40 anos
Ingresso da Mulher na Marinha

MARINHA DO BRASIL

GABINETE DO COMANDANTE DA MARINHA
Esplanada dos Ministérios, Bloco "N", 2º Andar
CEP 70055-900 – Brasília – DF
(61) 3429-1020 – gcm.secom@marinha.mil.br

Ofício nº 20-180/GCM-MB
20/995

Brasília, DF, 19 de agosto de 2020.

A Sua Senhoria o Senhor
ALBER VALE DE PAULA
Secretário-Executivo da Comissão Parlamentar de Inquérito - CPIOLEO
Câmara dos Deputados - Anexo II, Sala 165, Ala B
70160-900 - Brasília - DF

Assunto: **Reitera requisição de informações/documentos**

Senhor Secretário-Executivo,

1. Em atenção aos Ofícios nº 328/2020-Pres, de 16 de julho de 2020, e nº 338/2020-Pres, de 17 de julho de 2020, incumbiu-me o Comandante da Marinha de transmitir a Vossa Senhoria as análises anexas, inerentes às respostas aos Requerimentos nº 17/2019 e 10/2020.

2. Por oportuno, aproveito para reiterar meus protestos de elevada estima e consideração.

Respeitosamente,

ALEXANDRE BESSA DE OLIVEIRA
Capitão de Mar e Guerra
Assessor-Chefe de Relações Institucionais

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Brasília 20 de agosto de 20
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MARINHA DO BRASIL

CHARACTERIZATION AND COMPARISON OF SAMPLES COLLECTED IN THE ENVIRONMENT IN BRAZIL

FINAL REPORT

L.20.03/ 5290 JG / JR February 2020

715 rue Alain Colas - CS 41836
F - 29218 BREST CEDEX 2
+33 (0)2 98 33 10 10
contact@cedre.fr

CENTRE DE DOCUMENTATION, DE RECHERCHE ET D'EXPERIMENTATIONS SUR LES POLLUTIONS ACCIDENTELLES DES EAUX

715, rue Alain Colas - CS 41836 - 29218 BREST CEDEX 2 - FRANCE
Tél. : 02 98 33 10 10 - Fax : 02 98 44 91 38 - E-mail : contact@cedre.fr
International : 33 2 98 33 10 10 - Fax : 33 2 98 44 91 38

ANALYSES REPORT

Report L.20.03	Date: 11th of February, 2020	Contact : Julien Guyomarch julien.guyomarch@cedre.fr

Analyses required

Organisation: Marinha Do Brasil Contact: Commander Felipe MESSIAS Gonçalves Lourenço	Objective: characterization and comparison of oil samples collected in the environment in Brazil

Samples

Received: 13/01/2019	Type: Emulsified oils and contaminated sediments	References: Contaminated sediments (HC-20-02 and HC-20-03) Emulsified oil samples (HC-20-04 and HC-20-05)

Report

Written by: J. Guyomarch *Approved*	Read by: N. Tamic *Approved*	External diffusion: Marinha Do Brasil	Internal copies: Analysis & Resources Dpt. Confidential: ☒

Summary

Four samples, collected in the framework of a significant pollution of the shoreline in Brazil, and sent by the Brazilian Government, were received at Cedre for analyses. These samples consist in two contaminated sediment and two emulsified oils.
The objective was to determine the oil fingerprint of those samples and to compare them in order to establish common origins. In addition, as the source of this pollution remains unknown, physical-chemical characterizations were performed in order to specify the nature of the spilled oil (crude oil or heavy refined product).

The comparison of the various samples show that they have very similar fingerprints and chemical composition.
Qualitative analyses, consisting in looking at specific distributions of molecules obtained during the GC/MS analysis, show that the various patterns are in agreement with profiles generally obtained for refined products.
The detailed quantitative analysis shows a high concentration in PAH, particularly for the high molecular weights, and a great proportion of resins and asphaltenes, the heaviest fraction of the oil.

All these elements are in agreement with a heavy fuel oil, obtained by refining processes, rather than a heavy crude oil.

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CHARACTERIZATION AND COMPARISON OF OIL SAMPLES COLLECTED IN THE ENVIRONMENT IN BRAZIL

1 CONTEXT AND OBJECTIVES

Four samples, collected in the framework of a significant pollution of the shoreline in Brazil, and sent by the Brazilian Government, were received at Cedre for analyses. These samples consist in two contaminated sediment and two emulsified oils.

The objective was to determine the oil fingerprint of those samples and to compare them in order to establish common origins. In addition, as the source of this pollution remains unknown, physical-chemical characterizations were performed in order to specify the nature of the spilled oil (crude oil or heavy refined product).

2 SAMPLES

References of the samples received at Cedre are presented in *Table 1* and pictures taken at the samples reception are presented in *Figure 1*.

Table 1 *Origins and references of the samples*

Cedre's **Reference**	**Nature**	**Sampled**	**Sampling location**
HC-20-02	Contaminated sediment	19/11/2019	PRAIA DE JAPARATINGA
HC-20-03	Contaminated sediment	19/11/2019	ESTUARIO DO RIO MAMUCABAS-BARREIROS-PE
HC-20-04	Emulsified oil	20/11/2019	ESTUARIO DO RIO PERSINUNGA - divisa entre PE e AL
HC-20-05	Emulsified oil	21/11/2019	PRAIA DER ITAPUAMA - cabo de Santa Augustinho

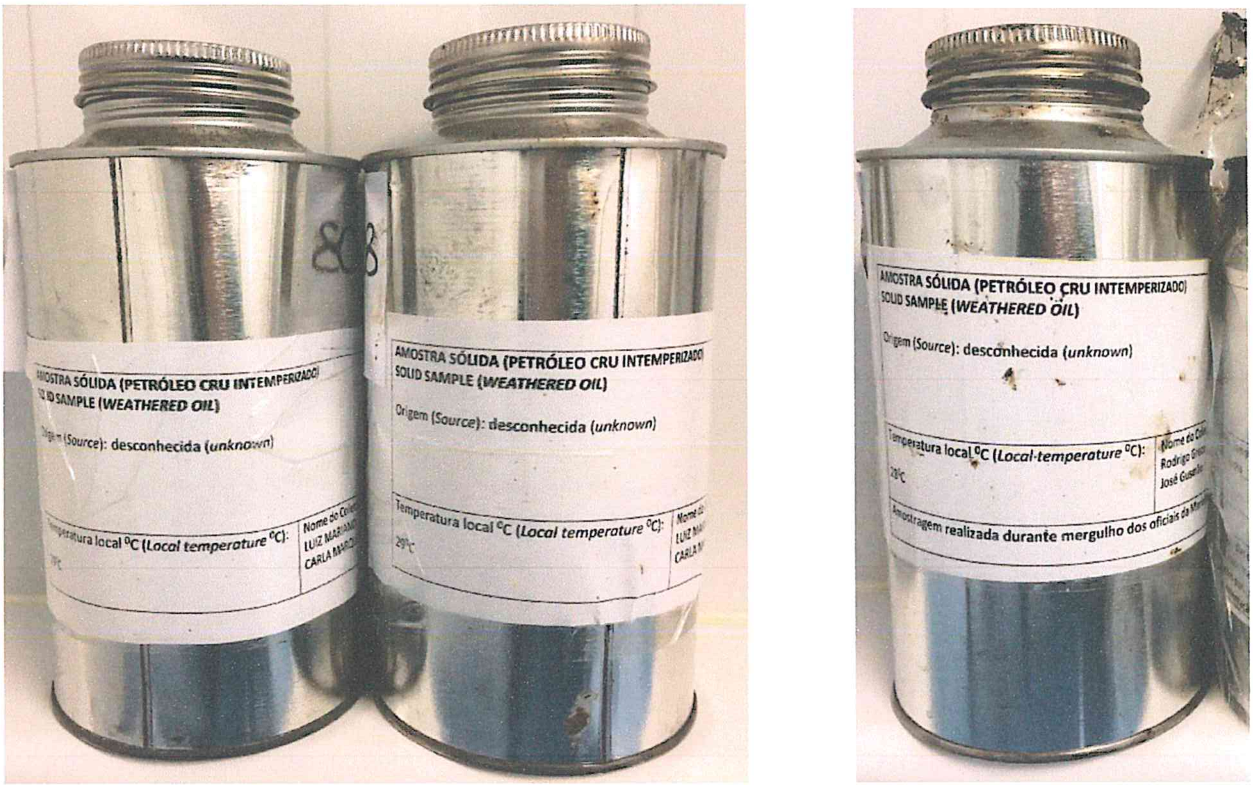


Figure 1 *Reception of the samples*

3 MATERIALS AND METHODS

3.1 Comparison and nature of oil samples

Samples were prepared and analysed in accordance with the recommendations of the CEN Technical Report (European committee for standardization) "Oil Spill Identification – Waterbone petroleum and petroleum products – Part 2: analytical methodology and interpretation of results based on GC-FID and GC-MS low resolution analyses". As this standard cannot be communicated to a third party, general principles are described hereafter. Detailed analytical conditions are presented in Appendix 1.

Oil was extracted from sediment samples (HC-20-02 and 03) with dichloromethane using an ultrasonic bath. For emulsified oils, samples were directly diluted in dichloromethane and the water was removed using a separating funnels. For all the samples, the extracts were dried over sodium sulphate and concentrated in order to obtain a final concentration in dichloromethane of approximately 5 mg/mL prior to analysis.

3.1.1 Principle of the samples comparison

In general, GC-FID analysis is used in a first phase for the screening of the samples (general shapes of the oils and *n*-alkanes distributions). Based upon the visual comparison of the chromatograms, source samples that are clearly different from spill samples can be discarded. Due to the limited number of samples, GC-MS analyses were directly performed, both in SCAN and SIM modes. SCAN modes provides a general view of the samples patterns, and is used as a screening method, while the SIM mode enables reliable comparisons based on various families of compounds.

The principle of the GC-MS analyses used for oil spill identification is to analyze different compounds using gas chromatography coupled to a mass spectrometer. Those compounds have to be conservative, *i.e.* should be as less as possible subjected to evaporation, solubilization and should be only slightly affected by natural degradation processes (especially biodegradation). The term "conservative" relates to the timescale considered. However, "non-conservative" molecules are also analyzed due to their interest for the characterization of the oil sample (presence of compounds typical of cracking processes, for example), but also to demonstrate the extent of some degradation phenomena (mainly biodegradation and photo-oxidation).

Compounds of interest are either polycyclic aromatic hydrocarbons (PAHs), saturates (linear alkanes and isoprenoids), or geochemical markers (biomarkers: hopanes, steranes/diasteranes and triaromatic steranes). Analysis of those specific compounds allows the calculation of 25 indices (presented as ratios) for each sample. Each ratio is calculated as the average of 2 injections of the same sample on the GC/MS.

The data treatment consists, then, in the comparison of the 25 ratios obtained for 2 samples, and the evaluation of a significant (or not) difference between those ratios, thanks to criteria defined by the method.

Additionally, relative abundances of those specific compounds are compared in order to estimate the importance of degradation processes. This evaluation can explain some differences between samples, due to degradation processes highlighted when comparing the different ratios.

3.1.2 Calculation of ratios

Several chemical compounds are analysed in order to characterize each sample. From the abundance of those molecules, ratios (R) are calculated following the general formula:

$$R = \frac{A}{B} \times 100$$

A and B represent either the height or the area of 2 target compounds as a function of their chemical nature (areas for the PAHs, alkanes and isoprenoids, height for the hopanes and other biomarkers).

3.1.3 Comparison of ratios

Ratios calculated for two samples collected in the environment are compared as follows:

- For each ratio, the absolute difference (AD) between the 2 values is calculated:

$$AD = \left| R_{Sample\ x} - R_{Sample\ y} \right|$$

- For each ratio, ADs are compared to the ratio average and a relative difference (RD) is calculated:

$$RD = \frac{AD}{R_{mean}} \times 100$$

Those RDs are presented as a graph on which 2 limits appear: 14% and 28%. A significant difference between the 2 samples is exhibited if the relative difference is higher than 14% for sufficiently abundant and well resolved peaks. The threshold of 28% corresponds to differences hardly compatible with a common origin, except if processes such as evaporation, biodegradation, or photo-oxidation can explain them.

3.1.4 Comparison of the abundances

In order to evaluate the impact of evaporation or any other degradation process on the calculated values following the timescale considered, compounds abundances of the samples collected in the environment are compared with the ones of the suspected sources (or with a second spill sample if no source has been identified). These abundances are normalized to a non-weathered compound, hopane (compound 30ab) in order to compare samples despite their different concentrations.

This sample comparison is illustrated thanks to a graph on which:

- The X-axis represents the retention time of the compounds during the analysis. This parameter is related to the molecular weight of the analysed compounds. The heavier molecules have the greatest retention times.
- The Y-axis represents the compounds abundances of the spill sample normalized to the reference sample (potential source), expressed in %.

In case of « match » between 2 samples, and if no evaporation occurs, all the values are located around 100%, with an error range that can vary according to the abundance of the compound used for normalization. In case of low hopane abundance, a margin of 20% is acceptable. If evaporation affects the spill sample, the distribution will be slightly modified, with lower values for the lighter compounds, progressively reaching 100% while the molecular weight increases. Those explanations are illustrated on an example, on *figure 2*.

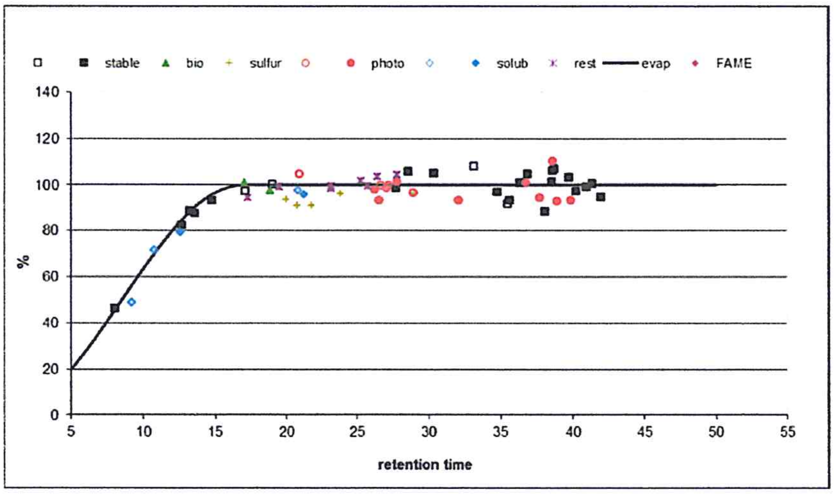


Figure 2 *Example of a match between a spill and a source samples, the spill sample being only affected by evaporation process (for compounds eluting before 15 min)*

3.2 Physical-chemical characterization of samples

3.2.1 Viscosity, water content and density of oil (emulsified oils)

The viscosity of the emulsified oil samples (HC-20-04 and HC-20-05) was measured at 50°C by using an Anton Paar Rheolab QC viscosimeter at 10 s^{-1}. The equipment was calibrated by analysing reference oils.

The density of the emulsified oil samples was determined according to the ASTM method D5002 Standard Test Method for density and relative density of crude oils by digital density analyzer (ASTM, 2013). This measurement was performed using an Anton Paar D4500 analyzer.

Emulsification was assessed by measuring the water content in the oil samples according to the water that is distilled using the ISO 3733 Dean & Stark method, equivalent to the ASTM D95-05 (2010).

3.2.2 PAH and *n*-alkanes

The PAHs and *n*-alkanes concentrations were measured in the four samples.
10 mg of the oil sample were spiked with internal standards (perdeutarated PAHs and eicosane). Compounds were then analyzed by Gas Chromatography coupled to Mass Spectrometry (GC-MS). The GC was an HP 7890 series II (Hewlett-Packard. Palo Alto. CA. USA) equipped with a Multi Mode Injector (MMI) used in the pulsed splitless mode (Pulse Splitless time: 1 min. Pulse Pressure: 15 psi). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 320°C (20 min) at 3°C/min. The carrier gas was Helium at a constant flow of 1 ml/min. The capillary column used was a HP 5-ms (Hewlett-Packard.Palo Alto. CA. USA): 50 m x 0.25 mm ID x 0.25 µm film thickness. The GC was coupled to a HP 7000 triple quadripole used in the Electronic Impact mode (Electronic Impact: 70 eV. voltage: 2000V). PAHs and *n*-alkanes quantifications were done using Single Ion Monitoring mode with respectively the molecular ion of each compound and a common fragment (generally m/z = 57) at

a minimum of 2 cycles/s. PAHs and *n*-alkanes were quantified relatively to the perdeuterated PAHs and eicosane introduced at the beginning of the sample preparation procedure.

3.2.3 SARA (Saturates/Aromatics/Resins/Asphaltenes) analysis

The oil composition was assessed by fractionation into 4 chemical families (saturates, aromatics, resins and asphaltenes). Asphaltenes were precipitated in n-pentane and were filtered on a glass fibre filter. The maltene fraction was the separated on a silica-alumina column. Saturates were eluted with *n*-pentane, aromatics with a *n*-pentane/dichloromethane 80/20 mixture, and resins with a mixture methanol/ dichloromethane 50/50. The various fractions were weighed after evaporation of the solvent and stabilization of the masses. The mass balance was calculated assuming that saturates and aromatics evaporates similarly whereas resins and asphaltenes do not evaporate.

4 RESULTS OF OILS COMPARISONS

4.1 Qualitative analyses and nature of the oils

GC/MS patterns point out the most significant differences or similarities between samples, by comparing the general composition of the oil and of the *n*-alkanes distributions. Chromatograms of the 4 environmental samples are presented on *figure 3*. Peaks eluting regularly on *figure 4* correspond to linear alkanes (*n*-alkanes). Hopanes and triaromatic steranes are illustrated appendix 4 (HC-20-02).

All the 4 samples look very similar based on the visual observations. Samples are characterized by a significant Unresolved Complex Mixture (UCM), which corresponds to the hump located below the peaks as illustrated *figure 4*. The methylphenanthrenes/anthracenes (m/z=192) in *figure 5 (left)* show a significant abundance of methylanthracene (peak in the centre), which could have been generated during a cracking process. In addition to this compound, the relative abundances of the methylphenanthrenes (two doublets) is characteristic of the cluster generally found in heavy fuel oils (these aromatic compounds are produced by cracking processes). In addition, the tetramethylphenanthrenes (m/z=192), illustrated on *figure 5 (left),* do not show the presence of retene (such aromatics with slightly longer side chains are not produced in higher-temperature processes).

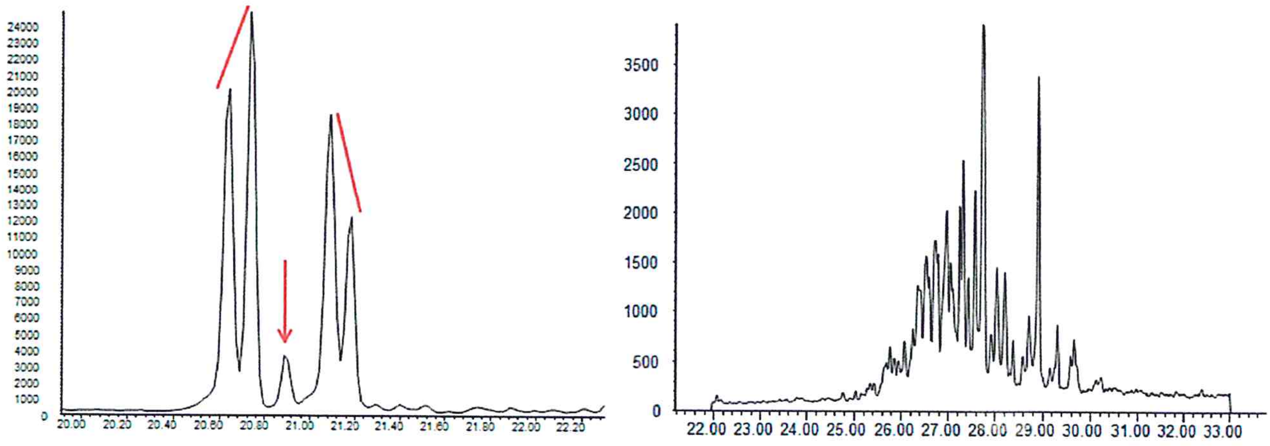


Figure 5 *GC/MS chromatograms of the contaminated sediment HC-20-02*
Methylphenanthrenes/anthracenes (left) and tetramethylphenanthrenes (right)

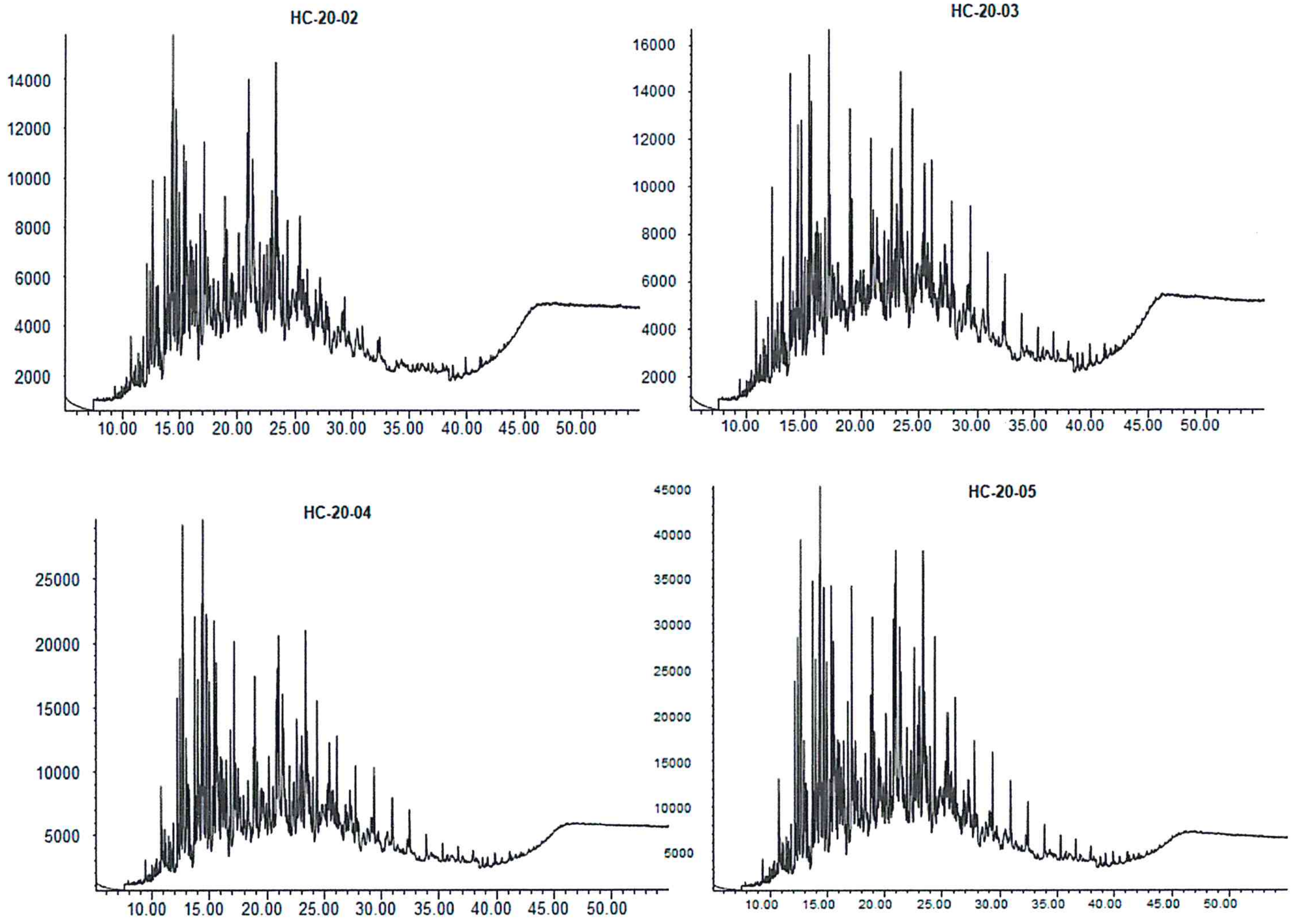


Figure 3 *GC/MS chromatograms of the samples (TIC)*

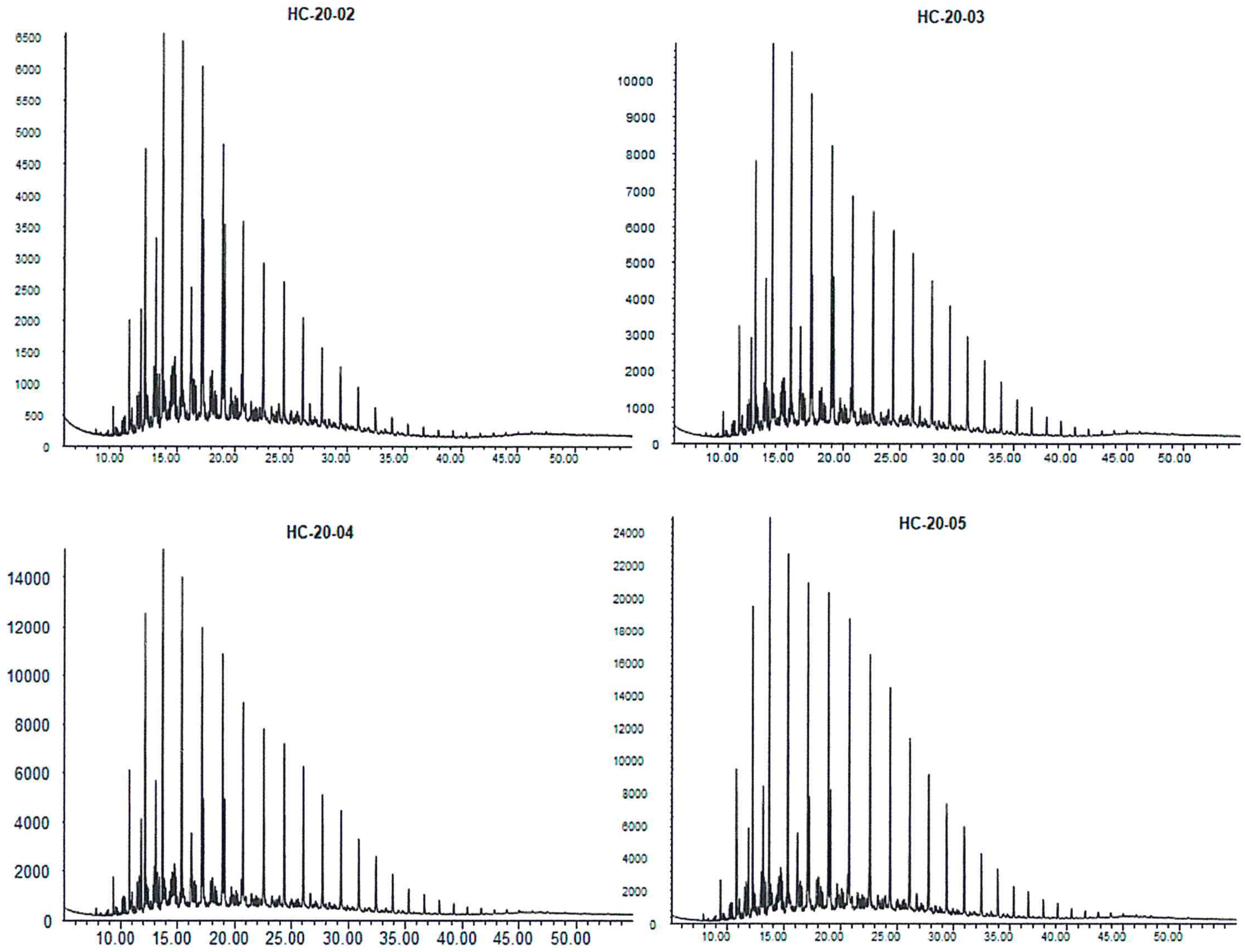


Figure 4 *GC/MS chromatograms of the samples (m/z=85)*

4.2 Comparison of oil samples

4.2.1 Comparison of sediment samples

The relative differences between the normative ratios obtained for the two sediment samples are all below or close to 14% (*Figure 6*), except the 27Tm/30ab, nC_{17}/pristane and nC_{18}/phytane ratios. These last two ratios, calculated between linear alkanes and isoprenoids, are the most sensitive ones to biodegradation and evaporation processes, which explain these variations. The variation of the 27Tm/30ab ratio can be due to the influence of the matrix, and also explained by the low abundance of hopanes.

Comparison of the abundances (*Figure 7*) shows important similarities between these two field samples with some variations, also explained by the low abundance of hopanes (abundances are normalised on the 30ab hopane).

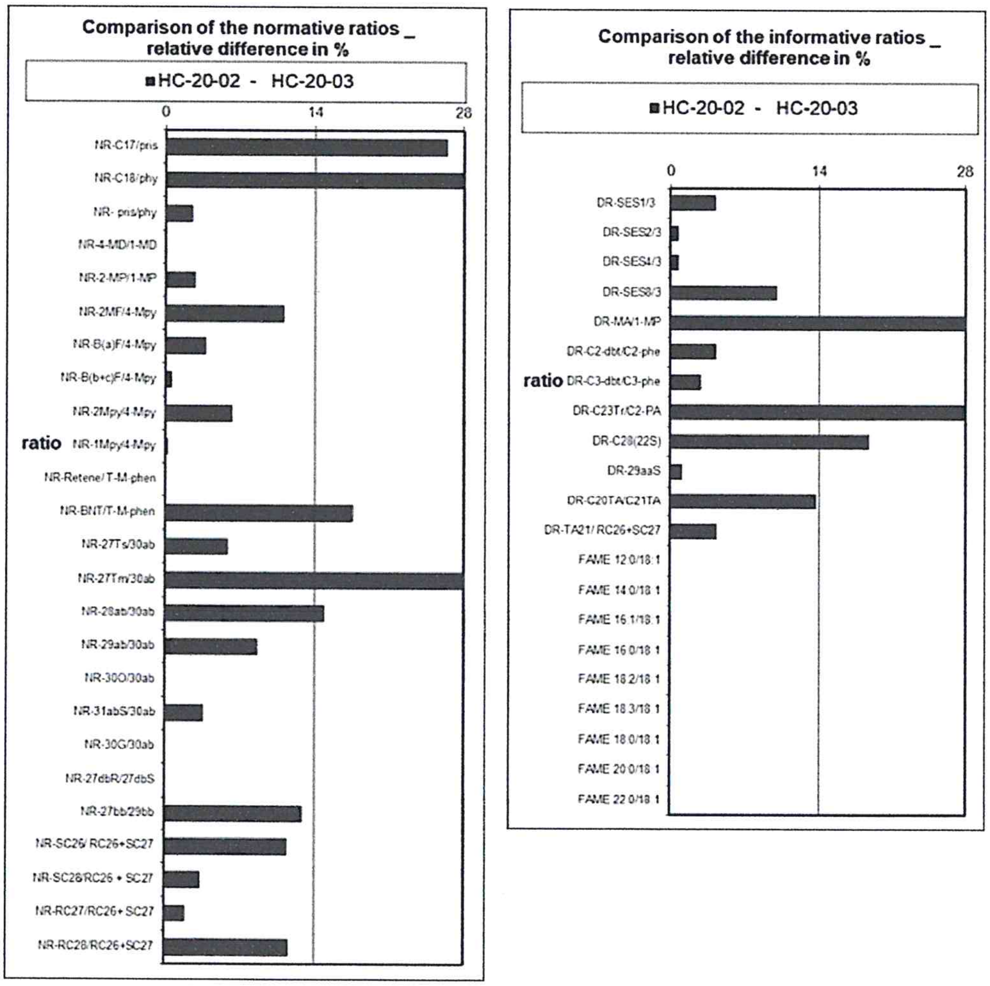


Figure 6 *Relative difference in the normative ratios between the contaminated sediments (HC-20-02 and HC-20-03)*

Based on these comparisons, it appears that oils extracted from these two sediment samples have the same origin, but show different levels of weathering, either evaporation or biodegradation.

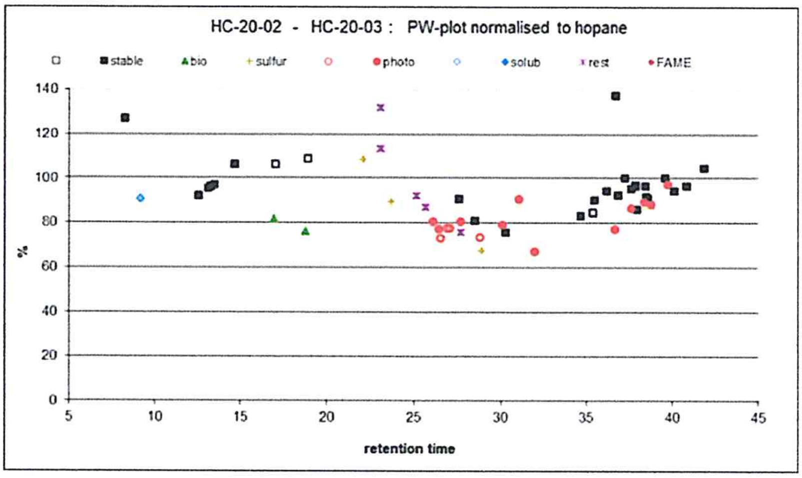


Figure 7 *Abundances comparison between then the contaminated sediments (HC-20-02 and HC-20-03)*

4.2.2 Comparison of emulsified oil samples

The relative differences between the normative ratios obtained for the two emulsified oil samples are all below or 14% (*Figure 8*), and the same goes for the informative ratios.
Comparison of the abundances (*Figure 8*) shows important similarities, all the compounds being between 80% and 120%.
Based on these comparisons, it appears that oils from these two samples have the same origin.

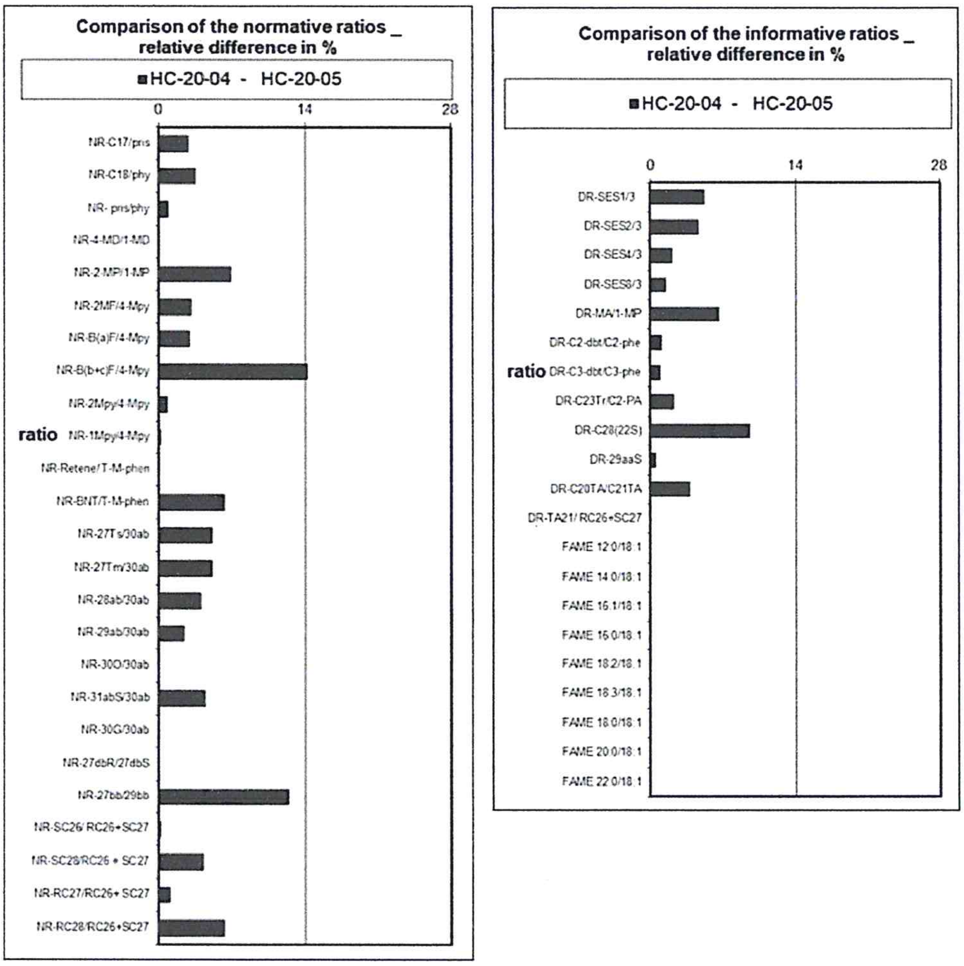


Figure 8 *Relative difference in the normative ratios between the two emulsified oil samples*

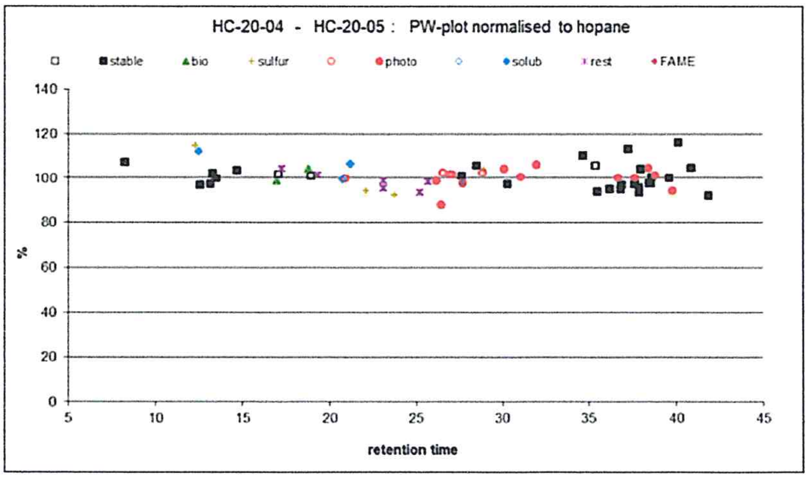


Figure 9 *Abundances comparison between the two emulsified oil samples (HC-20-04 and HC-20-05)*

4.2.3 Comparison of emulsified oils and sediment samples

The relative differences between the normative ratios obtained for the two sediment samples are all below or close to 14% (*Figure 10*), except the 27Tm/30ab, the BNT/T-M-Phen, nC_{17}/pristane and nC_{18}/phytane ratios. These last two ratios, calculated between linear alkanes and isoprenoids, are the most sensitive ones to biodegradation and evaporation processes, which explain these variations. The variation of the 27Tm/30ab ratio can be due to the influence of the matrix, and also explained by the low abundance of hopanes. The BNT/T-M-Phen ratio is known to be very sensitive to weathering.

Comparison of the abundances (*Figure 11*) shows similarities between these two field samples with some variations, which can be explained by the low abundance of hopanes (abundances are normalised on the 30ab hopane), and also by the influence of the matrix which affects differently the two samples.

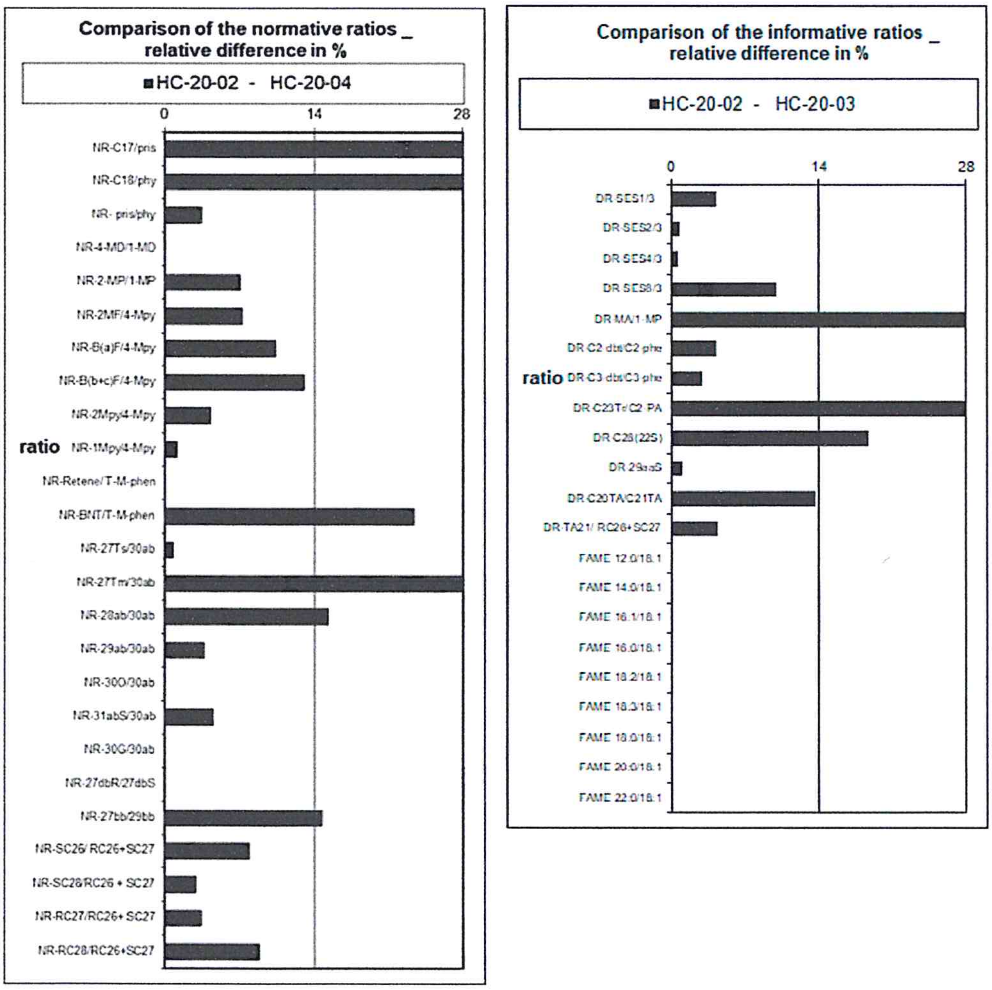


Figure 11 *Relative difference in the normative ratios between one contaminated sediment sample (HC-20-02) and one emulsified oil sample (HC-20-04)*

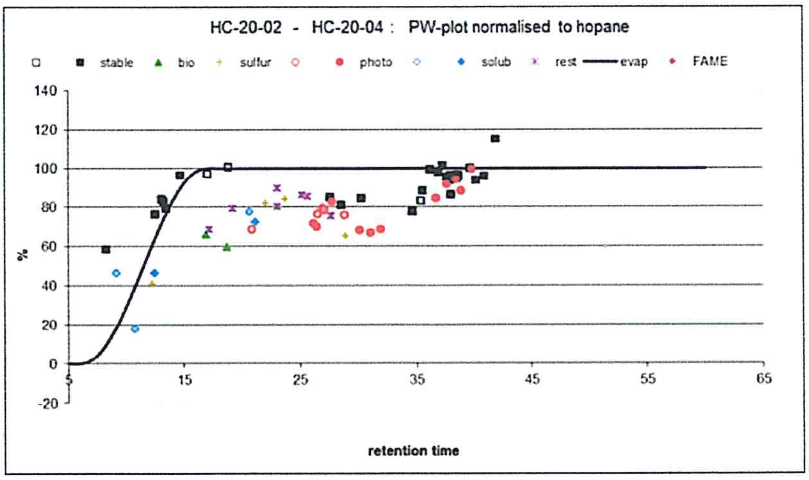


Figure 12 *Abundances comparison between one contaminated sediment sample (HC-20-02) and one emulsified oil sample (HC-20-04)*

4.3 Characterization of oil and sediment samples

4.3.1 Physical characterization of emulsified oils (viscosity, density and water content)

The two emulsified oils could only be characterized at 50°C due to their very high viscosity. Densities are in the range 0.945-0.950, and the viscosity is around 150 000 mPa.s at 10 s^{-1}. These very high values are due to the intrinsic high viscosity of the oil, and also by the significant water content, around 45%, which makes the oil more viscous.

Table 2 *Viscosity, density and water content of the emulsified samples*

Characterizations		HC-20-04	HC-20-05
50°C	Density	0,945	0,949
	Viscosity (10s-1)	132 906	151 076
	Water content (%)	47	43

4.3.2 Chemical characterization of emulsified oils and sediment samples

<u>PAH and n-alkanes</u>

Concentrations of various polyaromatic hydrocarbons (PAH) and *n*-alkanes are illustrated respectively in *figures 13* and *14*. The PAH concentrations are relatively high and in the range of concentrations that can be obtained for heavy fuel oil (see *appendix 3* for the comparison with the *Erika* heavy fuel oil). In addition, the abundance of high molecular weights compounds is relatively high.

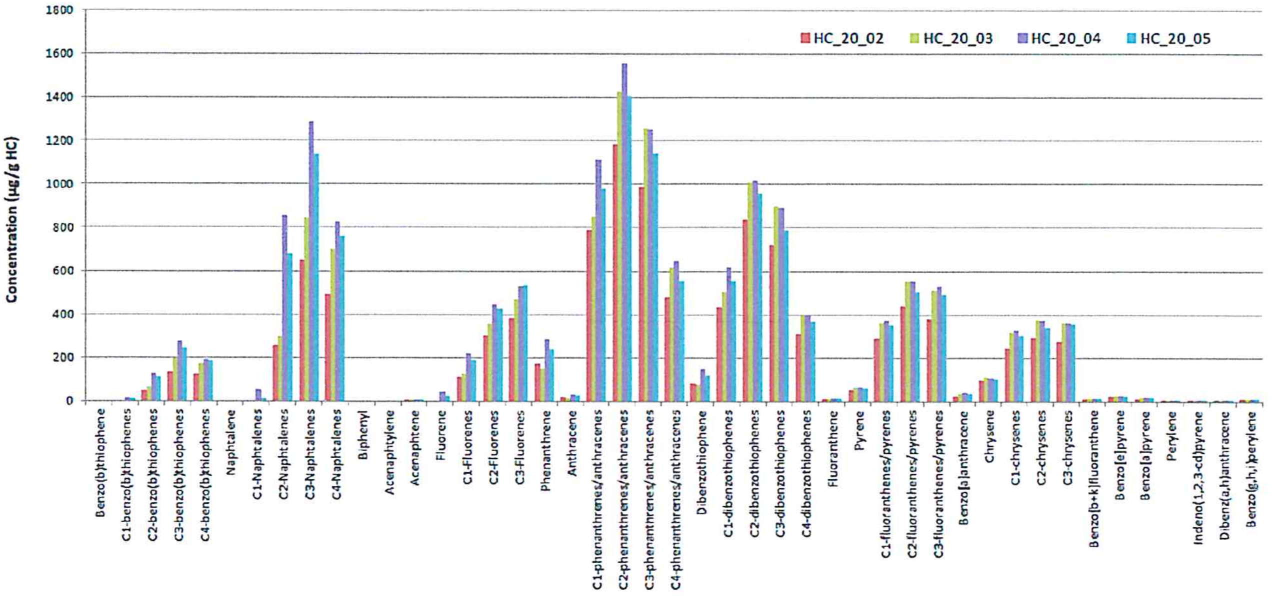


Figure 13 *PAH concentrations (µg/g or ppm)*

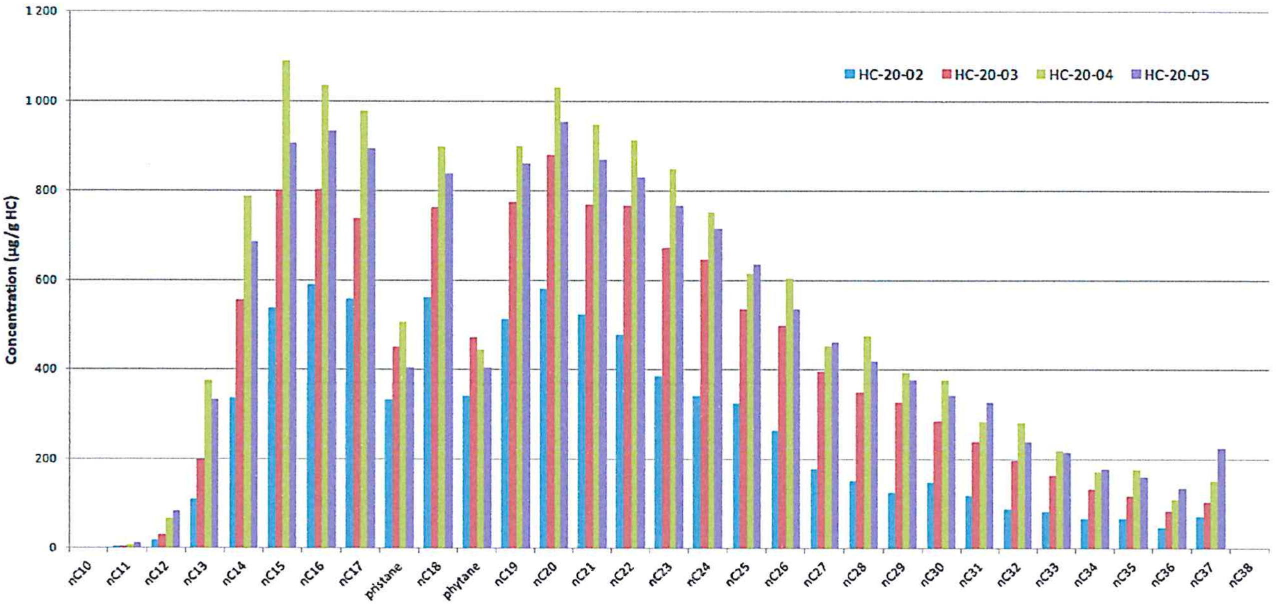


Figure 14 *n-alkanes concentrations (µg/g or ppm)*

SARA

Proportions of the various chemical families of compounds constitutive of petroleum products (Saturates/Aromatics/Resins/Asphaltenes), known as SARA analysis, are illustrated *table 3* for the various sediment and emulsified samples. The sum of resins and asphatenes is representative of the heavier fraction of oils, and is around 45%. This very high value can be obtained for heavy products such as heavy crude oils, bitumens or heavy fuel oils.

Table 3 *SARA analysis of sediment and emulsified samples*

Characterizations	HC-20-02	HC-20-03	HC-20-04	HC-20-05
		SARA analysis		
Saturates	22,2	18,6	20,0	31,0
Aromatics	34,8	29,8	29,2	32,3
Resins	22,1	25,6	26,0	14,3
Asphaltenes	20,9	26,0	24,7	22,4

5 CONCLUSION

The comparison of the various samples show that they have very similar fingerprints and chemical composition. In particular, the two emulsified oils, less affected by the matrix effects such as the ones observed for sediments, are very close to each other, and no significant difference could be pointed out. This homogeneity shows that the oils most probably do not come from an operational release from a ship as these spills are generally mixtures of products with the presence of lubricating oil (not present in the samples), and not homogeneous (the two emulsified oil samples are very similar).

The investigations carried out in order to identify the nature of the oil were conducted from both qualitative and quantitative points of views.
Qualitative analyses consisted in looking at specific distributions of molecules obtained from the GC/MS analysis. These various patterns were in agreement with profiles generally obtained for refined products. Heavy fuel oils are obtained by mixing various oil cuts, in particular fractions generated by cracking processes, and several aromatic distributions are specific to these processes.
The detailed quantitative analysis shows a high concentration in PAH, particularly for the high molecular weights, and a great proportion of resins and asphaltenes, the heaviest fraction of the oil. The very high viscosity of the emulsified oils is in agreement with these chemical properties.

All these elements are in agreement with a heavy fuel oil obtained according to refining processes, rather than a heavy crude oil.

APPENDICES

APPENDIX 1

GC/MS conditions of analyses

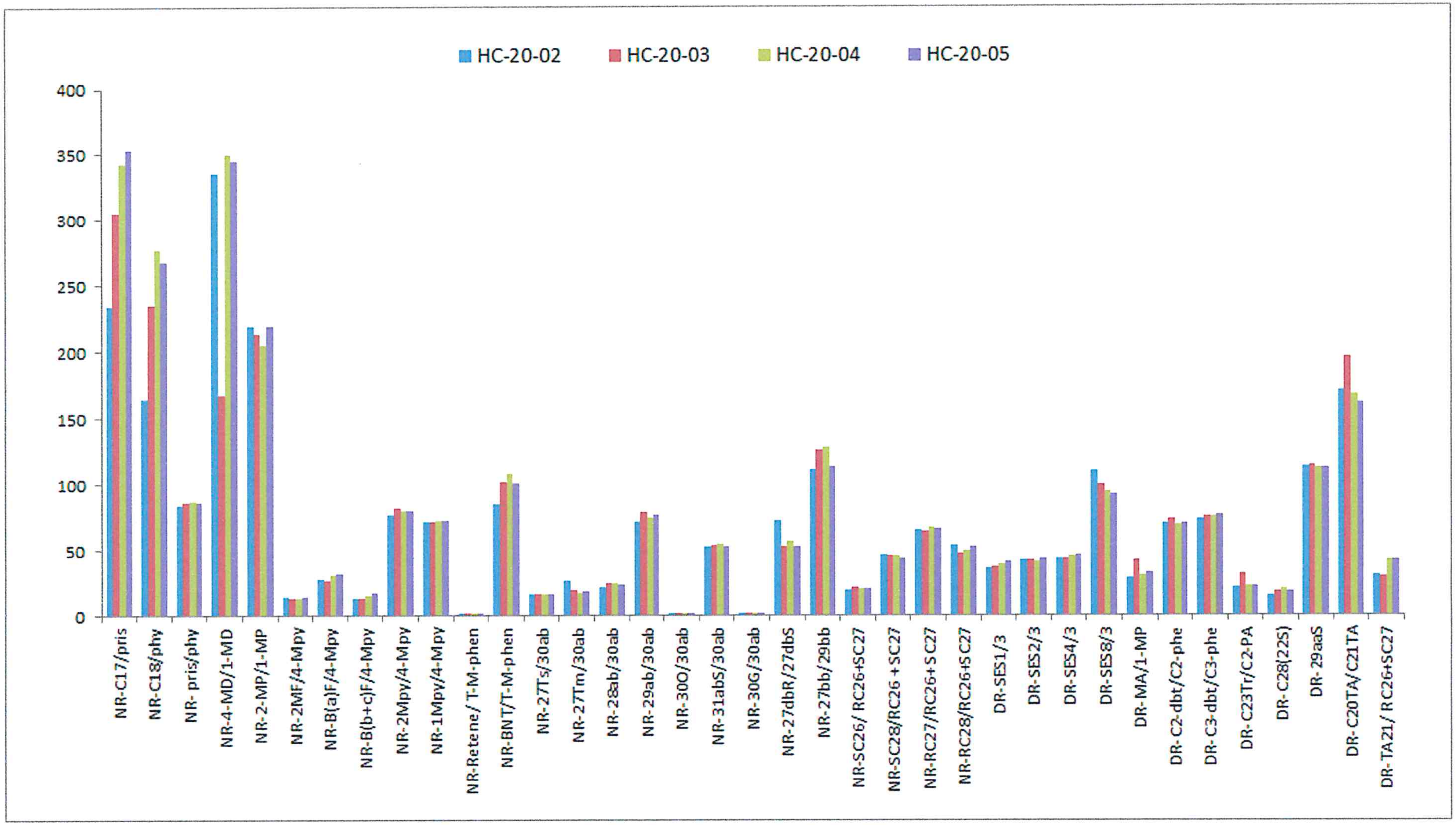
GC/MS (Gas Chromatography/Mass Spectrometry detector)

The analysis was performed by Gas Chromatography coupled to Mass Spectrometry (GC/MS). The GC was an HP 7890N (Hewlett-Packard, Palo Alto, CA, USA) equipped with a CIS-4 injector used in "pulsed splitless" mode (Splitless time: 1 min, flow 54 mL/min). The injector temperature was maintained at 300 °C. The interface temperature was 300°C. The GC temperature gradient was: from 50°C (1 min) to 150°C at 10°C/min, then 320°C (10 min) at 5°C/min. The carrier gas was Helium at a constant flow of 1 mL/min. The capillary column used was a HP-5 ms (HP, Palo Alto, USA): 30 m x 0.25 mm ID x 0.25 µm film thickness. The GC was coupled to an Agilent 5975 Mass Selective Detector used in SIM mode (Electronic Impact: 70 eV, voltage: 2000 V). Saturates and PAHs semi-quantifications were done using Single Ion Monitoring mode with the most representative fragment (saturates) or the molecular ion (PAH) of each compound at a minimum of 2 cycles/s.

APPENDIX 2

Diagnostic ratios

Table 1 Diagnostic ratios



APPENDIX 3

PAH and n-alkanes concentrations Comparison with the Erika heavy fuel oil

Table 1 *PAH and n-alkanes concentrations (average of emulsified samples) and comparison with the Erika heavy fuel oil*

		Erika	**Emulsified oil samples**
Benzo(b)thiophene	BT	311,4	0,0
C1-benzo(b)thiophenes	BT1	612,6	11,3
C2-benzo(b)thiophenes	BT2	629,1	118,7
C3-benzo(b)thiophenes	BT3	515,1	259,8
C4-benzo(b)thiophenes	BT4	175,8	187,2
Naphtalene	N	1137,6	0,0
C1-Naphtalenes	N1	2980,9	31,7
C2-Naphtalenes	N2	3978,4	766,6
C3-Naphtalenes	N3	2791,3	1212,3
C4-Naphtalenes	N4	1377,3	793,5
Biphenyl	B	0,0	0,0
Acenaphtylene	ANY	0,0	0,0
Acenaphtene	ANA	130,5	2,8
Fluorene	F	211,4	32,3
C1-Fluorenes	F1	449,4	203,7
C2-Fluorenes	F2	673,5	436,6
C3-Fluorenes	F3	671,2	532,3
Phenanthrene	P	760,3	263,6
Anthracene	A	161,5	30,9
C1-phenanthrenes/anthracenes	P1	2218,5	1045,6
C2-phenanthrenes/anthracenes	P2	2828,8	1480,0
C3-phenanthrenes/anthracenes	P3	2510,9	1195,2
C4-phenanthrenes/anthracenes	P4	1455,1	600,0
Dibenzothiophene	D	259,0	133,0
C1-dibenzothiophenes	D1	810,6	586,4
C2-dibenzothiophenes	D2	1233,3	987,1
C3-dibenzothiophenes	D3	1160,6	839,6
C4-dibenzothiophenes	D4	551,1	382,3
Fluoranthene	FL	41,5	12,8
Pyrene	PY	238,7	61,0
C1-fluoranthenes/pyrenes	FL1	1106,7	361,0
C2-fluoranthenes/pyrenes	FL2	1586,1	530,2
C3-fluoranthenes/pyrenes	FL3	1534,6	511,6
Benzo[a]anthracene	BA	321,0	37,0
Chrysene	C	541,1	102,3
C1-chrysenes	C1	1926,0	314,4
C2-chrysenes	C2	2354,0	355,0
C3-chrysenes	C3	2147,3	357,3
Benzo[b+k]fluoranthene	BBF	89,2	14,1
Benzo[e]pyrene	BEP	174,3	25,0
Benzo[a]pyrene	BAP	228,4	17,3
Perylene	PE	117,0	5,6
Indeno(1,2,3-cd)pyrene	IN	76,9	1,3
Dibenz(a,h)anthracene	DBA	99,1	4,1
Benzo(g,h,i)perylene	BPE	70,4	9,1
TOTAL (µg/ml)		**43 248**	**14 852**
N - N4		18%	18%
BT - C3		81%	81%
B(b+k)F - BPE		1%	1%

	Erika	**Emulsified oil samples**
nC10	156	0
nC11	261	9
nC12	291	75
nC13	341	354
nC14	341	735
nC15	344	998
nC16	377	984
nC17	164	936
pristane	425	455
nC18	205	868
phytane	536	424
nC19	697	880
nC20	936	992
nC21	1297	907
nC22	1778	871
nC23	2078	807
nC24	2063	734
nC25	2108	625
nC26	1779	570
nC27	1344	456
nC28	1049	446
nC29	929	385
nC30	721	359
nC31	739	303
nC32	472	258
nC33	333	217
nC34	266	175
nC35	255	168
nC36	0	123
nC37	0	187
nC38	0	0
TOTAL	**22 285**	**15 301**

APPENDIX 4

Chromatograms of hopanes and triaromatic steranes

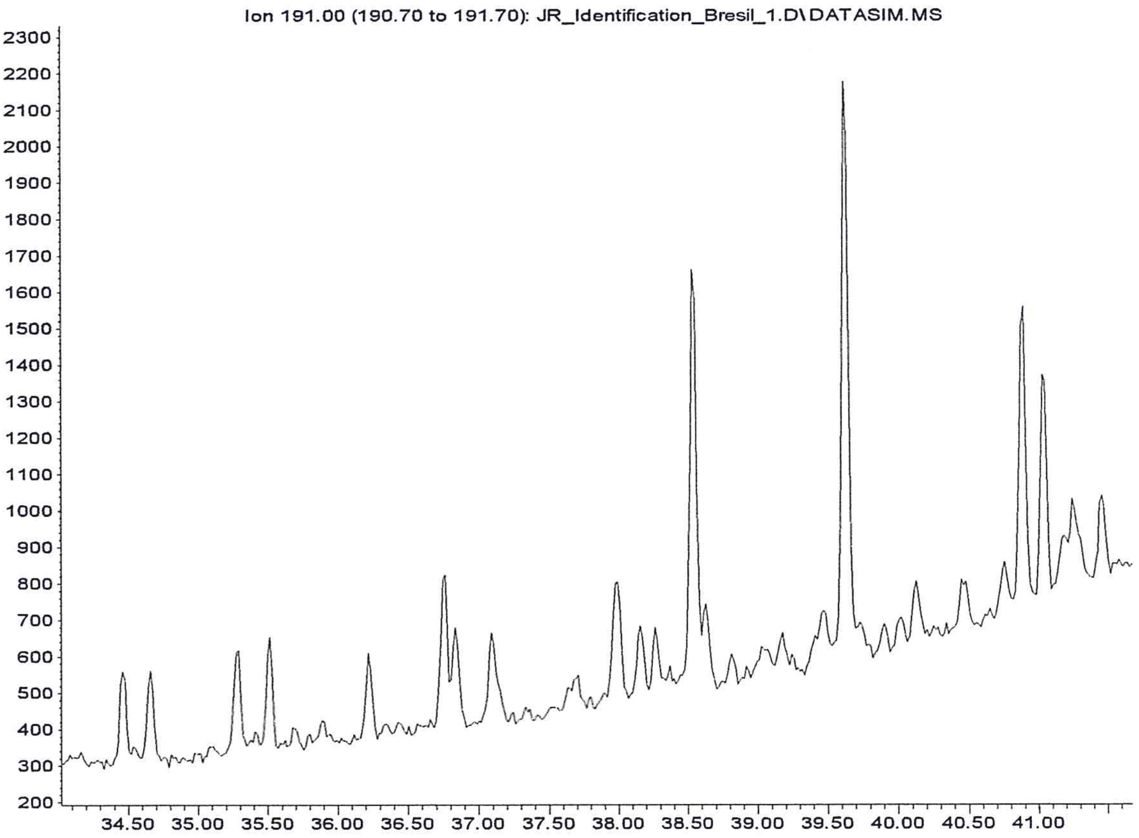


Figure 1 *Chromatogram of hopanes (m/z=191)*

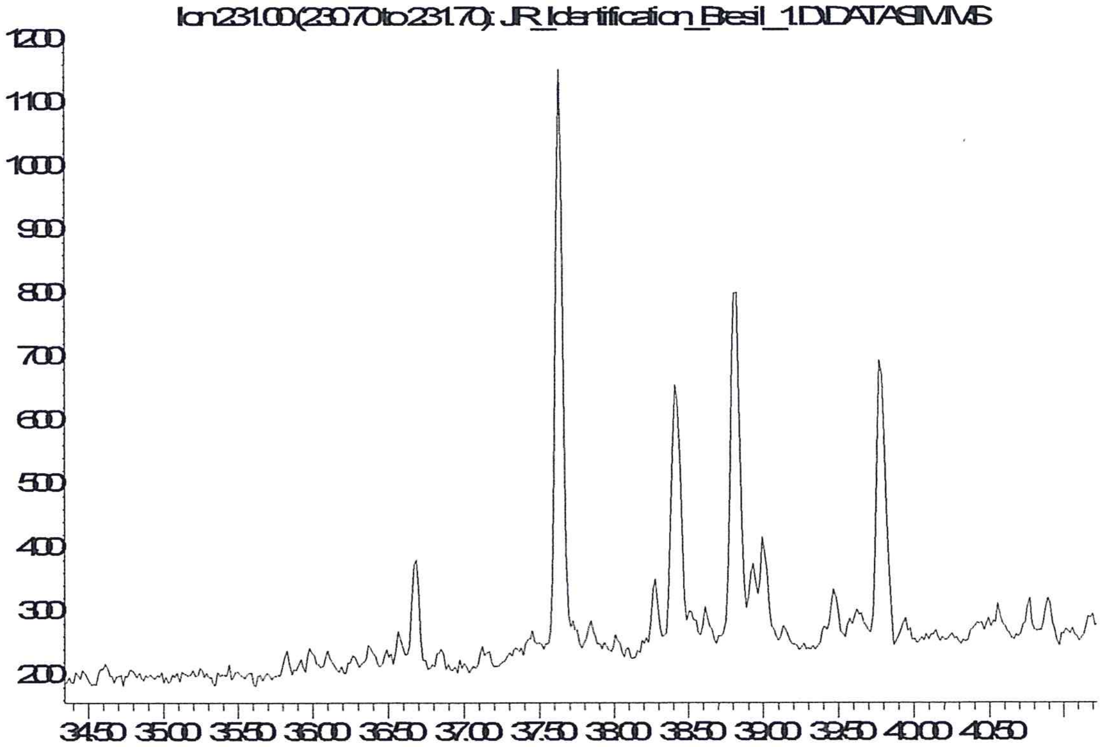


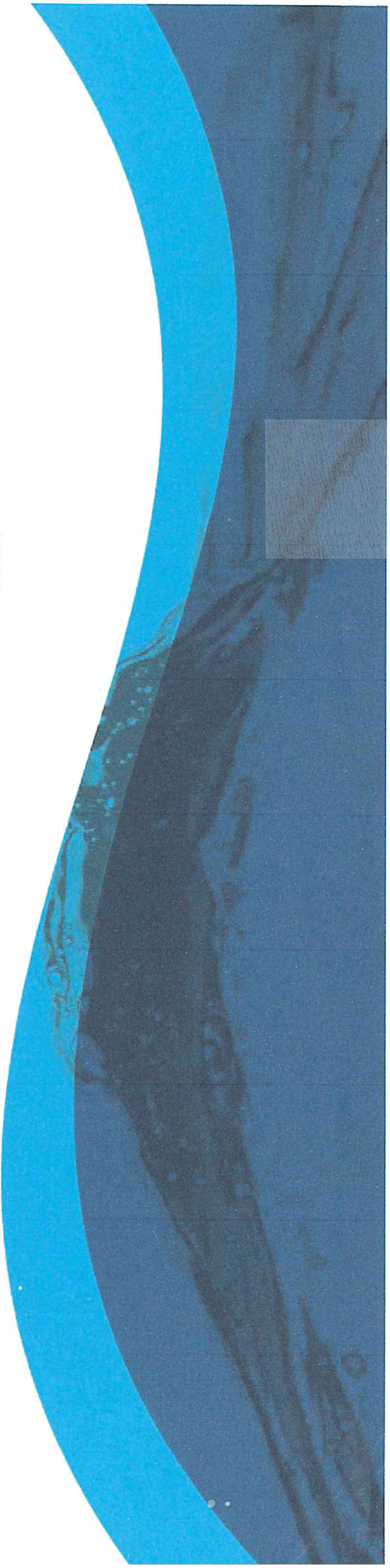
Figure 2 *Chromatogram of triaromatic steranes (m/z=231)*

SINTEF Ocean AS
SINTEF Ocean AS
Address: Postboks 4762 Torgarden
NO-7465 Trondheim NORWAY
Switchboard: +47 46415000

Oil Spill NE Brazil

Final Report

2020-03-05



In partnership with

ISDB

Avenida Rio Branco 89, sala 802
CEP: 20040-004, Centro
Rio de Janeiro-RJ-Brazil
Phone: +55 32394850

SINTEF Ocean AS
Address:
Postboks 4762 Torgarden
NO-7465 Trondheim
NORWAY
Switchboard: +47 46415000

Enterprise /VAT No:
NO 937 357 370 MVA

Report

Oil Spill in Brazil

Fingerprinting analysis and physicochemical properties of oil samples

REPORT NO.	PROJECT NO.	VERSION	DATE
OC2020 F-026	302005245	Final	2020-03-04

AUTHOR(S)
Liv-Guri Faksness
Marianne U. Rønsberg, Kjersti Almås

CLIENT(S)
Brazilian Navy, Oil Spill Inquiry

CLIENT'S REF.	NUMBER OF PAGES:
Frigate Captain Messias	27

CLASSIFICATION	CLASSIFICATION THIS PAGE	ISBN
Restricted	Restricted	

ABSTRACT

An oil spill in north-eastern Brazil has affected Brazilian jurisdictional waters and over 2,250 km of the coastline. The spill was first reported on August 30, 2019, and has impacted 675 locations in 116 municipalities, and 6,000 tons of oily materials are recovered so far (Mongabay, 2019). The origin of the oil spill is still unconfirmed.

SINTEF has analysed 8 samples collected at different locations along the coastline of Brazil from November 9 to 13, 2019.

According to the criteria given in CEN (2012), the GC/MS fingerprinting analysis indicated that the spill samples were refined products (residual blends, e.g. HFO) and not crude oils, and that the analysed spill samples seem to have the same origin.

PREPARED BY	CHECKED BY	APPROVED BY
Liv-Guri Faksness	Per S. Daling	Mimmi Throne-Holst

Table of Contents

1 Introduction

An oil spill in north-eastern Brazil has affected Brazilian jurisdictional waters and over 2,250 km of the coastline. The spill was first reported on August 30, 2019, and has impacted 675 locations in 116 municipalities, and 6,000 tons of oily materials are recovered so far (Mongabay, 2019). The origin of the oil spill is still unconfirmed.

The objective was to characterise oil spill samples taken from different shoreline locations at the coastline of Brazil to answer questions by the analysis a) whether each of the samples originates from crude or bunker fuel oil (refined product), and if they are from the same source b) weathering degree to indicate how long the samples have been weathered at sea; c) physico-chemical properties of the oil samples that may be relevant for the response operation and estimating the oil spill budget.

SINTEF received a total of 8 samples collected on different locations as indicated on the map in Figure 1.1. The samples were analysed according to CEN (2012) "Oil spill identification" methodology. The spill samples are usually compared with suspected sources. However, as no suspected source samples is available, the method is used to find out if the spill samples are from the same source. Due to the content of sediment particles, viscosity and density measurements were not possible.

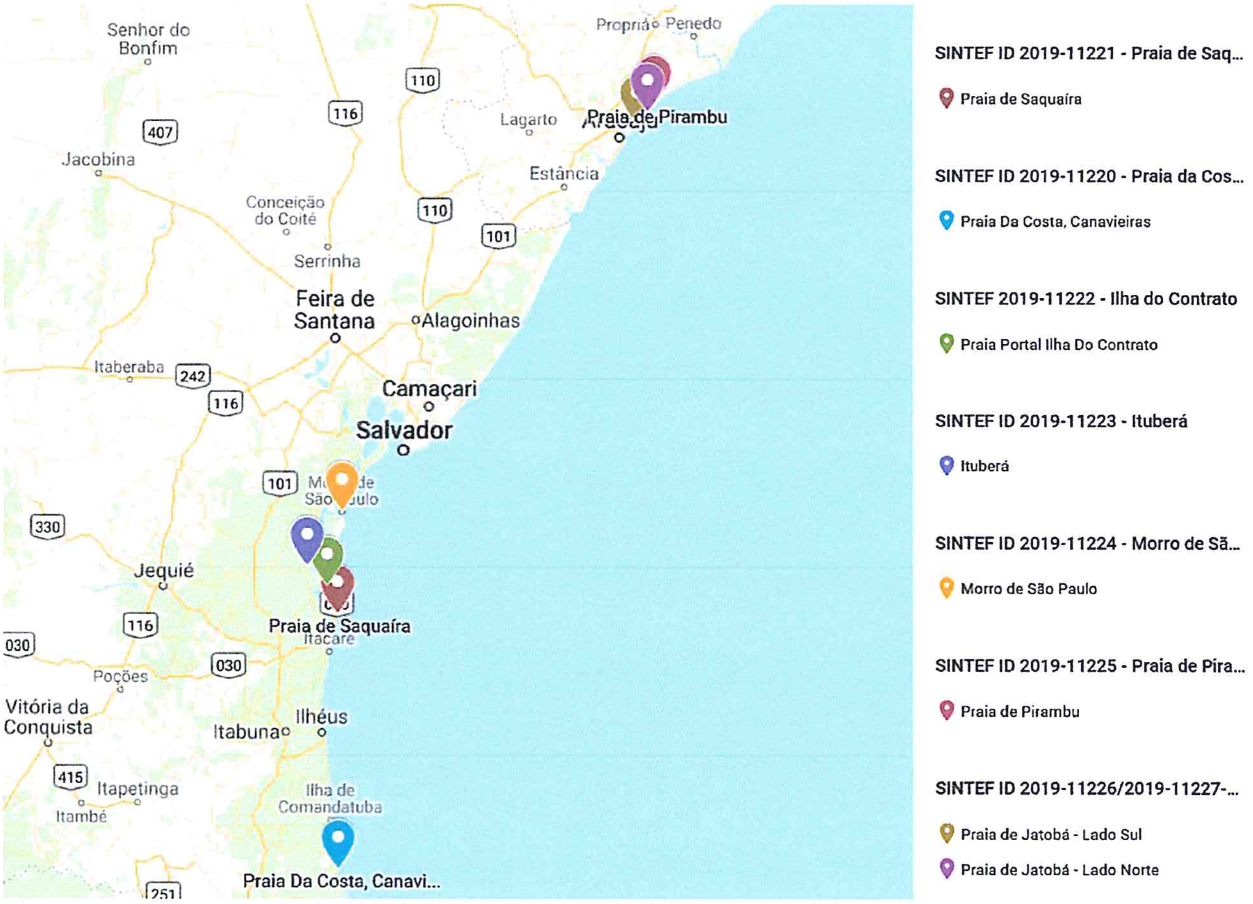


Figure 1.1 Map indicating the sampling locations (Google Map from J. Carneiro, ISDB)

2 Sample information

SINTEF received 8 samples from Equinor Brazil on December 20, 2019. The samples were collected from November 9 to 13, 2019, and are described in Table 2.1. Photos of the samples when arriving SINTEF are shown in Figure 2.1.

In addition, three crude oil samples from Venezuela and Brazil have been analysed to get more knowledge about the forensic fingerprinting of the crudes from this area.

Table 2.1 Overview over the analysed samples with information from the original labelling. A map indicating the sampling locations are shown in Figure 1.1. The three crude oils from Venezuela and Brazil are not directly related to the spill.

SINTEF ID	Sample ID	Sampling site	Samling date	GPS coordinates	GC/FID	GC/MS
2019-11220	Canavierias	Praide da Costa, Canavierias/BA	11-Nov-19	15°37'24"S; 38°56'24"S	X	X
2019-11221	Marau	Praida de Saquaira, Marau/BA	9-Nov-19	14°2'22"S; 38°56'58"N	X	X
2019-11222	Igrapuina	Ilha do Contrato - Igrapiuna	12-Nov-19	13°53'42"S; 39°1'18"W	X	
2019-11223	Itubera	Itubera - BA	12-Nov-19	13°43'56"S; 39°8'29"W	X	
2019-11224	Cairu	Moro de São Paulo, Cairu, BA	11-Nov-19	13°22'45"S; 38°54'46"W	X	X
2019-11225	Pirambu	Praia de Pirambu - Rebio Santa Isabel	13-Nov-19	10°41'2,0" ; 36°46'49,92"	X	X
2019-11226	Jatoba Sul	Praia de Jatoba - Lado Sul do TMIB	12-Nov-19	10°49'58,3" ; 36°56'1,6"	X	X
2019-11227	Jatoba Norte	Praia de Jatoba - Lado Norte do TMIB	12-Nov-19	10°49'42,1" ; 36°55'49,3"	X	
2019-10659	Zuata	Crude oil from Venezuela		From Equinor, Trondheim	X	x
2019-10640	Peregrino	Crude oil from Brazil		From SINTEF Storage	X	
2019-10624	BCF-17	Crude oil from Venezuela		From SINTEF Storage	X	x

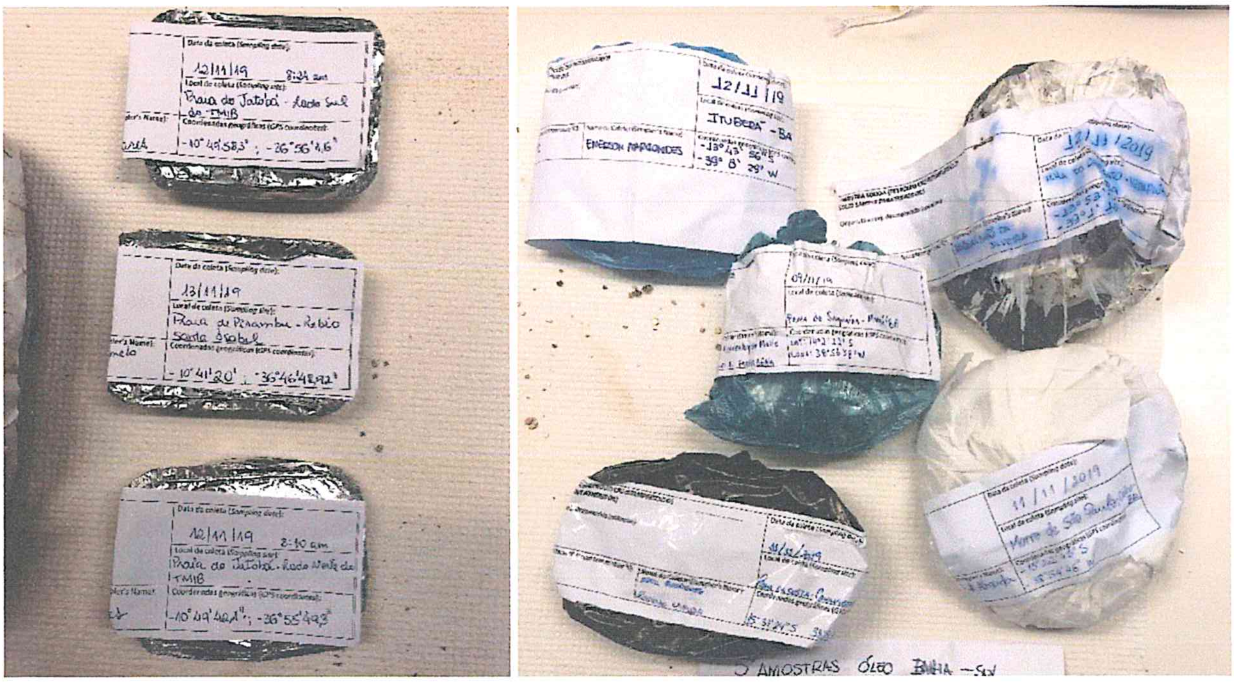


Figure 2.1 The samples when they arrived the SINTEF laboratory.

3 Methods

3.1 Physical characteristics of the spill sample

Due to that the samples contained sediment particles, viscosity and density measurements were not possible, as the particles will interfere with the instrumentation.

As it was not possible to measure oil density, a simple sinking test of the sample material was performed: An aliquot of the spill sample was transferred to bottles with seawater (3.4% salinity) and tap water (20 °C). If the sample does not float, the density (g/mL) is higher than in the water (1.024 and 1.0, respective).

The amount of sediment in the samples were quantified by "washing" a weighted aliquot in a solvent (dichloromethane, DCM). The sediment was filtrated out, rinsed by methanol, dried at 50 °C overnight, and weight.

Water content in the samples were measured by Karl Fisher titration.

3.2 Chemical characterisation

The samples were analysed according to CEN (2012) "Oil Spill Identification"-methodology.

An aliquot of the spill sample was transferred to a vial (40 mL), added DCM (25 mL), followed by 10 min. in an ultrasonic bath. Particles and water were removed by filtration over Bilson wool with sodium sulphate, Na_2SO_4.

The sample extracts were analysed on gas chromatograph with flame ionisation detector (GC/FID) and gas chromatograph with mass spectrometer (GC/MS). GC/FID was used for screening analysis and GC/MS for detailed fingerprinting analysis. The same sample extracts were used in both GC/FID and GC/MS analysis.

According to CEN (2012) duplicate analysis shall be performed for at least one of the samples. Results and evaluation of the duplicate analysis are shown in Appendix D.

The decision chart for the oil spill identification methodology applied in the CEN guideline is shown in Appendix E.

4 Results and discussion

4.1 Physical characteristics of the spill sample

There was a significant amount of sand particles in the samples. The simple "sinking test" was performed both in seawater and in tap water. As shown in Figure 4.1, the samples sank directly to the bottom (same observation in tap water), indicating that their densities were higher than 1.

Figure 4.1 *"Sinking test" of the spill samples in seawater.*

The amount of sediment (sand) in the samples varied between 9 and 71%, and the water content between 13 and 47% (Table 4.1). The content of oil varied between 16 and 44 in the spill samples. The total percentage of water/oil emulsion in the sample were from 29 to 91%, if the entire amount of water was emulsified in the oil phase. This resulted in 40 to 52 % water in the emulsions, or an average water content of 46 (±5) wt% in the oil.

Table 4.1 *Physical characteristics of the samples. Water contents were measured in the samples prior to removal of sediment particles. It was assumed that the entire amount of water was emulsified in the oil phase when estimating the water content in the oil.*

SINTEF ID	Sample ID	Water content in sample (wt. %)	Sand (wt. %)	Oil (wt. %)	Total emulsion (wt. %)	Water content in o/w wt. %)
2019-11220	Canavierias	30	32	38	67	45
2019-11221	Marau	47	9	44	91	52
2019-11224	Cairu	33	31	36	69	48
2019-11225	Pirambu	13	71	16	29	44
2019-11226	Jatoba - Sul	18	56	26	45	40

4.2 GC screening analysis

The GC chromatograms of all spill samples are given in Appendix A (Figure A 1 to Figure A 8). One of the samples did not contain any hydrocarbons (Figure A 8). This sample was labelled Jatoba Norte do TMIB (SINTEF ID 2019-11227).

The chromatographic patterns of the remaining samples were quite similar:

- The GC chromatograms show a distribution of oil components from nC12 and up to the chromatographic GC-limitation of around nC38. This indicated that there was a significant amount of heavy oil components (e.g. asphaltenes and heavy waxes) in the samples that are larger than C38, but they are not possible to analyse by GC. This indicate a relative heavy oil.

- All samples show high similarities in the lower end of the chromatogram, indicating that the samples may have undergone a low degree of evaporation. However, we do not know if the oil contained any lighter components when spilled. Therefore, it is not possible to estimate any trends in variation in weathering degree between the different samples and their locations.
- The significant content of n-alkanes suggests that the oils were not biodegraded. This can also be indicated by the relative high ratios of isoprenoids n-C17 and pristane, and n-C18 and phytane.
- One of the samples, collected in Cairu, has similar GC chromatogram as the other samples, but seems to contain additional peaks between C18 and C21 (Figure A 5).

The GC chromatogram of the sample collected in Marau (Figure 4.2) indicates that it was less weathered the other samples (see peak height difference between C15 and C17). The GC chromatogram of a sample collected in Pirambu (Figure 4.3) indicates that it was slightly more weathered than the other samples. These two spill samples were compared with two crude oils from Venezuela, shown Figure 4.4 and Figure 4.5, and one crude from Brazil (Figure 4.6). The GC chromatograms indicate that the oils are significant different.

The chromatographic patters in the spill samples were similar, indicating that they could have the same origin. To confirm this, GC/MS fingerprinting analysis were performed, followed by calculating and evaluating diagnostic ratios by a simple statistical method, in accordance with CEN (2012).

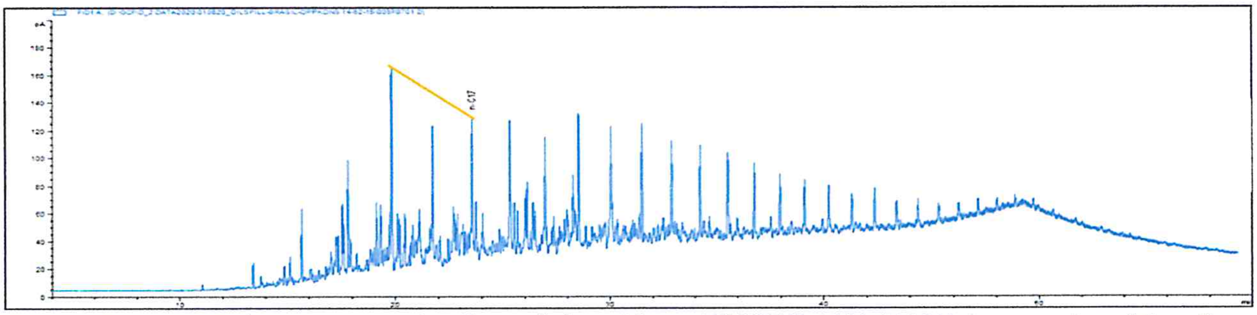


Figure 4.2 *GC chromatogram of spill sample from Marau (SINTEF ID 2019-11221). Less weathered than the other samples. Peak hight difference between C15 and C17 indicated with orange line.*

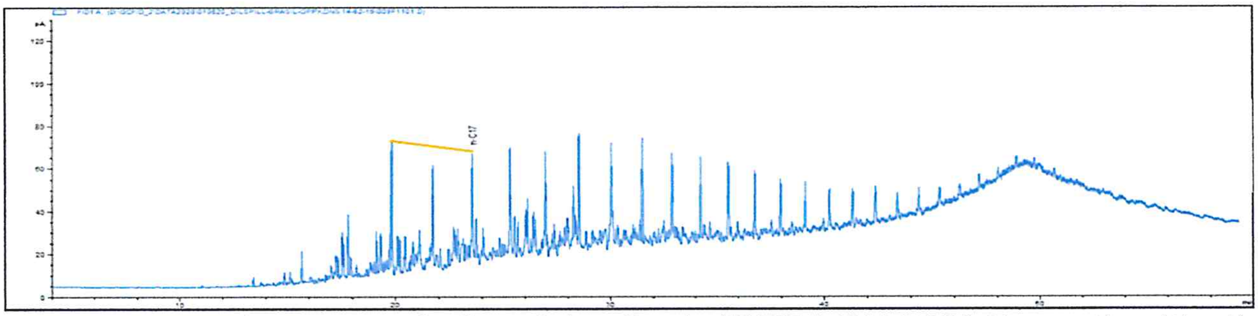


Figure 4.3 *GC chromatogram of spill sample from Pirambu (SINTEF ID 2019-11225). More weathered than the other samples.*

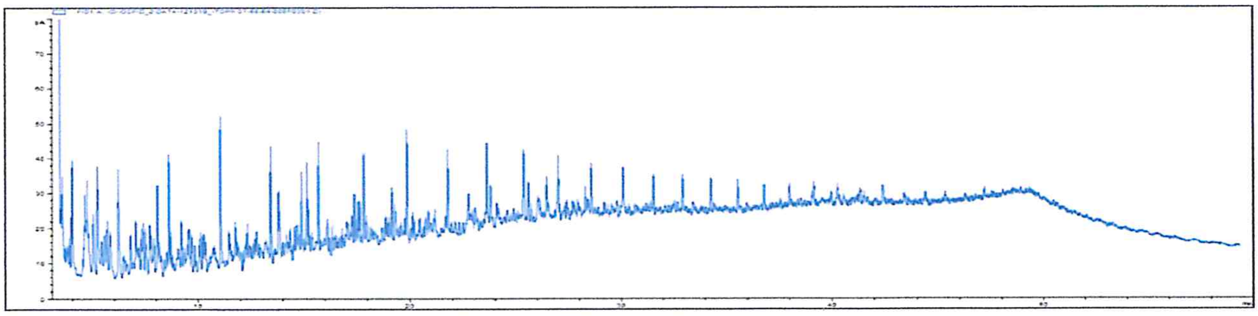


Figure 4.4 *GC chromatogram of BCF-17 (SINTEF Id: 2019-10624)*

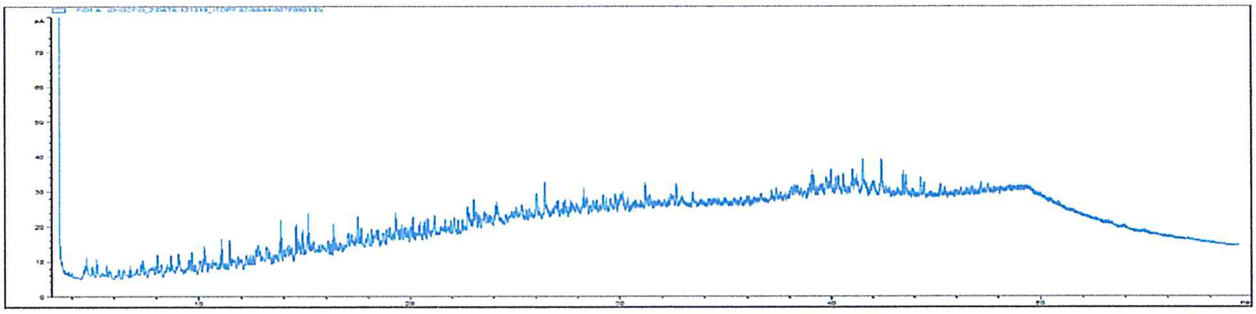


Figure 4.5 *GC chromatogram of Zuata (SINTEF Id: 2019-10659)*

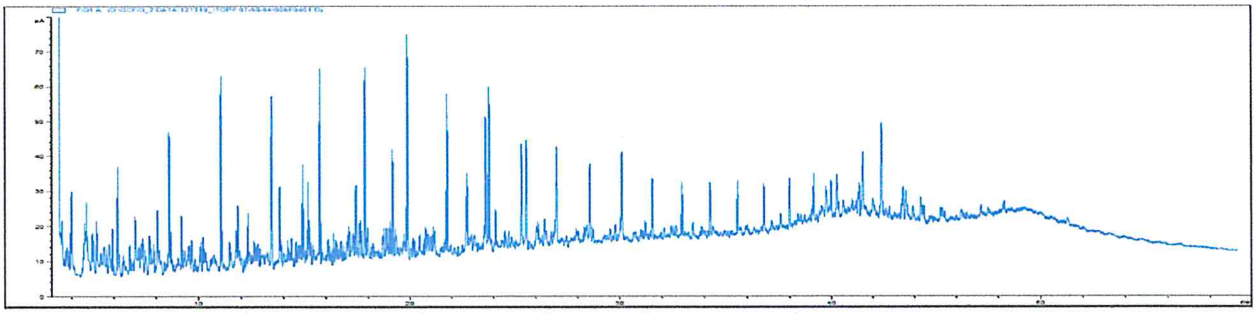


Figure 4.6 *GC chromatogram of Peregrino (SINTEF Id: 2019-10640)*

4.3 GC/MS fingerprinting

GC/MS fingerprinting analysis were performed in accordance to CEN (2012) on five of the received samples. Selected ion chromatograms are given in Appendix B. Examples of ion chromatograms are shown for the most weathered sample (Pirambu) in Figure 4.7, Figure 4.10, and Figure 4.11.

GC/MS fingerprinting can be used to indicate if an oil is a crude oil or a refined product. The refinery cracking processes lead to distinct clusters of isomers if it is a refined product as conversion refinery processes can alter the distribution of the of methyl phenanthrene isomers and create new compounds typically absent in the feedstock. Specifically, catalytic cracking can reduce the proportion of the less stable (9-, 4-, and 1-) methyl-phenanthrenes (MP, the second duplet in Figure 4.7) and produce methyl-anthracene (MA) that generally are absent or present in only low concentrations in crude oil (Uhler et al., 2007).

According to CEN (2012), there are two specific features that indicate a refined product:

- Methyl-phenanthrenes (m/z 192): The first duplet is higher than the second duplet, and it contains a distinct methyl-anthracene (MA) peak.
- Retene is usually not present in the C4-phenanthrenes (m/z 234), as it is strongly reduced during refinery cracking (Radovic et al., 2012).

In a crude oil, the first duplet is lower than the second duplet and the methyl anthracene peak is not as distinct. However, if retene is not present, it could still be a crude, as several crudes only contain traces of retene.

The C1-phenathrenes in the spill sample are shown in Figure 4.7 , and as it can be seen, the first duplet is higher than the second duplet, and MA is present, indicating that the oil is a refined product. In Figure 4.8 and Figure 4.9, the ion chromatograms of the Venezuelan crudes BCF-17 and Zuata are shown and it can be seen that the methyl-anthracene peak is not as distinct as in the spill sample.

An ion chromatogram of the C4-phenanthrenes in the spill sample from Pirambu is shown in Figure 4.10. Retene was not present in any of the samples (expected location is given).

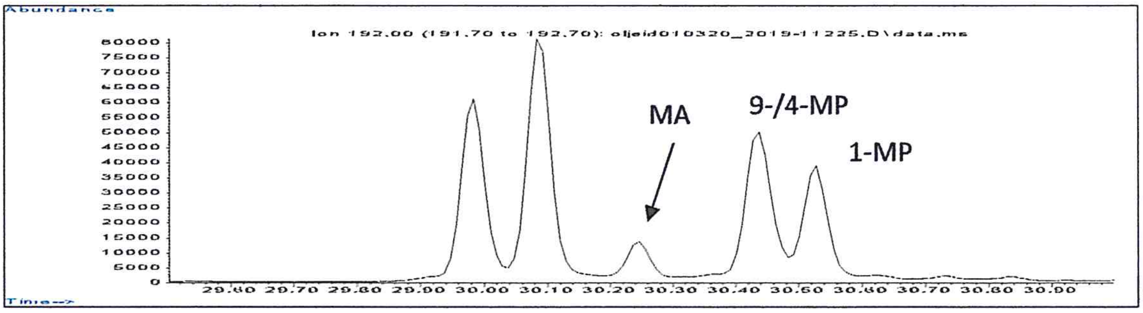


Figure 4.7 *Ion chromatogram of C1-phenanthrenes (m/z 192) in the spill sample from Pirambu (2019-11225)*

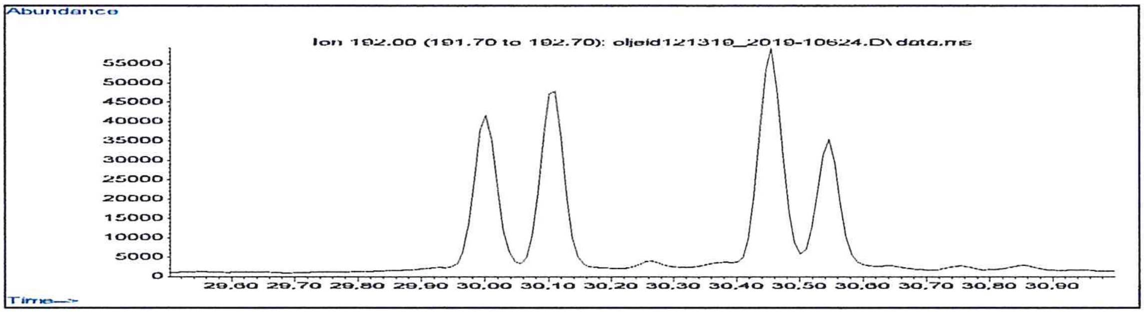


Figure 4.8 *Ion chromatogram of m/z 192 in the Venezuelan crude oil BCF-17 (SINTEF ID 2019-10624)*

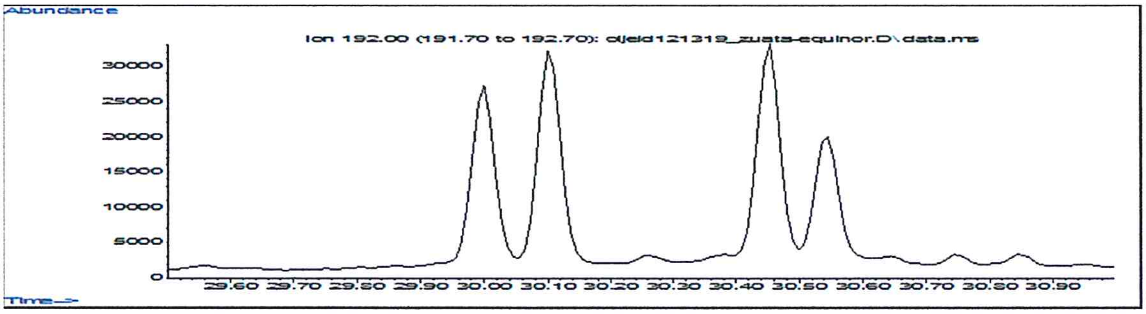


Figure 4.9 *Ion chromatogram of m/z 192 in the Venezuelan crude oil Zuata (SINTEF ID 2019-10659).*

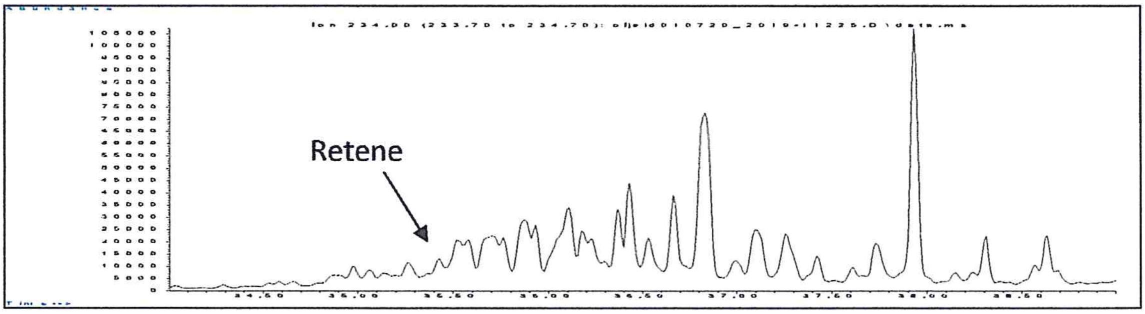


Figure 4.10 *Ion chromatogram of C4-phenantrenes with the expected location of retene in sample from Pirambu (SINTEF ID 2019-11225).*

In addition, several other PAHs and geochemical biomarkers were analysed, as described in CEN (2012). The biomarker hopanes (m/z 191) in the spill sample from Pirambu are shown in Figure 4.11. The hopanes can indicate the oils origin, and the present oil contains the biomarker oleanane (30O), which indicates that the oil may origin from a terrestrial source rock. For comparison, the hopanes in the Venezuelan crudes BCF-17 and Zuata are shown in Figure 4.12 and Figure 4.13. They contain oleanane too, but there were several visual differences in the ion chromatograms of the hopanes, some of them indicated with a red arrow.

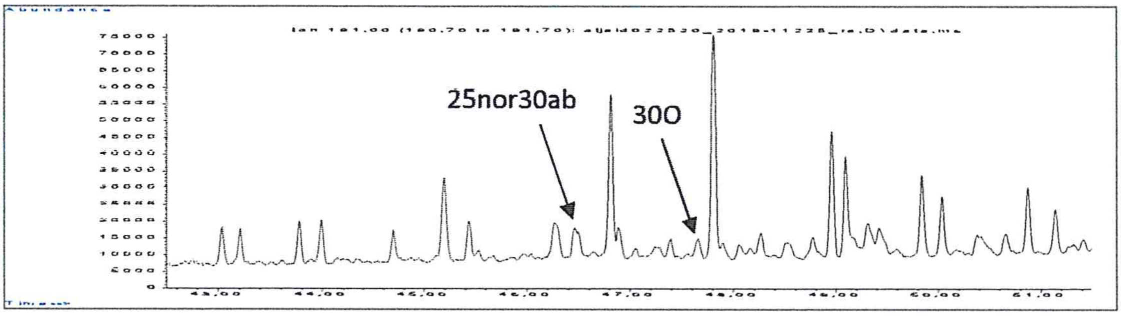


Figure 4.11 *Ion chromatogram of hopanes (m/z 191) in the spill sample from Pirambu (SINTEF ID 2019-11225).*

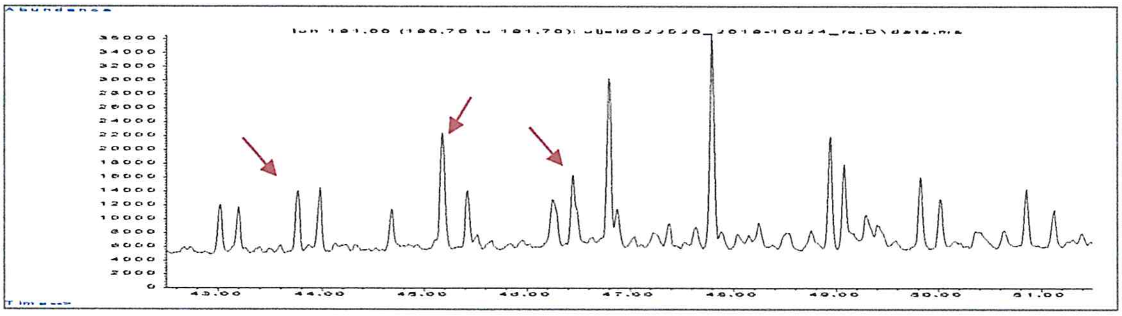


Figure 4.12 *Ion chromatogram of m/z191 of the Venezuelan crude BCF-17 (SINTEF Id: 2019-10624). Red arrows indicate visual differences when compared with the spill sample 2019-11225.*

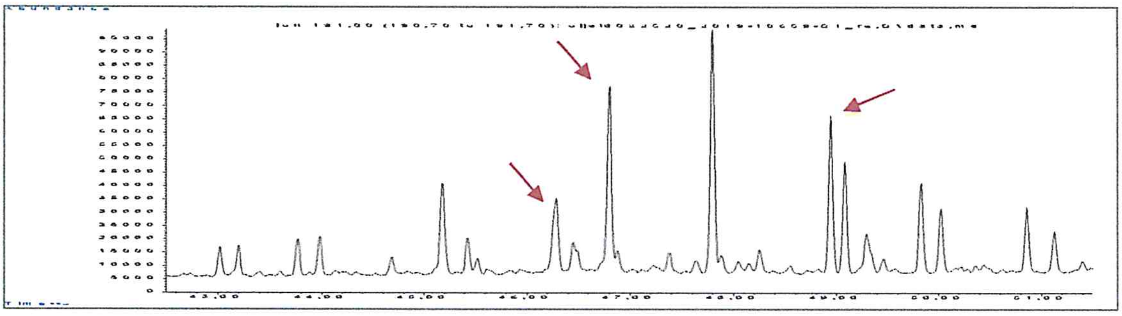


Figure 4.13 *Ion chromatogram of m/z191 of the Venezuelan crude Zuata (SINTEF Id: 2019-10659).). Red arrows indicate visual differences when compared with the spill sample 2019-11225.*

Overlaying ion chromatograms of m/z 191 and m/z 177 are given in Figure 4.14, indicating that the peak of 25nor30ab is the first in the duplet at a retention time of 46.45 min. This is also in accordance with an internal reference oil, the so-called "SINTEF-mix".

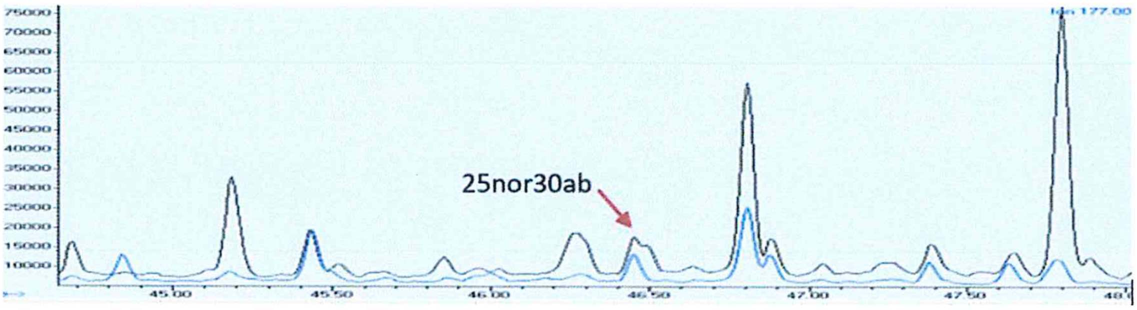


Figure 4.15 *Overlaying ion chromatograms of m/z 191 (black line) and m/z 177 (blue line) in the spill sample from Pirambu (SINTEF ID 2019-11225). The peak of 25nor30ab is the first in the duplet with a retention time of 46.45 min (red arrow).*

4.3.1 Visual inspection of selected ion chromatograms

The following ion chromatograms are given in Appendix B:

- m/z 192 (C1-phenanthrenes/anthracenes) are shown in Figure B 1 to Figure B 5 (spill samples),
- m/z 191 (hopanes) in Figure B 6 to Figure B 12 (spill samples and the crudes Zuata and BCF-17),
- m/z 217 and 218 (steranes and disteranes) in Figure B 13 to Figure B 19 (spill samples and the crudes Zuata and BCF-17),
- m/z 216 (C1-fluoranthenes/pyrenes) in Figure B 20 to Figure B 24 (spill samples),
- m/z 231 (triaromatic steranes) in Figure B 25 to Figure B 29 (spill samples).
- Ion chromatograms of C4-phenanthrenes (m/z 234) are not given, as retene was not present in any of the samples.

There were no obvious differences when comparing the ion chromatograms of the spill samples visually, indicating that they may have the same origin.

The next step in CEN (2012) is usually to compare the spill sample with the suspected sources by calculations of diagnostic ratios and evaluating the ratios by using a simple statistical method. However, as no samples from suspected sources are available, the method is used to confirm that the spill samples are from the same source.

4.3.2 Evaluation of samples

The GC/MS data was treated as described in CEN (2012), and an Excel spreadsheet prepared by the Bonn Agreement OSINET group was used to compare and evaluate the samples.

So-called PW-plots (percentage weathering) of PAH and biomarker compounds were generated (Figure 4.16, left graph). The PW-plots are used to evaluate results and to visualize the analytical data by showing potential similarity of oil samples and the impact of weathering. A data point in the PW-plot represents the concentration of a compound or compound group in the spill sample relative to the concentration of the same compound or compound group in the suspected source. When comparing two samples by means of a PW-plot, a compound that is robust to weathering is used as a normalization compound, in this case hopane (C30) is chosen. According to CEN (2012), the assessment to estimate the variance of the PW-plot results in a range of 85% to 118%. This range is assigned as a maximum acceptable range when comparing two samples.

Diagnostic ratios (DR) for numerical comparison were calculated (CEN, 2012). DR are ratios between the peak height or peak area of single compounds or compounds groups selected by their diversity in chemical composition and on their known behaviour in weathering processes. When calculating critical difference between two DR a fixed value of 14% of the mean value of a ratio is used, which is based on the maximum allowable relative standard deviation of 5% for the ratios. Consequently, any measured difference in a DR between two samples (i.e. the absolute different in percent based on the mean of the two ratios) higher than 14% should be regarded as significant, meaning that these two ratios are statistically different. The ratio comparison graphs shown in Figure 4.16, illustrate the relative difference between normative ratios (middle graph) and informative ratios (right figure).

In Figure 4.16, the two spill samples that were least (Marau) and most weathered (Pirambu) than the other samples were compared as described above. The PW-plot and the comparison of normative DR where within the acceptance criteria for positive match according to CEN (2012).

In Appendix C, the samples were compared with the sample from Marau, as it seemed less weathered than the other samples according to visual comparison of the GC chromatogram. The PW-plot and the comparison of normative and informative DR where within the acceptance criteria for positive match according to CEN (2012) for all samples. As mentioned above, the GC chromatogram of the sample collected in Cairu (2019-11124), was like the other samples, but contained some additional peaks. This could indicate that this sample is contaminated or contains traces of another oil product in addition to the main source. However, only one of the normative DR has a relative difference of more than 14%, and it is the small peak of oleanane 30O). As the similarities are significant, it is no reason to believe that this sample has another source than the other samples.

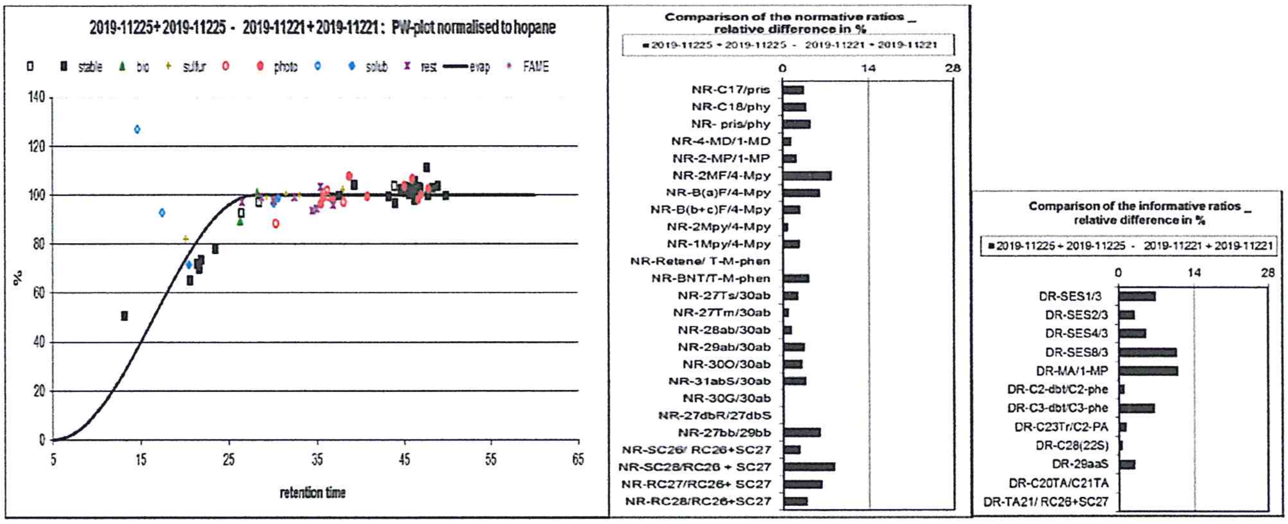


Figure 4.16 *PW-plots and comparison of normative and informative diagnostic ratios: Spill samples from Pirambu (most weathered sample) and Marau (least weathered sample). Duplicate analyses of both samples are compared.*

5 Conclusions

SINTEF received a total of 8 samples from Equinor Brazil on December 20, 2019. The samples were collected from November 9 to 13, 2019, at different locations along the coastline of Brazil.

The samples were analysed and evaluated according to the criteria given in CEN (2012). The GC screening analysis showed that the sample labelled Jatoba Norte do TMIB did not contain any hydrocarbons. The chromatographic patterns of the remaining 7 samples were quite similar. The GC/MS fingerprinting analysis indicated that the spill samples were relatively heavy refined products (residual blends, e.g. HFO) and not crude oils. The spill samples were compared by calculating diagnostic ratios and the ratios evaluated by a simple statistical method. The results showed that all spill samples seem to have the same origin and that the source is a refined oil product.

Due to the content of sediment particles in the samples, viscosity and density measurements were not possible. A simple test showed that the spill samples were heavier than seawater, indicating a density higher than 1. The water content in the emulsions were between 40 to 52 %.

6 References

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Mongabay (2019). https://news.mongabay.com/2019/11/voyager-i-tanker-identified-as-possible-brazil-oil-spill-perpetrator/ (Accessed January 8, 2020)

Radovic, J.R., C. Dominguez, K. Laffont, S. Diez, J.W. Readman, J. Albaiges, and J.M. Bayona (2012). Compositional properties characterizing commonly transported oils and controlling their fate in the marine environment. J. Environ. Monit. 14: 3220-3229.

Uhler, A.D., S.A. Stout, G.S: Douglas (2007). Chemical heterogeneity in modern marine residual fuel oils. *In* Wang Z. and S.A. Stout (eds): Oil spill environmental forensics. Fingerprinting and source identification. Academic Press, ISBN 678-0-12-369523-9, pp. 327-348.

A Appendix A GC chromatograms

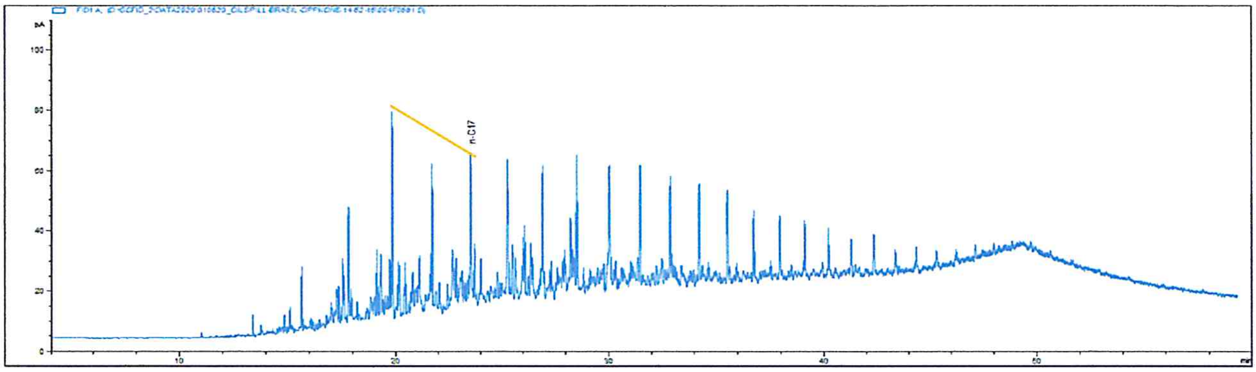


Figure A 1 *GC chromatogram of spill sample from Canavierias (SINTEF ID 2019-11220)*

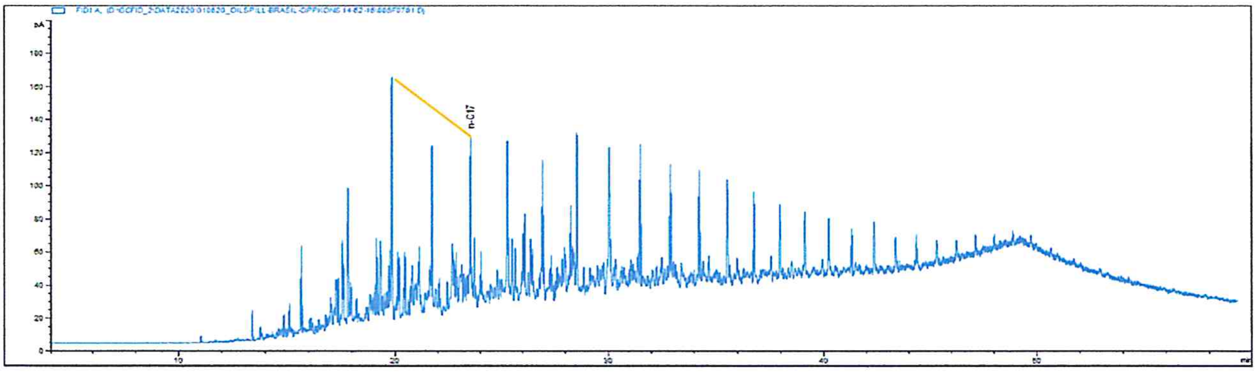


Figure A 2 *GC chromatogram of spill sample from Marau (SINTEF ID 2019-11221)*

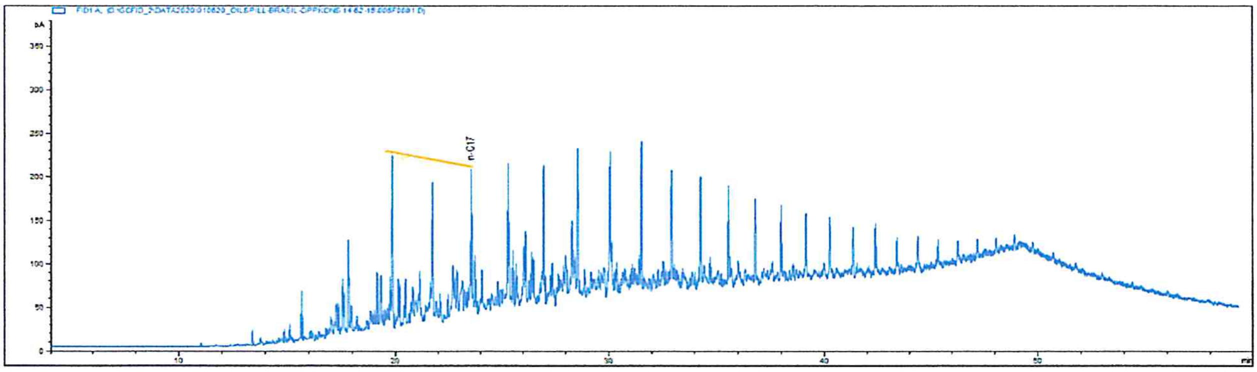


Figure A 3 *GC chromatogram of spill sample from Igrapuina (SINTEF ID 2019-11222)*

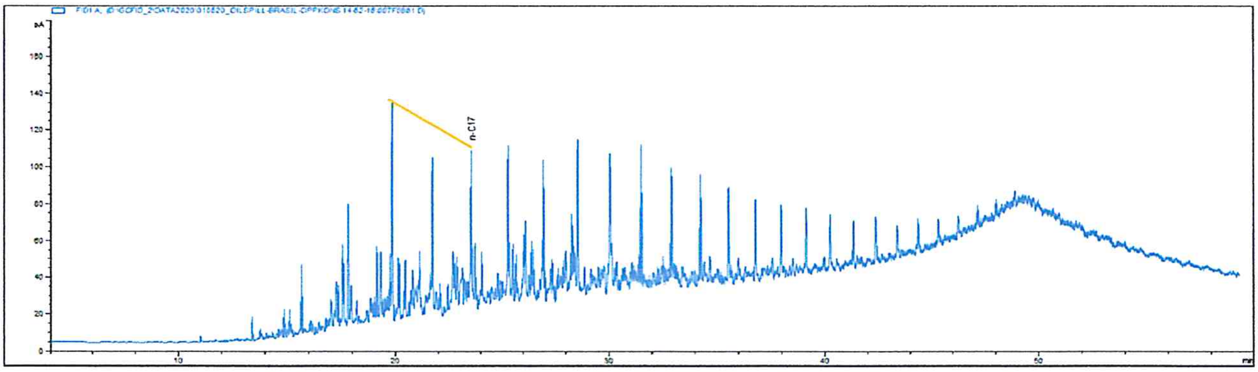


Figure A 4 *GC chromatogram of sample from Itubera (SINTEF ID 2019-11223)*

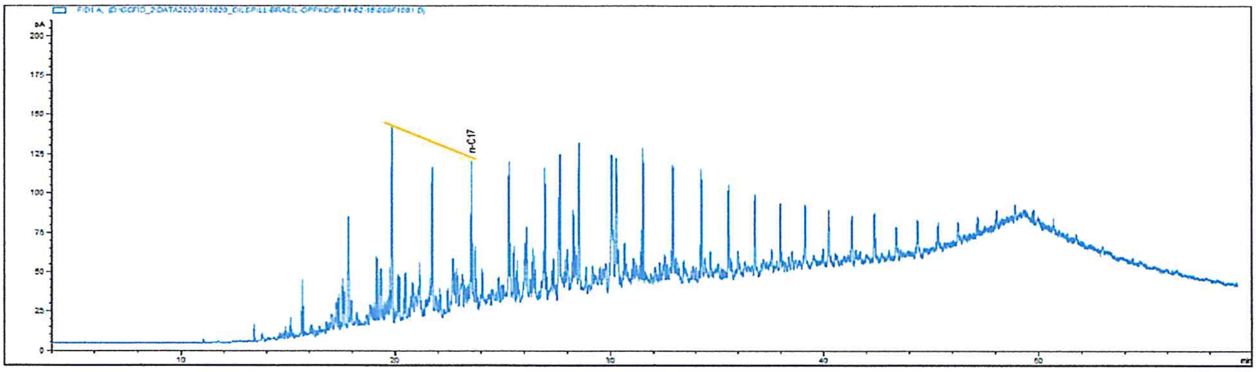


Figure A 5 *GC chromatogram of spill sample from Cairu (SINTFE ID 2019-11224)*

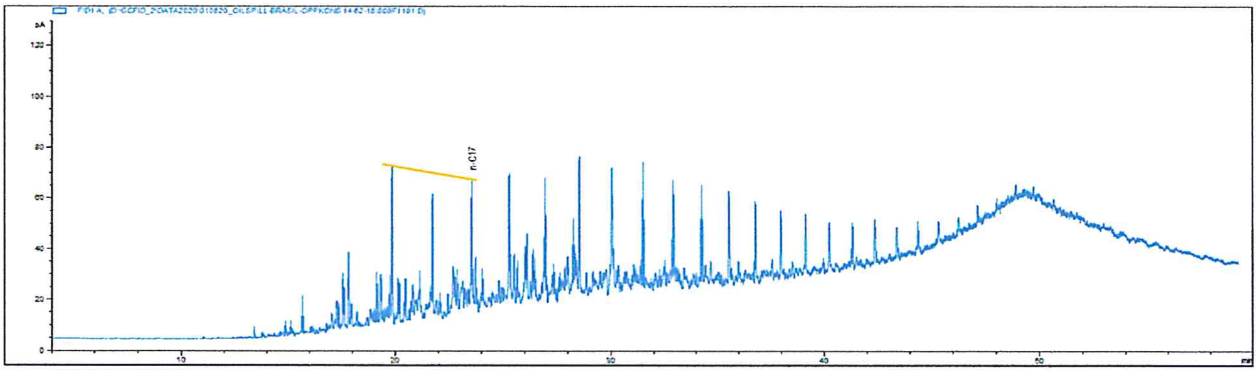


Figure A 6 *GC chromatogram of spill sample from Pirambu (SINTEF ID 2019-11225)*

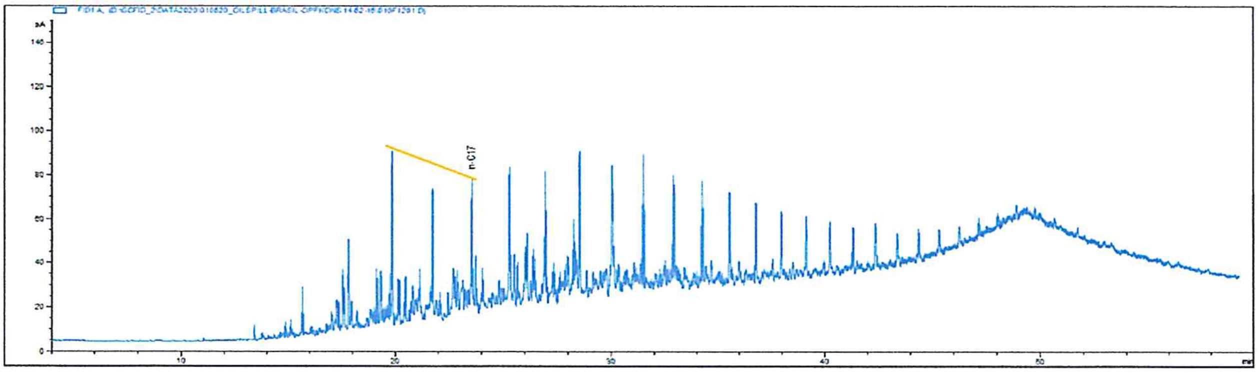


Figure A 7 *GC chromatogram of spill sample from Jatoba Sul do TMIB (SINTEF ID 2019-11226)*

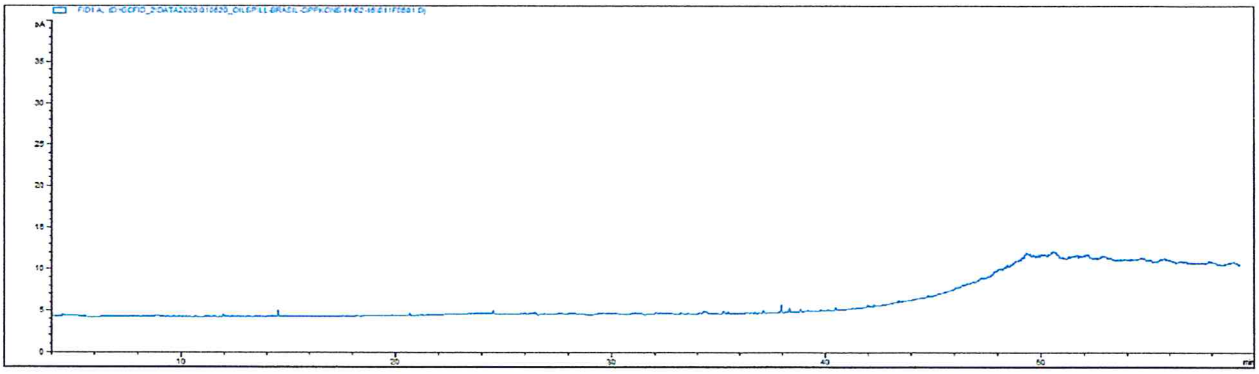


Figure A 8 *GC chromatogram of spill sample from Jatoba Norte do TMIB (SINTEF ID 2019-11227)*

B Appendix B Ion chromatograms

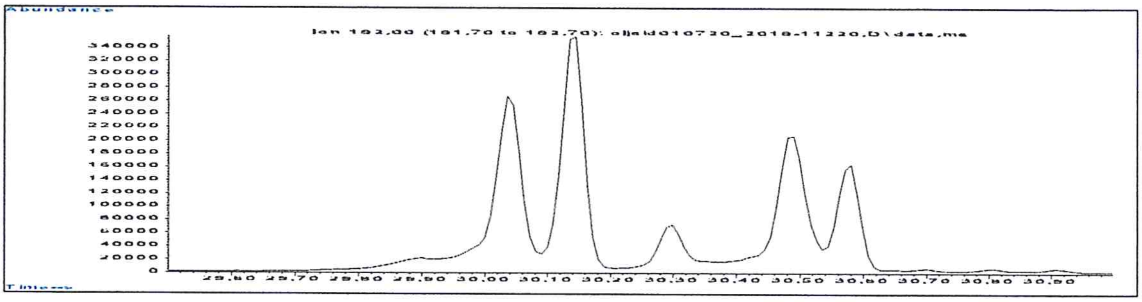


Figure B 1 *C1-phenantrenes-anthracenes (m/z 192) from Canavierias (SINTEF Id:2019-11220)*

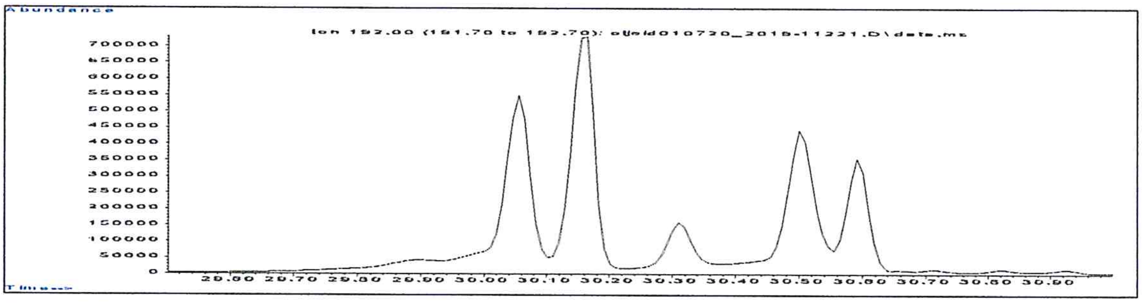


Figure B 2 *C1-phenantrenes-anthracenes (m/z 192) from Marau (SINTEF Id: 2019-11221)*

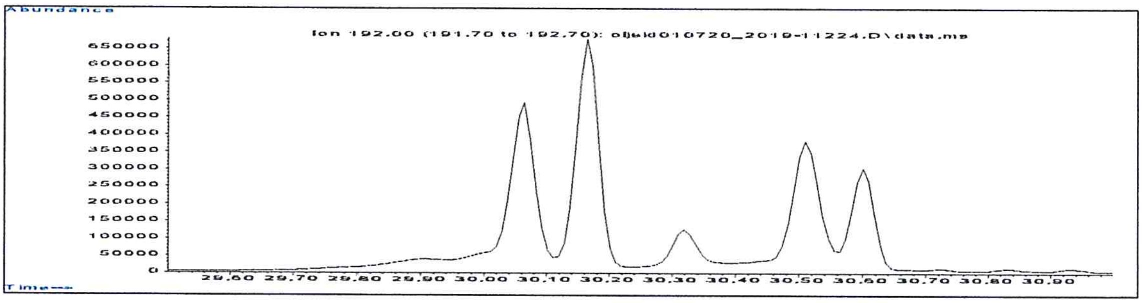


Figure B 3 *C1-phenantrenes-anthracenes (m/z 192) from Cairu (SINTEF Id: 2019-11224)*

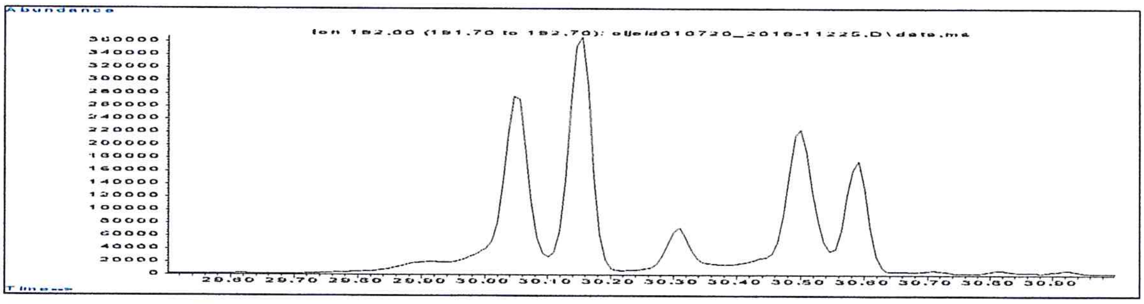


Figure B 4 *C1-phenantrenes-anthracenes (m/z 192) from Pirambu (SINTEF Id: 2019-11225)*

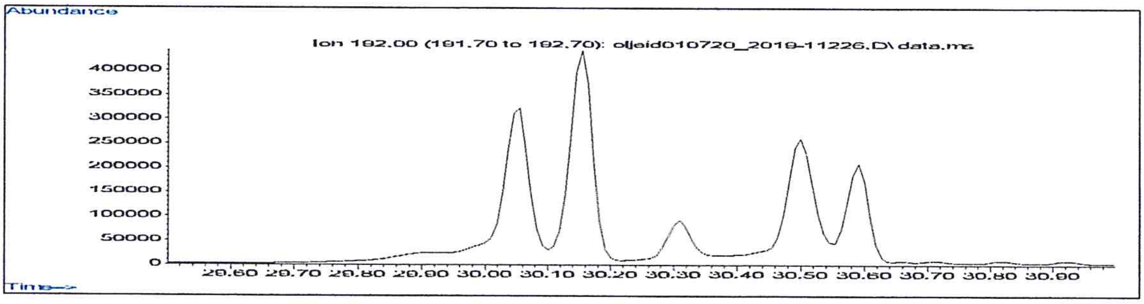


Figure B 5 *C1-phenantrenes-anthracenes (m/z 192) from Jatoba Sul do TMIB (SINTEF Id: 2019-11226)*

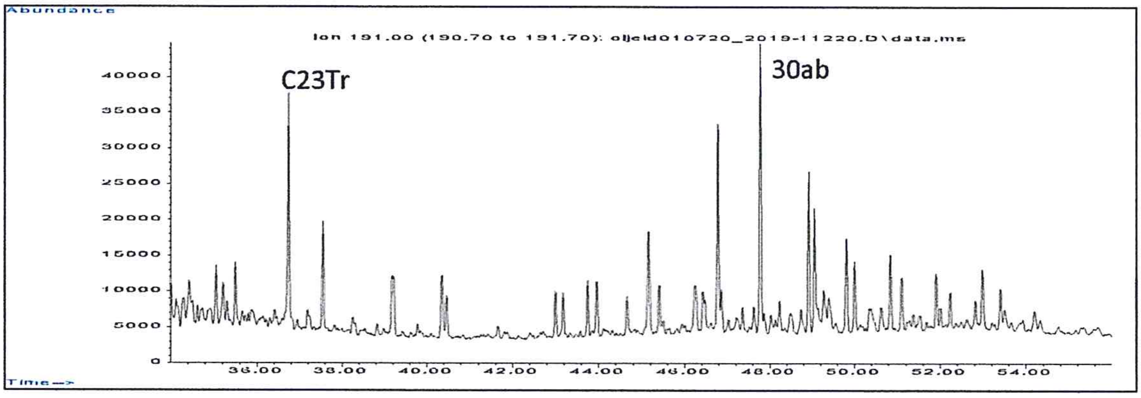


Figure B 6 *Hopanes (m/z191) from Canavieiras (SINTEF Id: 2019-11220). Earlier retention time interfere with alkylated phenanthrenes, which have higher abundance than the hopanes.*

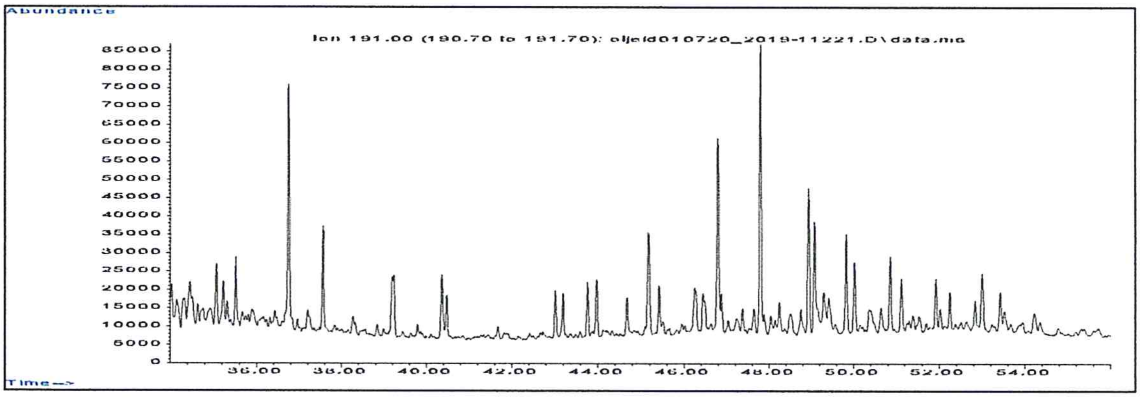


Figure B 7 *Hopanes (m/z191) from Marau (SINTEF Id: 2019-11221)*

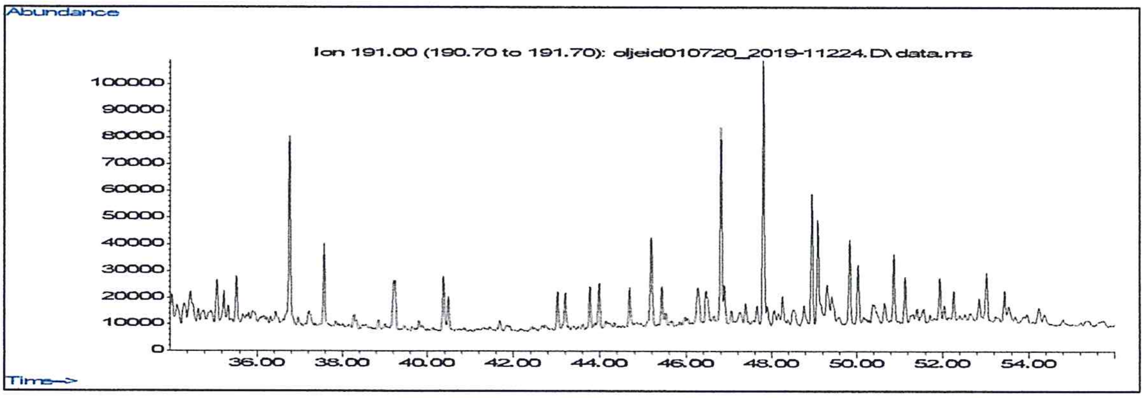


Figure B 8 *Hopanes (m/z191) from Cairu (SINTEF Id: 2019-11224)*

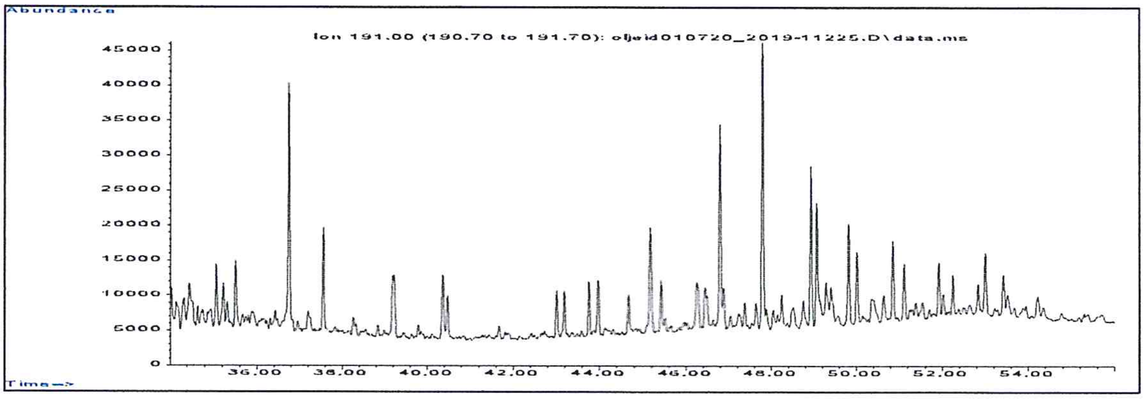


Figure B 9 *Hopanes (m/z191) from Pirambu (SINTEF Id: 2019-11225)*

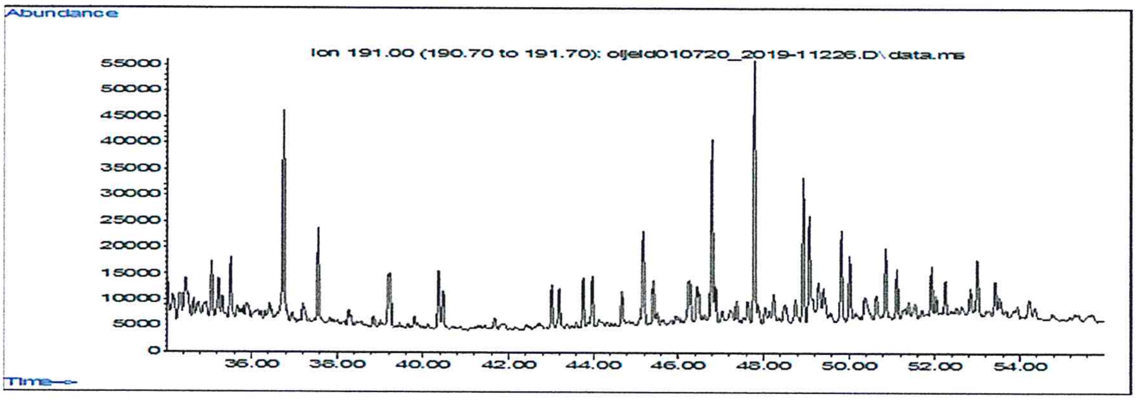


Figure B 10 *Hopanes (m/z191) from Jatoba Sul do TMIB (SINTEF Id: 2019-11226)*

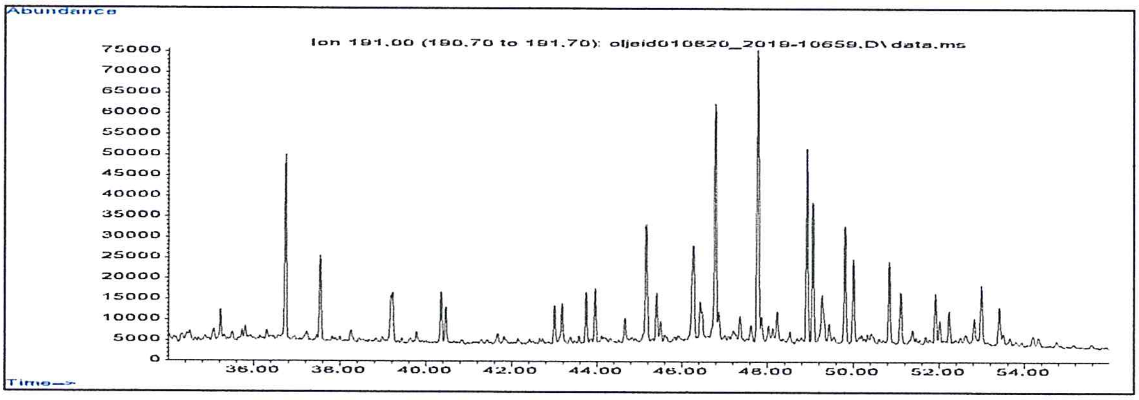


Figure B 11 *Hopanes (m/z191) from Zuata oil (SINTEF Id: 2019-10659)*

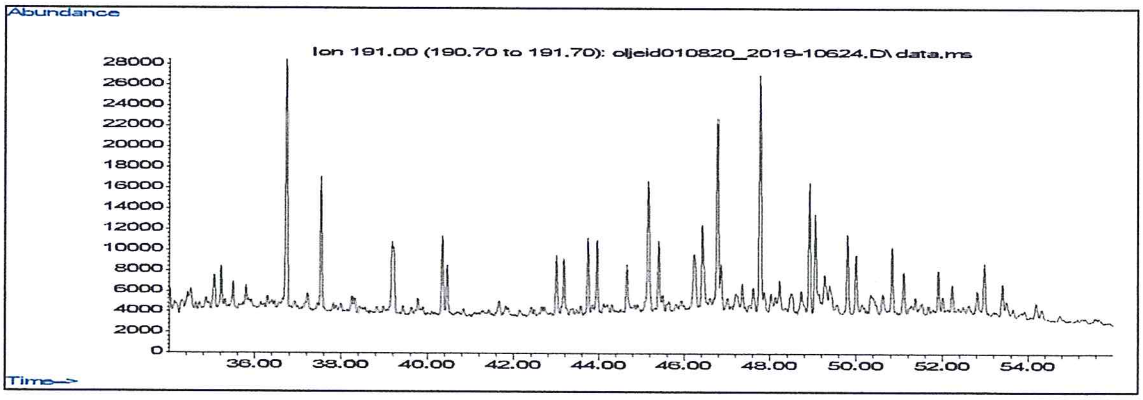


Figure B 12 *Hopanes (m/z191) from BCF 17 (SINTEF Id: 2019-10624)*

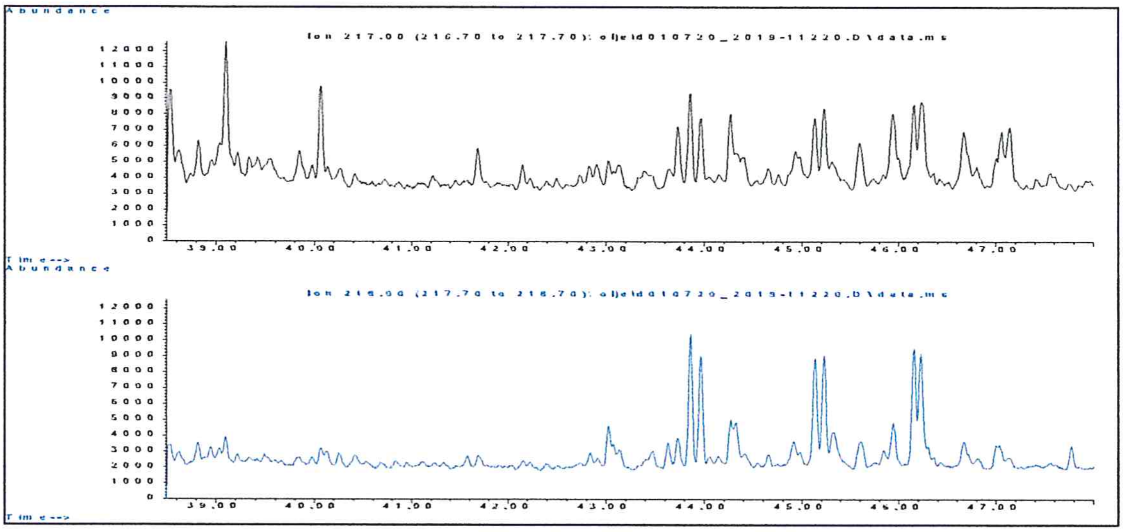


Figure B 13 *Steranes and disteranes (m/z 217 and m/z218) from Canavieiras (SINTEF Id: 2019-11220)*

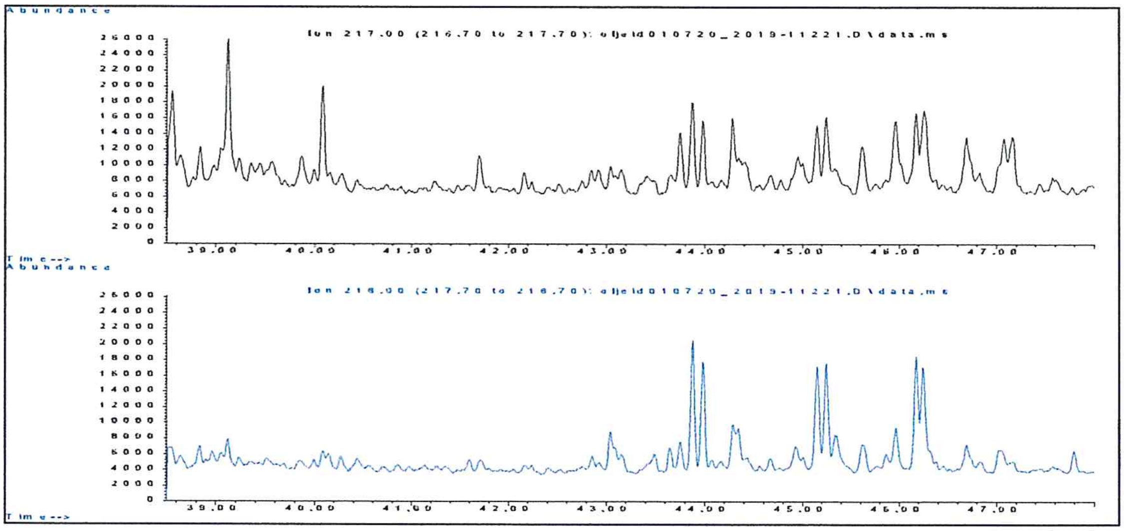


Figure B 14 *Steranes and disteranes (m/z 217 and m/z218) from Marau (SINTEF Id: 2019-11221)*

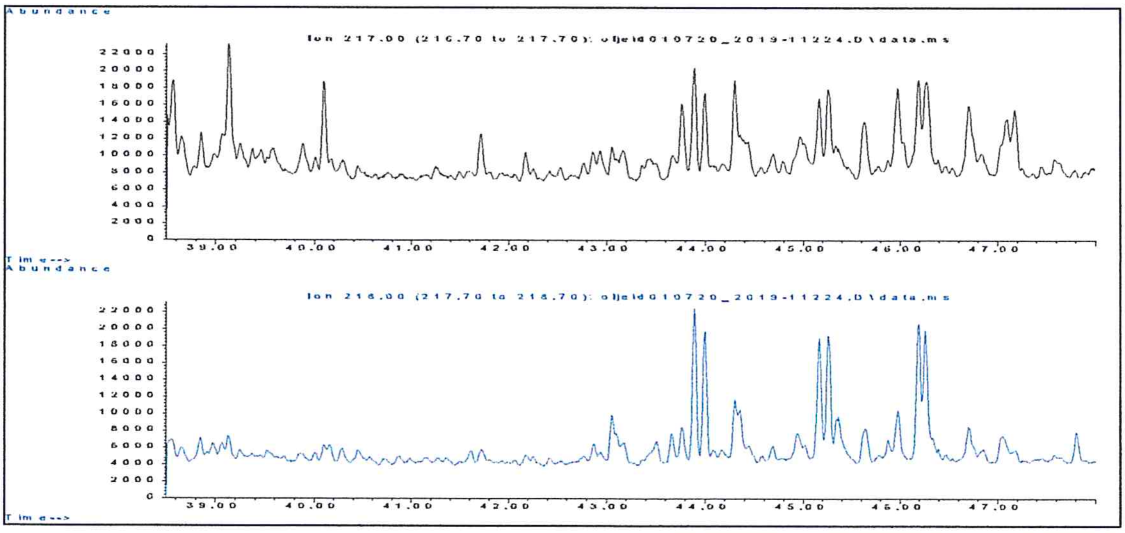


Figure B 15 *Steranes and disteranes (m/z 217 and m/z218) from Cairu (SINTEF Id: 2019-11224)*

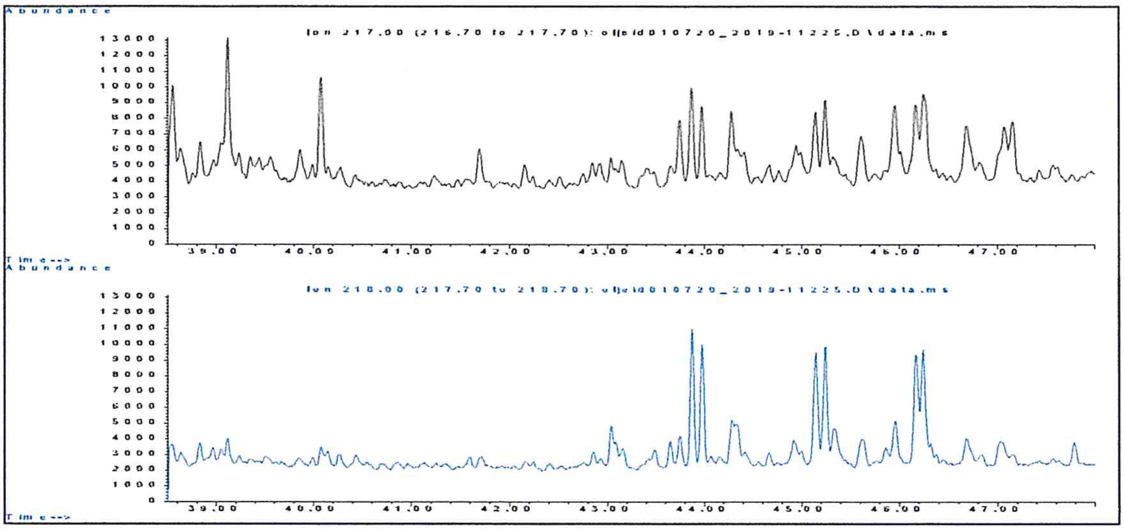


Figure B 16 Steranes and disteranes (m/z 217 and m/z218) from Pirambu (SINTEF Id: 2019-11225)

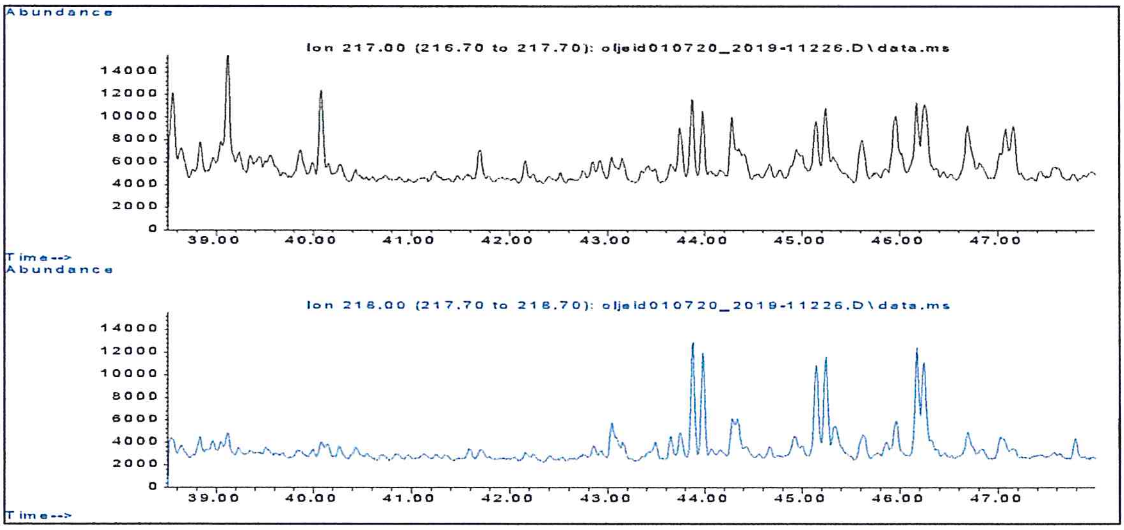


Figure B 17 Steranes and disteranes (m/z 217 and m/z218) from Jatoba Sul do TMIB (SINTEF Id: 2019-11226)

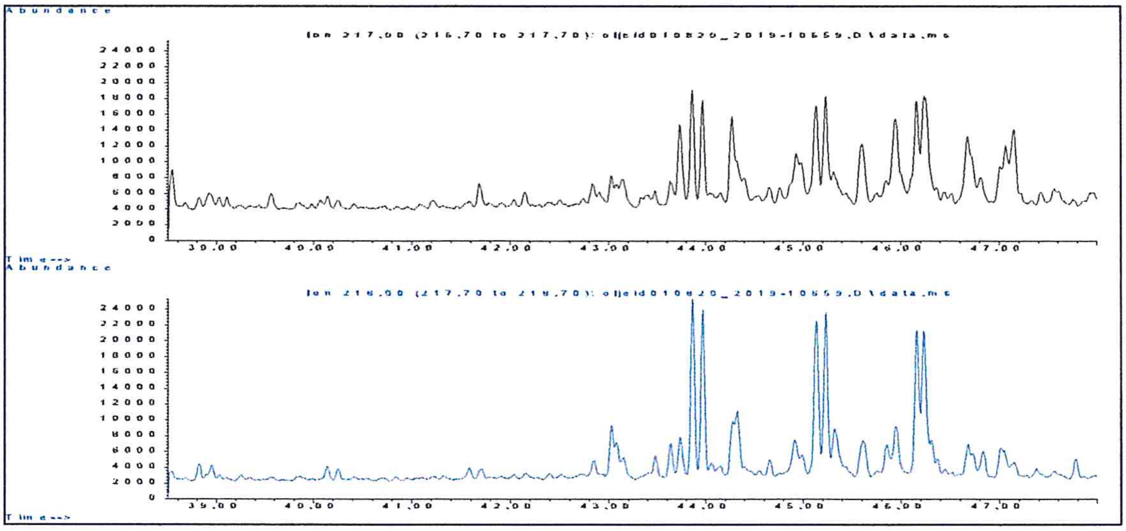


Figure B 18 Steranes and disteranes (m/z 217 and m/z218) from Zuata oil (SINTEF Id: 2019-10659)

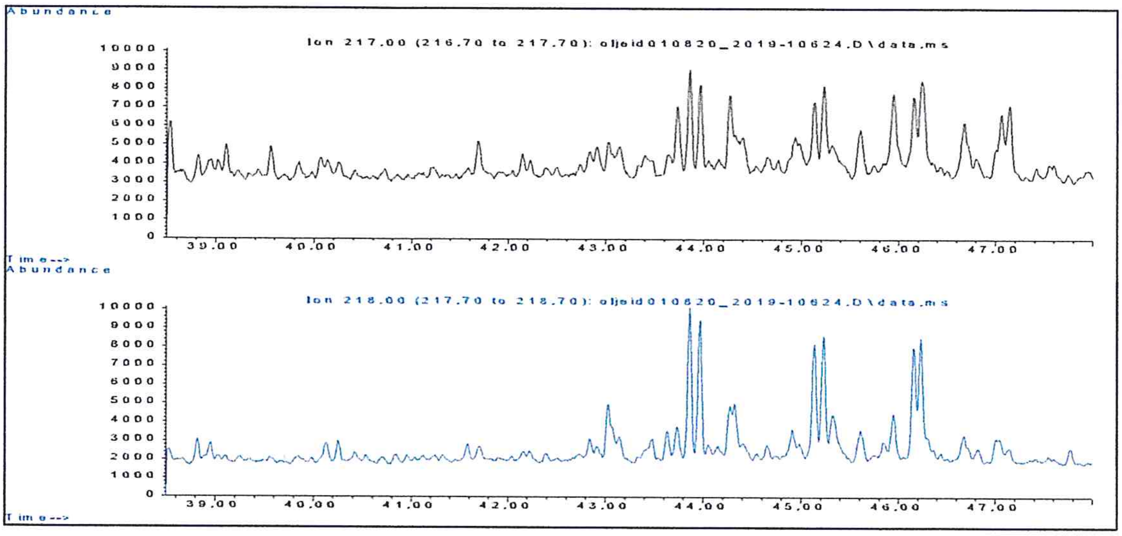


Figure B 19 *Steranes and disteranes (m/z 217 and m/z218) from BCF 17 (SINTEF Id: 2019-10624)*

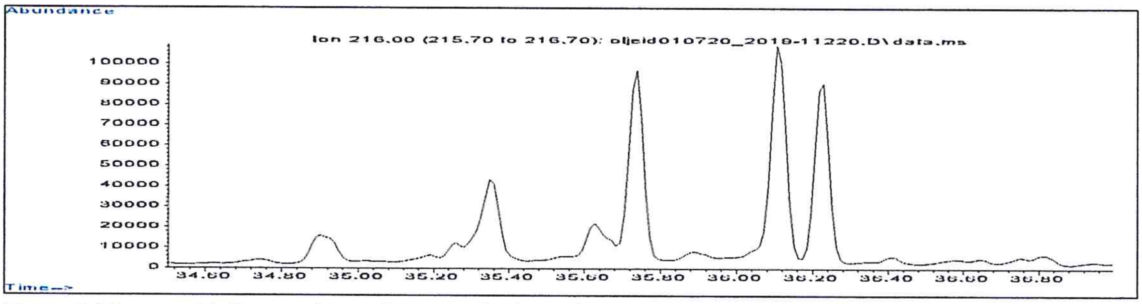


Figure B 20 *C1-fluoranthenes/pyrenes (m/z 216) from Canavierias (SINTEF Id: 2019-11220)*

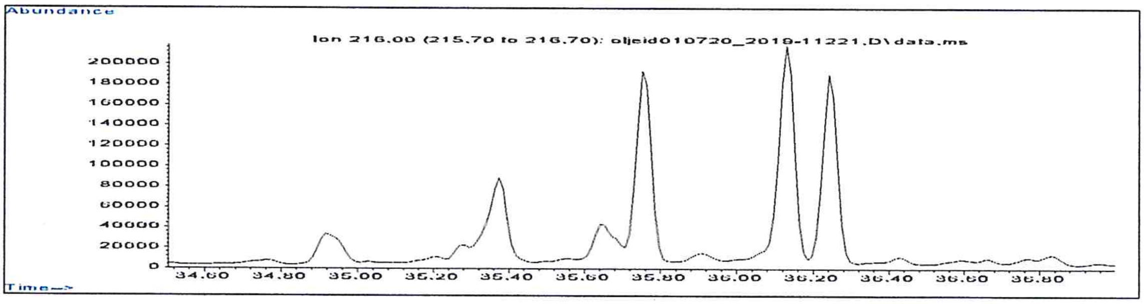


Figure B 21 *C1-fluoranthenes/pyrenes (m/z 216) from Marau (SINTEF Id: 2019-11221)*

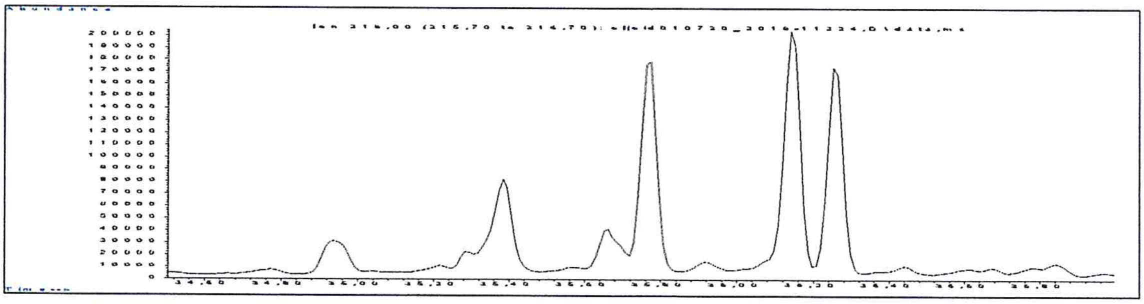


Figure B 22 *C1-fluoranthenes/pyrenes (m/z 216) from Cairu (SINTEF Id: 2019-11224)*

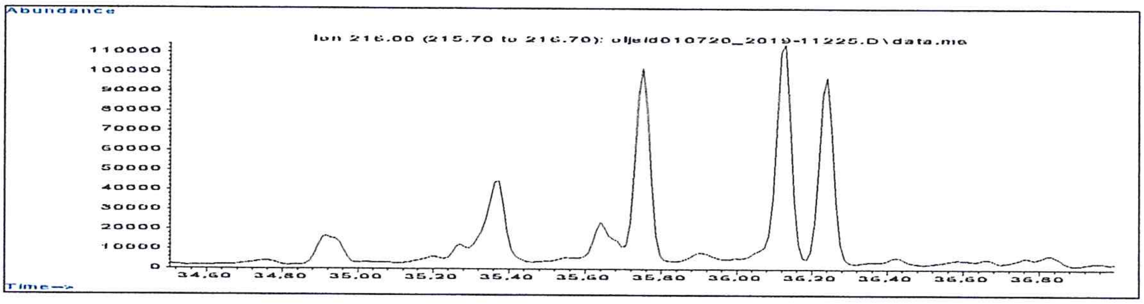


Figure B 23 *C1-fluoranthenes/pyrenes (m/z 216) from Pirambu (SINTEF Id: 2019-11225)*

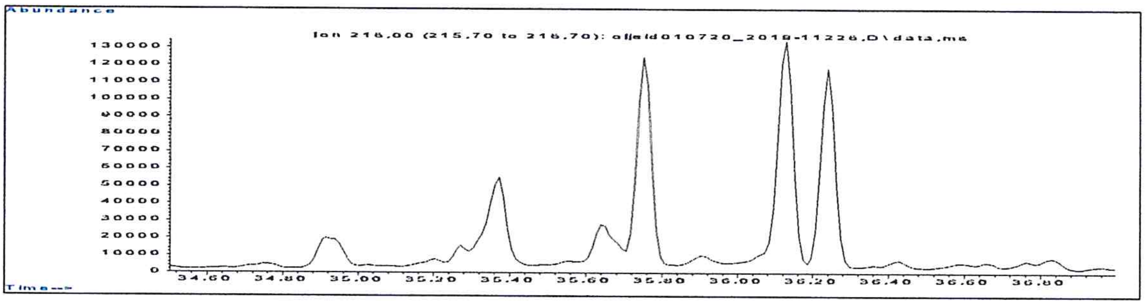


Figure B 24 *C1-fluoranthenes/pyrenes (m/z 216) from Jatoba Sul do TMIB (SINTEF Id: 2019-11226)*

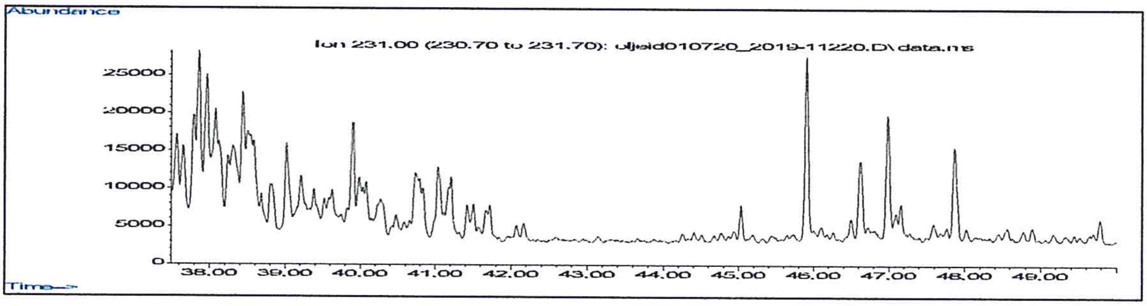


Figure B 25 *Triaromatic steranes (m/z 231) from Canavierias (SINTEF Id: 2019-11220)*

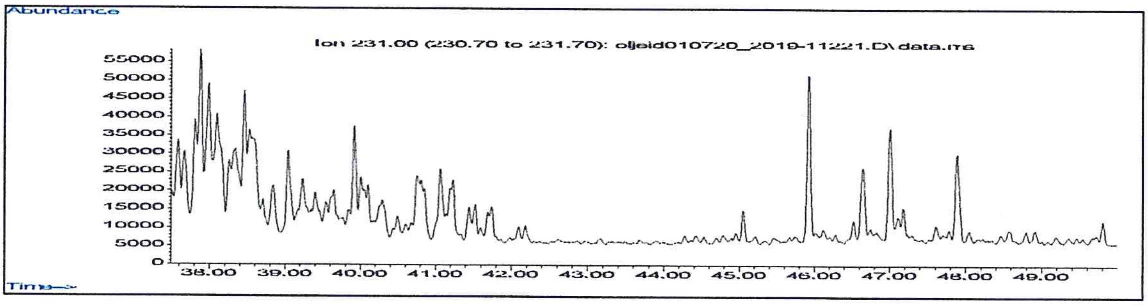


Figure B 26 *Triaromatic steranes (m/z 231) from Marau (SINTEF Id: 2019-11221)*

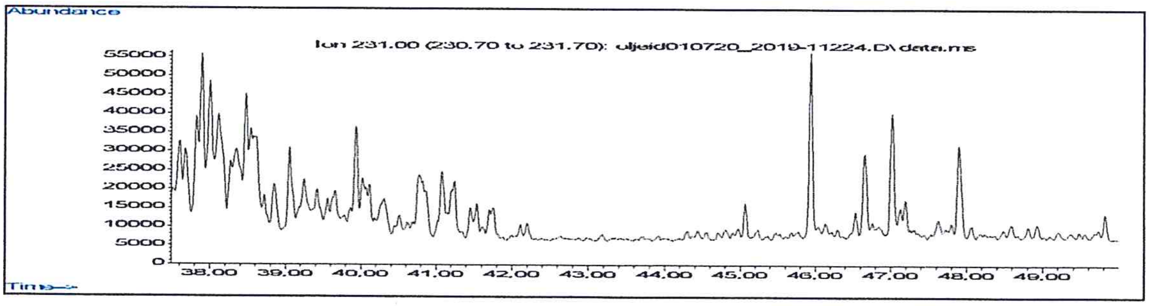


Figure B 27 *Triaromatic steranes (m/z 231) from Cairu (SINTEF Id: 2019-11224)*

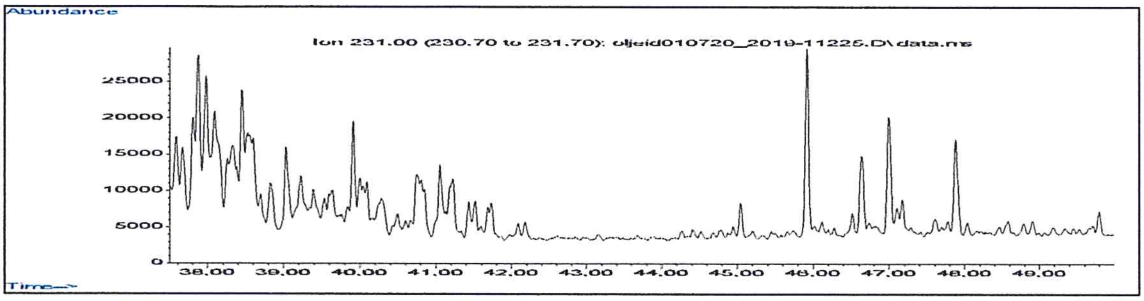


Figure B 28 *Triaromatic steranes (m/z 231) from Pirambu (SINTEF Id: 2019-11225)*

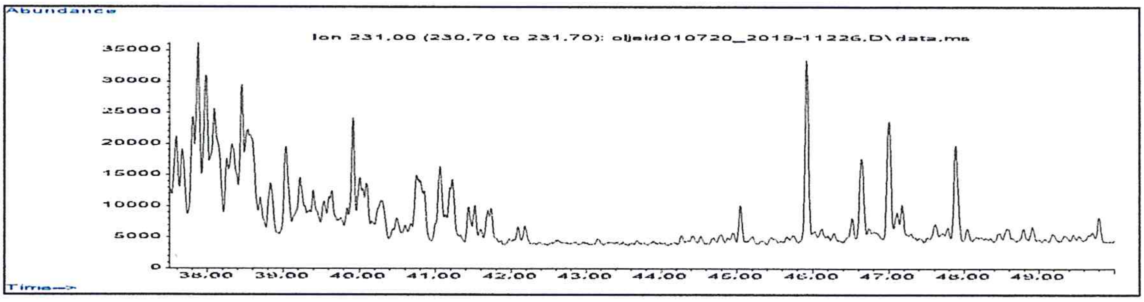


Figure B 29 *Triaromatic steranes (m/z 231) from Jatoba Sul do TMIB (SINTEF Id: 2019-11226)*

C Appendix C Comparison of samples: PW-plots and diagnostic ratio

Duplicate analysis was performed for all samples and the average of the duplicates are used to compare the samples. The samples were compared to the sample from Marau (2019-11121), as it seemed less weathered than the other according to visual comparison of the GC chromatograms.

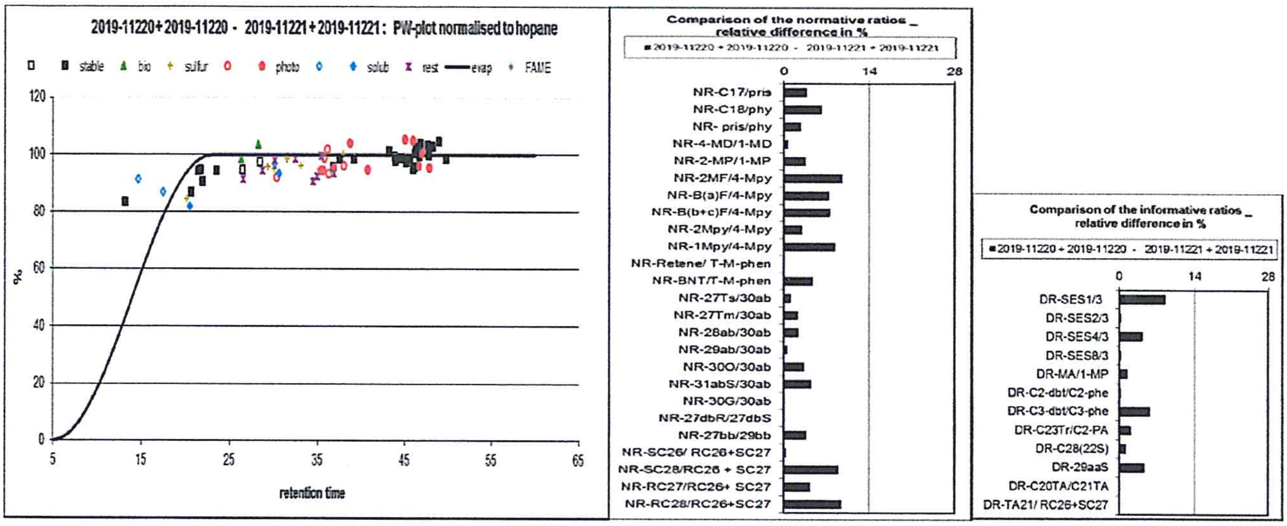


Figure C 1 *PW-plots and comparison of diagnostic ratios: Spill samples from Marau (2019-11221) and Canavierias (2019-11220).*

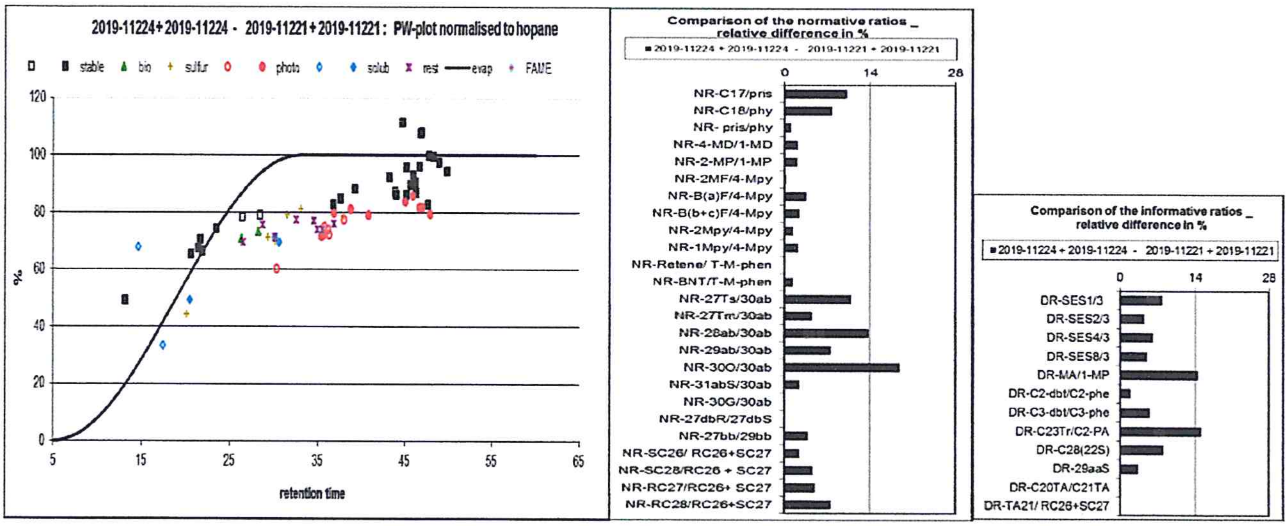


Figure C 2 *PW-plots and comparison of diagnostic ratios: Spill samples from Marau (2019-11221) and Cairu (2019-11224).*

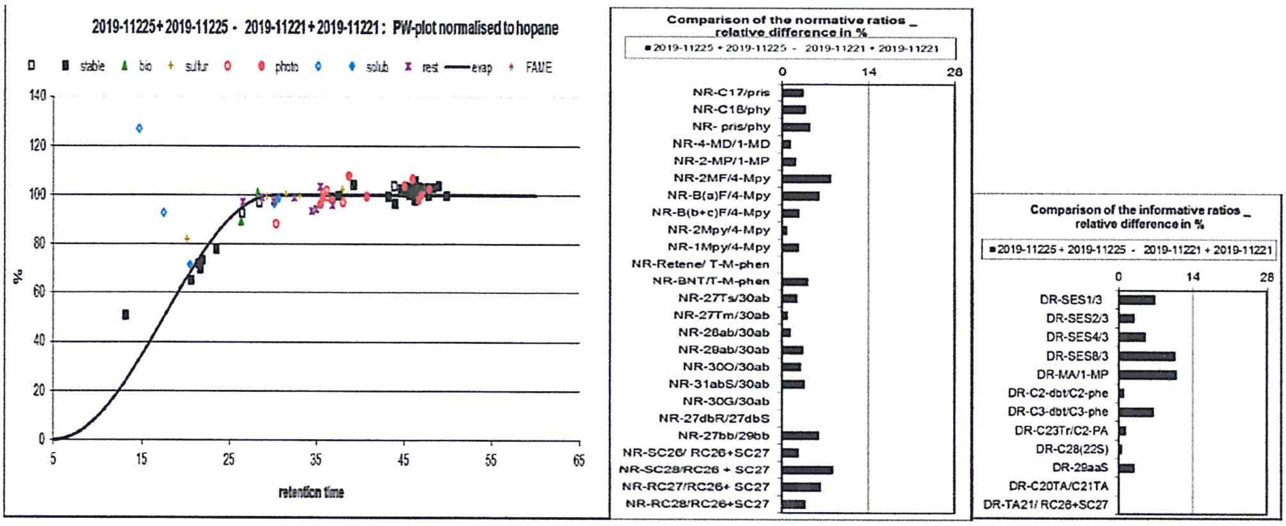


Figure C 3 *PW-plots and comparison of diagnostic ratios: Spill samples from and Marau (2019-11121) and Pirambu (2019-11125).*

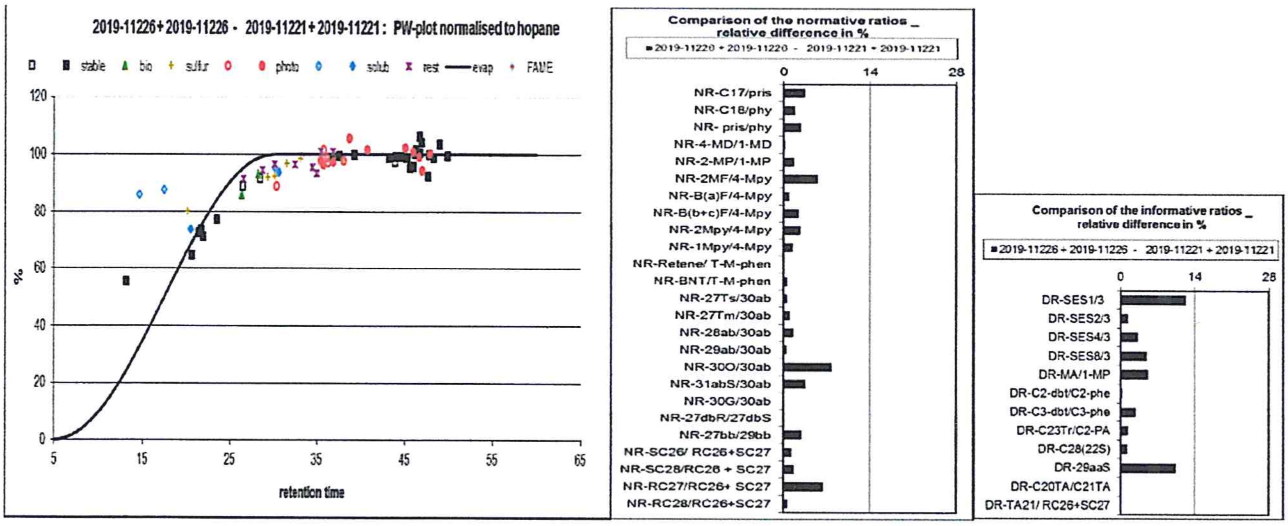


Figure C 4 *PW-plots and comparison of diagnostic ratios: Spill samples from Marau (2019-11221) and Jatoba lado Sul (2019-11226).*

D Appendix D Evaluation of duplicate analysis

According to CEN (2012), duplicate analysis shall be performed of at least one of the samples. The PW-plots and the ratio comparison from duplicate analysis of the sample from Canavierias (2019-11220) are shown in Figure D 1. The PW-plot and the comparison of normative and informative DR where within the acceptance criteria for positive match according to CEN (2012).

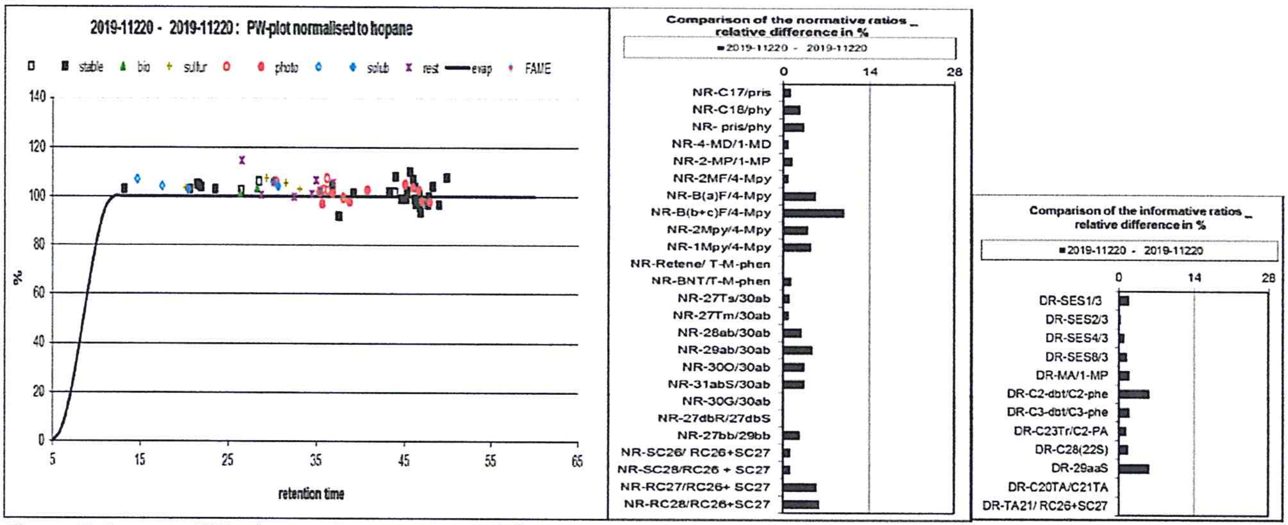
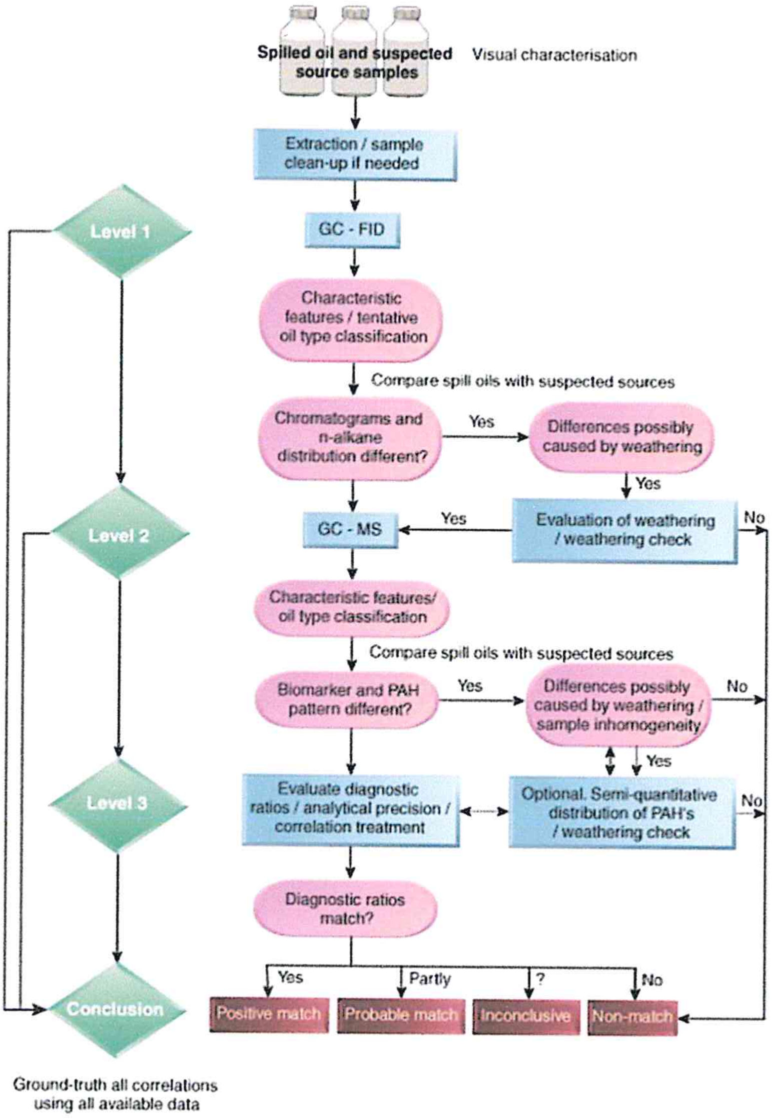


Figure D 1 *PW-plots and comparison of diagnostic ratios: Duplicate analysis of sample from Canavierias (SINTEF ID 2019-11220).*

Table D 1 *Eliminated diagnostic ratios and reasons for elimination.*

Eliminated ratios	*Reason for elimination*
Retene/T-M-phen	Retene not detected
30G/30ab	30G not detected (indicate hyper salinity source rock if present)
27dbR/27dbS	Too low concentrations (below signal-to-noise)
Informative ratios	
C20TA/C21TA	Too much interference from other components for 20TA and TA21
TA21/ RC26+SC27	Too much interference from other components for TA21

E Appendix E Decision chart for oil spill identification



Decision chart for oil spill identification applied in the CEN guideline.