27.3	29.1	31.2
4-Mpy/30ab					m/z	36.1	36.6	38.0	37.5	36.9

Table 8
Indicated ratios sorted on the average of the height and area RSD's.

The results have been shown at the meeting. It was decided that working group 3 will further work on this issue.

4. Conclusions

. . . .

The results of the participants including comments and remarks are shown in Chapter 2.
General issues still not complete solved after finishing CEN/TR 12255-2, learnings from the contributions of the participants and some goals for the future are discussed in Chapter 3.

At the workshop in Trondheim the concept report has been used as a guide to go through all the individual reports and the issues of chapter 3 leading to the following conclusions:

3.1.1 At the meeting it was decided, that the name Heavy Fuel Oil should be used to describe this product. It is applicable for both the use on board of ships as for other purposes like energy plants.

3.1.2 At the workshop in Trondheim, possible explanations for the differences between source 2 and spill 4 were controversially discussed, including the possibility of inhomogeneous distributions (different amounts of cutter stocks, mixing of oil from different compartments of the ship during the salvage operation). At the end, there was agreement that nobody would swear at court that the samples originated from the same source.

3.2 and 3.4 All 19 participants have found a correct match between sample So1 and Sp 5, but the high temperature treatment of So1 resulting in Sp 6 has led to seven conclusions ranging from inconclusive to non-match.
Many participants indicated a strong relationship between So2 and Sp 4. Because it are real samples the correct answer cannot be given, but it can be concluded that it is very useful to study the homogeneity of the heavy fuels oils ships have on board in the fuel tanks.

3.3 It can be concluded that the PW plots of the GCMS results are very useful to estimate weathering and are essential in oil spill identification.

3.4 The meeting was positive about the use of the table of SKL to describe the conclusion, but it was generally agreed that more guidance is needed in order to come to the same conclusions when having the same information about the samples.

3.5.1 The meeting concluded about the cleanup of HFO samples, that the text in the guideline must be changed from **advised** into **prescribed** because deterioration of the column can influence the final conclusions.

3.7 For intra-laboratory comparison of samples the temperature program and the applied column phase is less important, but for co-operation and mutual assistance in difficult cases, the exchange of results and especially also for building a database a common method is essential.

3.8 and 3.9 The list of ratios mentioned in the CEN guideline is still under discussion. Working paper **WP3ratios comment Paul Kienhuis.doc** and the results of RR2007 will be used by working group 3 to answer questions like
ratios for specific oil types
ratios based on only large peaks
ratios based on peaks from the different m/z values
ratios based well separated peaks,
ratios based close eluting peaks
ratios based on height or area

During the workshop 5 working groups were formed to study the following issues:

WG_1	Pre-injection
	Clean-up - Reason for why not using fractionation: F1/F2: sat/aro (?)
WG_2	Harmonization of chromatographic conditions
	Quality management - Instrumental aspects
WG_3	Selection of CR's
	Further refinement of Gerhards table (WP3) - Selection of compound ratios
WG_4	Common Data-base
	possibility / needs for it - at which level ? - Multivariate Treatment
WG_5	Conclusion definitions.
	Further refinements of suggested terms - Statistics

Coordinator	Gerhard Dahlmann
Time frame	First quarter of 2008

5. References

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Annex: Proposal for the text of the Bonn website section Bonn-OSInet

The Bonn-OSInet expert group intends to make documents available on www.bonnagreement.org
A part of the documents will be password protected.
Below a proposal for the text and the documents.
This action is scheduled for the first half of 2008.

Bonn-OSInet expert group

The SEVENTEENTH MEETING OF THE CONTRACTING PARTIES; OSTEND: 27 – 29 SEPTEMBER 2005 decided to create a forum of BONN experts on oil-spill identification with Dr Gerhard Dahlmann (BSH, Germany) as convenor.
As recommended by the workshop, the forum should aim to provide mutual assistance in difficult cases, to promote quality assurance in oil-spill identification (especially through ring-tests, development of common reference materials (CRMs), and sample exchanges) and consider the possibility of a common database of oil sources.

The expert group exists of experts from the Bonnagreement countries. Activities and meetings of the expert group are open to observers from other countries worldwide.

The first ring test, dealing with crude oil and Heavy Fuel oil, was organized in 2006 by Gerhard Dahlmann. 13 laboratories from 11 European countries participated.
The results were discussed at a the first workshop of the Bonn-OSInet expert group held at BSH in Hamburg ,DE: 9-10 November 2006.
Documents of the ring test and workshop:

Bonn-OSINET2006-1: Minutes of the first workshop of the Bonn-OSInet expert group held at BSH in Hamburg ,DE: 9-10 November 2006
Bonn-OSINET2006-2: Final report of the ring test of 2006 in zip format.
Bonn-OSINET2006-3: Contributions of the participants of RR2006 in zip format.

The second ring test, dealing with crude oil from the Tricolor case, was organized in 2007 by Paul Kienhuis (RWS-RIZA, NL) and Gerhard Dahlmann(BSH, DE).
19 laboratories from 16 countries worldwide participated.
The results were discussed at a the second workshop of the Bonn-OSInet expert group held at SINTEF in Trondheim,NO: 7-9 November 2007.
Documents of the ring test and workshop:

Bonn-OSINET2007-1: Minutes of the workshop of the second workshop of the Bonn-OSInet expert group held at SINTEF in Trondheim,NO: 7-9 November 2007.
Bonn-OSINET2007-2: Final report of the ringtest of 2007 in zip format.
Bonn-OSINET2007-3: Contributions of the participants of RR2007 in zip format.

The third workshop of the Bonn-OSInet expert group will be organized at the RWS-Waterdepartment, Lelystad, NL: end of May 2008.