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GEOSCIENCES

Chronic oil spills revealed by the most important set of samples from the incident in northeastern Brazil, 2019

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Abstract: In 2019, an oil spill of unprecedented dimensions and unknown source reached the Brazilian coast. Such incident, which occurred somewhere in the ocean and was detected only when the first oil patches reached the beaches in the northeastern region, is recognized as one of the most serious oil spills in the country. From the chromatographic analysis of the oily residues using n-alkanes, polycyclic aromatic hydrocarbons (PAH), and oil biomarkers, it was possible to characterize their coverage. The results confirmed that an oil of the same specification reached a length of coastline higher than 3,000 kilometers. However, were also found oily residues that did not match with the product involved in that incident, evidencing the occurrence of different discharges. This study documents the extension of the affected coastline during the incident and assesses the possible origin of such different oils from their geochemical characteristics by selecting 21 samples from more than 300 samples previously collected and analyzed during the response actions. The unexpected occurrence of these residues suggest chronic events. The results highlighted that unrelated oily residues were found even in a region far from the coast, indicating that discharges of oil in the open sea occur more regularly than initially expected.

Key words: chemical fingerprinting, Forensic Geochemistry, Heavy oil, Oil spill.

INTRODUCTION

At the end of August 2019, reports of occurrences of oily stains on some beaches in northeast Brazil began to appear. Such reports were initially restricted to the states of Paraíba (PB), Pernambuco (PE), and Rio Grande do Norte (RN) (IBAMA, 2019). However, up to the end of September, the occurrences were recorded in other locations in the region, especially in Alagoas (AL) and Ceará (CE). In the beginning of October, as an unprecedented situation took shape (especially after the arrival of a significant amount of oil in Aracajú, Sergipe (SE), occurred in October 4th, 2019), the Brazilian National Contingency Plan (NCP) was activated. In the months that followed, oily residues were detected in all other states in the Northeast region, Bahia (BA), Piauí (PI), Maranhão (MA), and even in other regions as in the states of Espírito Santo (ES) and Rio de Janeiro (RJ), in the Southeast region. Despite not being the first oil spill in Brazilian waters, the incident is considered one of the most serious (if not the most serious) incidents that has ever occurred in Brazil in view of the large extent of the affected coastline.

The origin of the spill was not promptly identified, and there were no reports of incidents with ships or oil platforms that could be causing it. Thus, an investigation was conducted to

find its source and explain why these tarry oil stains, such as tar mats, continued to reach the northeastern coast at an increasing distance from the places where the first occurrences were observed. In this investigation, the Maritime Authority considered ships, oil platforms, onshore installations, and even some potentially polluting shipwreck as suspects. It also considered the possibility that oil from some farther source, perhaps on the African coast, having traveled greater distances with the sea currents, had come from that continent to the Brazilian coast (Folha de Pernambuco, 2020). Due to the lack of information about a recent wreckage or from a vessel in need of assistance at sea (perhaps informing of the need to dump part of its cargo as well as requesting help from the Coastal State), the possibility of an intentional spill became very plausible.

Early detection of the incident was ineffective. The spilled oil probably traveled below the seawater surface in the open sea, which may have hindered its early detection. Most of the strategies, tactics, and equipment in oil spill response are based on the principle that oil floats. However, oil does not always float. Occasionally, it becomes suspended in the water column or sinks to the bottom of the waterbody, or does all three: floats, suspends, and sinks. Furthermore, oil that has sunk to the bottom can become re-suspended by an increase in turbulence and spread by currents (API 2016).

"Weathering" is the term that combines a wide variety of physical, chemical, and biological processes that a spilled oil undergoes in the environment. The weathering processes include evaporation, emulsification, natural dispersion, dissolution, microbial degradation, photooxidation, and other processes, such as sedimentation and oil-suspended particle interactions (Hollebone 2015, Peters et al. 2005) that change its original composition. Its characteristics, a heavy and tarry oil slightly affected by weathering, explain why oily patches were detected only when close to the coast or after reaching the beaches. The spilled oil was presumably in temporary suspension due to turbulence and had refloated when sea conditions became milder (in the absence of the turbulence that probably made it over-washed). Although significant portions of submerged oil residues were not found during the response actions, it is possible that part of the originally spilled oil had permanently sunk to greater depths in the ocean. The Brazilian Navy research vessel "Vital de Oliveira" used sonar systems, a remotely operated vehicle (ROV), and other equipment to detect submerged oil, without success. Aircraft equipped with sensors (e.g., laser fluorosensors) for surface oil detection also did not detect oily stains when far from the coast.

Estimates based on computational modeling indicated that the incident occurred somewhere in international waters at a distance between 600 and 700 kilometers from the Brazilian coast, at a latitude near the border between Sergipe and Alagoas (Agência Brasil 2019), close or in the area where the South Equatorial Current (SEC) splits to form North Brazil Current (NBC) and Brazil Current (BC) (Stramma 1991, Silveira et al. 2000).

Even before the activation of the NCP, the Maritime Authority, Federal Environmental Agency (IBAMA), and other local officials investigated its causes and collected samples from the spilled oil. Along with the response actions, samples from all over the impacted area were sent for analysis in the Brazilian Maritime Authority forensic laboratory.

Probably due to the popular outcry and media attention that arose from the incident, reports from oil in beaches from the states of Maranhão (MA) to São Paulo (SP), including

the oceanic islands of Fernando de Noronha (a Brazilian national oceanic sanctuary), were registered. Some of these reports, from regions presumably non-affected by the incident, raised concern about the possibility of chronic or multiple spills, especially for those samples collected in the south of the São Tomé Cape (Fig. 1). In that region, especially close to 23 °S latitude, coastline orientation changes abruptly, starting to follow an east-to-west path instead of a north-to-south path (Albuquerque et al. 2014). Such coastline characteristics would probably hinder spilled oil from reaching more southern areas. Also, the most significant occurrences were restricted to the region between the states of Rio Grande do Norte and Bahia (Piauí 2019), while from the Abrolhos Bank (south of Bahia) to the south occurrences were very scarce.

The first sample was collected in September 2nd, 2019 (when the first communication was reported to the Maritime Authority officials in Pernambuco). Including the reoccurrence observed in some areas during southern hemisphere winter in the middle of 2020, the involved teams collected more than 300 samples of oily and other residues from all the impacted regions to investigate their origins (including a few samples composed of small debris of charcoal, plastic, and other strange materials, i.e., garbage). This constitutes

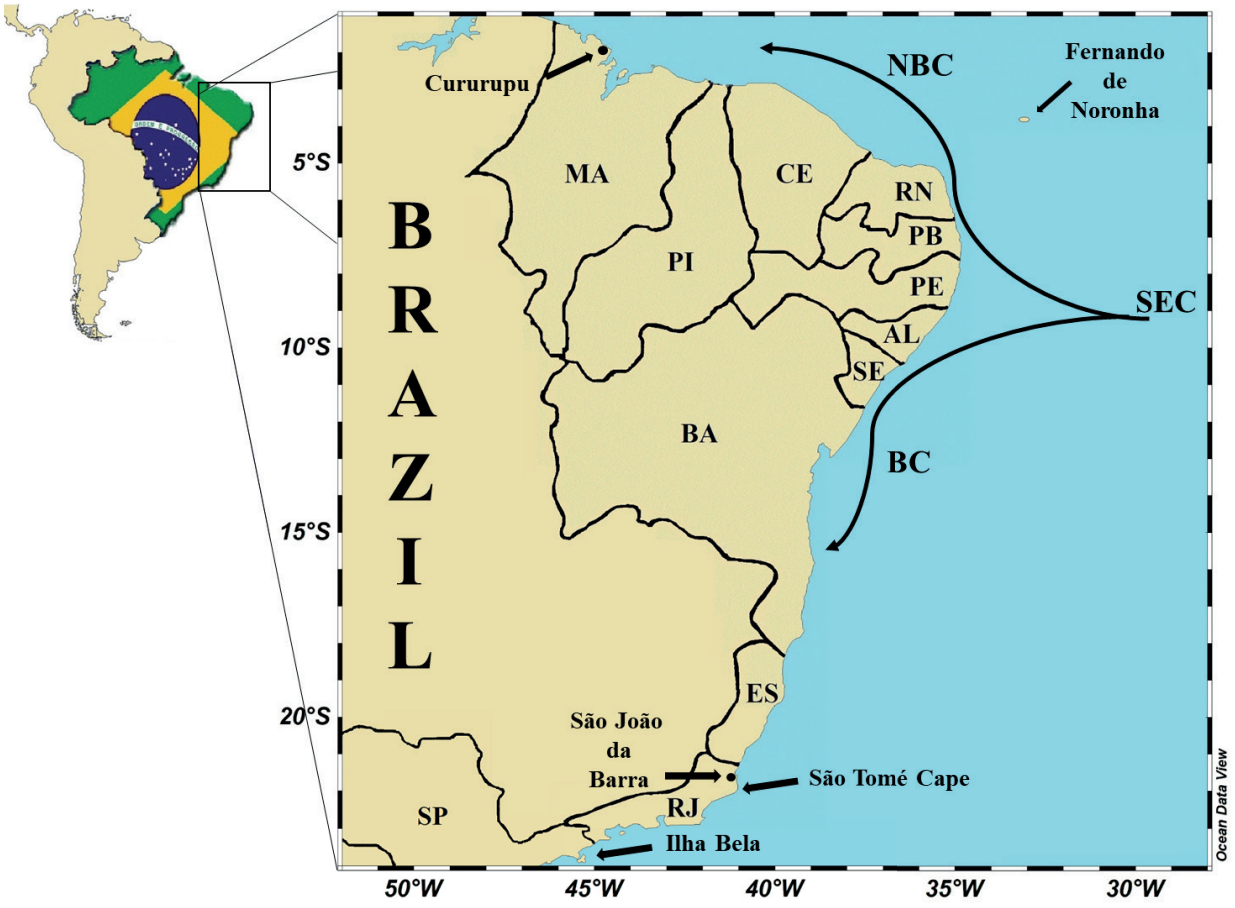

Figure 1. Affected area along the Brazilian coast. Legend: SEC – southern branch of the South Equatorial Current; NBC – North Brazil Current; BC – Brazil Current; MA – Maranhão; PI – Piauí; CE – Ceará; RN – Rio Grande do Norte; PB – Paraíba; PE – Pernambuco; AL – Alagoas; SE – Sergipe; BA – Bahia; ES – Espírito Santo; RJ – Rio de Janeiro; SP – São Paulo.

the most important set of samples from that incident, being a valuable source of information. From that sample analysis, it was possible to determine the real extension of the affected coastline during the incident, from Cururupu (MA) to São João da Barra (RJ). It was also possible to find evidence that — similar to other regions of the world — the Brazilian coast suffers from the presence of chronic oil spills that are more regular than initially expected.

MATERIALS AND METHODS

As will be evidenced from the results, the incident affected, to a greater or lesser extent, more than 3,000 km of coastline. Samples were collected from Cururupu (MA) to Ilha Bela (SP) (Fig. 1), including samples from Fernando de Noronha oceanic islands. Out of more than 300 samples previously collected and analyzed from the affected beaches along the coast and from suspected sources during the incident, 21 samples collected between September 2019 and January 2020 were chosen for this study (Table I). The chosen samples were collected at different places in the impacted areas and in other areas supposedly affected by the incident, both to characterize the coverage of the oil spill and to register the occurrence of chronic spills in Atlantic waters that occasionally reach the Brazilian coast.

Sample collection occurred during the response actions, following standard procedures and using collecting material described in CEN (2012a) and DPC (2020) for thick and emulsified oil samples. Briefly, oily samples were collected using glass or aluminum containers previously cleaned and decontaminated in a muffle furnace for 6 hours at 450°C. After sample collection, these containers were sealed, identified, and immediately sent for analysis. All samples considered in this study showed signs of weathering on visual examination, besides being mixed with sand, vegetation and, eventually, other materials.

Oily samples were purified using CEN (2012b) procedures for thick and emulsified oil samples. Briefly, water, sand and other particles were separated using solvent extraction (dichloromethane) after mixing the sample with sodium sulphate P.A. (previously dried in muffle furnace for 6 h at 450 °C) to clean-up the extracts. After oil separation, solvent was evaporated to dryness.

Sample preparation involved fractionation of the sample (20 mg to 50 mg of the purified oil) by gravity liquid chromatography on glass columns (1.2 X 30 cm) packed with 10 g of silica-gel topped with 1 g of sodium sulphate. The saturate fraction was obtained by percolation with 20 ml of n-hexane and the aromatics with 40 ml of a solution of n-hexane/dichloromethane (3/1, v/v). Both fractions were taken to dryness in Nitrogen flux and redissolved in dichloromethane.

A gas chromatograph fitted with a flame ionization detector (GC-17A, Shimadzu) with a capillary column DB-1 with 30m × 0.25mm (0.25µm film thickness) was used for n-alkanes and isoprenoids analysis. Initial temperature for the oven was 50 °C with heating rate of 6 °C.min^{-1} to 310 °C (hold for 10 min); injector and detector were held at 280 °C, with helium as carrier gas (1 mL.min^{-1}), and an injection volume of 1 µl in splitless mode.

A single quadrupole gas chromatograph mass spectrometer Clarus 600 GC-MS (Perkin Elmer) (operating in SIM mode with electron ionization source at 70 eV) was used. A capillary column DB-5 MS with 60m × 0.25mm (0.25µm film thickness) was used. Helium was used as carrier gas (1.5 ml.min^{-1}) and injection volume 1 µl in splitless mode. Initial temperature for the oven was 35 °C with heating rate of 20 °C.min^{-1} (up to 150 °C) and 1.5 °C.min^{-1} to 310 °C (hold for 6.58 min). Transfer line was at 310 °C and ion

Table I. Samples considered for this study.

Sample	Sampling date	Sampling Location	Lat/Long
DB01	09/03/2019	Piedade Beach, Jaboatão dos Guararapes – PE	08°10'31"S 34°54'56"W
DB06	09/04/2019	Do Amor Beach, Conde – PB	07°21'08"S 34°47'49"W
DB10	09/09/2019	Ponta Negra Beach, Natal – RN	05°49'41"S 35°10'54"W
DB13	09/17/2019	Pajuçara Beach, Maceió - AL	09°39'58"S 35°42'37"W
DB23	09/25/2019	Paracuru Beach, Paracuru - CE	03°26'24"S 38°57'00"W
DB39	09/23/2019	Taperai Beach, Alcântara - MA	02°23'28"S 44°22'35"W
DB61	10/08/2019	Porto do Sauípe Beach, Entre Rios - BA	12°23'09"S 37°52'52"W
DB76	10/12/2019	Itapuã Beach, Salvador - BA	12°57'06"S 38°22'10"W
DB83	10/12/2019	Caçacueira Island, Cururupu - MA	01°29'31"S 44°46'2"W
DB94	10/15/2019	Serra Grande Beach, Uruçuca - BA	14°29'33"S 39º03'17"W
DB132	10/31/2019	Brasiliana Beach, Itaúna - ES	18°32'13"S 39°43'41"W
DB162	11/06/2019	Eustáquio Beach, Ilha Bela - SP	23°50'13"S 45°14'37"W
DB192	11/22/2019	Grussaí Beach, São João da Barra - RJ	21°41'31"S 41°01'23"W
DB194	11/23/2019	Santa Clara Beach, São Francisco de Itabapoana - RJ	21°51'52"S 41°07'13"W
DB198	11/24/2019	João Francisco Beach, Quissamã – RJ	22°08'47"S 41°14'36"W
DB205	11/27/2019	Forte Beach, Cabo Frio - RJ	22°53'29"S 42°01'16"W
DB219	11/28/2019	Peró Beach, Cabo Frio - RJ	22°50'11"S 41°58'42"W
DB254	10/16/2019	Porto do Mangue Beach, Porto do Mangue - RN	05°04'06"S 36°46'51"W
DB256	11/18/2019	Fernando de Noronha Island – Sueste Bay – PE	03°51'57"S 32°25'24"W
DB268	12/30/2019	Caetanos Beach, Amontada - CE	03°05'7"S 39°32'32"W
DB281	01/23/2020	Pitimbu Beach, Pitimbu - PB	07°28'33"S 34°48'18"W

source at 220 °C. Same conditions were applied for saturate and aromatic compounds. The list of ions to be monitored by GC-MS was as usually reported on correlation studies of oil-spills (Peters et al. 2005, Wang et al. 2006) and covered straight-chain/branched alkanes and ubiquitous petroleum polycyclic compounds such as tricyclic and pentacyclic terpanes, steranes (regular, methylated, degraded and rearranged) as well as polynuclear aromatic hydrocarbons (parental compounds and alkylated homologs). Data were integrated using peak heights using the Turbomass 6.0 software.

Samples were analyzed in duplicates, as described in CEN (2012b). The names of the compounds are as described in the CEN (2012b) methodology. Comparison of oils from different locations was conducted by visual inspection of chromatographic profiles, multivariate statistical tests based on diagnostic ratios (DRs) (developed from peak heights of identified compounds, normalized by C_{30}-αβ hopane – 30ab) and by the acceptance criteria described in the CEN methodology (CEN 2012b). Based on that methodology, normative and informative DRs from different samples were compared, and those DRs that exceeded the 14% threshold of critical difference (CD), using a relative standard deviation (RSD) of 5%, were considered significantly different, usually indicating that compared samples were from different sources.

Samples were compared to the first sample collected during the incident (considered the reference sample) according to the CEN (2012b) methodology matching criteria. The possible long-term effects of weathering on the fingerprinting of spilled oil during the incident, which may lead to misinterpretation on source recognition, were not evaluated in this study. Such effects will be the object of a complementary article, reporting an experiment specifically designed to elucidate possible false negatives related to weathering. Such study is important in view of the possible reoccurrence of oil in the future, given that some compounds are more susceptible to weathering than others (Wenger & Isaksen 2002), to determine whether future arrivals of oil in the affected area are related to the original incident or represent another spillage.

Percentage weathering plots (PW-plots) were also considered in the evaluation, based on GC-MS results. The PW-plots present the results of the remaining percentage of the considered compounds (e.g., biomarkers and alkylated PAHs) when the two samples are compared. Two samples from the same origin, when compared to each other, might show significant differences only in the compounds affected by weathering. The PW-plots also shows the non-similarity of oil samples and are useful in recognizing whether specific differences are significant or not. Samples were collected as the oil reached the beaches along all the affected areas after drifting in the sea for an unknown time, which might be different from one sample to another. Thus, some DRs, mainly those developed for the investigation of spills involving light to medium oils, could have been affected by weathering. For PW-plots all samples were normalized by sample DB01, used as the reference oil.

Statistical analyses were conducted using Excel® and PAST 4.03 (Hammer et al. 2001) software. Calculated DRs were standardized before analysis. Cluster analysis was employed, as an additional tool, for a simultaneous analysis of the DRs (including saturate and aromatic compounds) used to evaluate the samples. Such analysis used single linkage clustering (nearest neighbor) and similarity indices for sample correlation. The results presented in the cluster analysis, for each sample considered in the current study, represent the average of two injections from the same sample.

RESULTS AND DISCUSSION

The chromatographic analysis using GC-FID and GC-MS revealed that most of the samples from the incident, sharing the same chromatographic profiles and DR values (also considering the CD criterion established in CEN 2012b), came from the same heavy and slightly altered oil that reached the Brazilian coast between Maranhão and Rio de Janeiro. Some samples have evidenced the occurrence of other spills, suggestive of chronic environmental contamination by the discharge of oil in the sea. Results of the DRs used to determine the relative difference (%) between samples are presented in Table II.

Characteristics of the spilled product

According to organic geochemical analysis, the spilled oil present strong correlation to some Venezuelan crudes instead of a Brazilian sourced oil (Fig. 2) as its biomarker profiles (Fig. 2a, 2b and 2c) are very similar to those reported by other studies (Lobão et al. 2010, López & Lo Mónaco 2017, Oliveira et al. 2020), including the high abundance of pregnanes (pregnane, S21 and homopregnane, S22), tricyclics (including C23Tr) and presence of oleanane. Also, according to Mello et al. (1988), that studied geochemical characteristic features of Brazilian crudes, the presence of Oleanane (which is a diagnostic marker of terrigenous inputs, as also described in Samuel et al. 2009) (Fig. 2a) preclude the possible origin in oils sourced in the Brazilian oil platforms from Potiguar basin, located in the area affected by the incident, initially considered as possible sources.

As the source of the product was not identified by the authorities, its characteristics had to be determined from the samples collected in the beaches, which were subjected to weathering effects that could cause considerable changes in its physical properties and chemical composition (Hollebone 2015, Peters et al. 2005, Stout & Wang 2007, Wang et al. 2006). Such samples of heavy and emulsified oil, with some loss of volatile compounds (as shown by depletion of n-alkanes below n-C_{11}-n-C_{13}, depending on the sample analyzed), prevented the determination of its original density (API gravity) due to the weathering state of received samples. Further, because of weathering and impurities, no viscosity tests were performed.

In terms of possible specification of the spilled product, the nature of crude oils and their products is highly variable around the World: normal alkanes ranging from *n*-C_5 to *n*-C_{40} are often the most abundant constituents in crude oils. Although some of the "primary" genetic chemical features of the naturally occurring *parent* petroleum are passed directly to the *daughter* petroleum products, the refining process can impart its own effects on the chemical composition of the resulting manmade petroleum, with effects on their chemical fingerprints (Stout & Wang 2016). The n-alkanes profile of the samples in this study suggests that the incident was caused by a spill of crude oil, due to the presence of n-alkanes from n-C_{11}-n-C_{13} to, at least, n-C_{37} (for GC-FID chromatographic profile, see Fig. 3a). However, as indicated in Uhler et al. (2007), the relative abundance of 2-methyl-anthracene (2-MA) and methyl-phenanthrenes (Fig. 2d) suggests the occurrence of rapid heating processes, indicative of catalytic cracking, related to refining processes. Heavy fuel oils (HFOs), similarly to many other oil products, are made from crude oils. However, in terms of refinery cuts, HFOs are not compositionally constrained as distillate fuels. Rather, heavy marine fuel oils are blended from residual oils, gas oil, and other economically advantageous stocks to achieve basic physical and chemical specifications (Uhler et al. 2007). Among the diverse specifications of HFOs, it is possible that some share chromatographic

and chemical similarities with evaporated or otherwise slightly weathered crude oils (Uhler et al. 2016). The presence and relative abundance of 2-MA in the mass chromatogram of the ion *m*/z 192 suggests that the incident might have been caused by a release of an HFO instead of crude oil. This is because 2-MA is generally absent or present in low relative concentrations in crude oils. Incidents involving HFO residues can also happen due to the huge number of ships traveling around the world to sustain international trade that obviously have to replenish their fuel tanks for the next trip. Relative preservation of methyl-fluoranthenes/pyrenes and benzofluorenes (m/z 216) (Fig. 2e) suggests the absence of significant changes associated with photo-oxidation, although its effects depend on the thickness of the exposed oil layer. The 1- and 2-methylpyrenes, as well as the benzofluorenes, are significantly reduced with respect to the 4-methylpyrene when exposed to photodegradation (Radović et al. 2014).

Another possibility is that the incident might have been caused by an upgraded crude oil spill. One of the world's largest reserves of heavy and extra-heavy biodegraded crude oil is found in the eastern basin of Venezuela (López et al. 2015). Heavy crude oils have high concentrations of coke promoters, sulfur, and high acidity, and are difficult to transport because they are very viscous or even solid when recovered from the producing wells. Further, traditional refineries are not suitable for their processing, which necessitates their transformation into synthetic crudes of similar composition, either light or medium crude oils (Carrilo & Corredor 2013). Further, according to Carrilo & Corredor (2013), well-known technologies are applied for heavy crude oil upgrading in both Orinoco Belt (Venezuela) and Alberta province (Canada). As the crude oil upgrade process may involve different steps, including catalytic cracking, there is a possibility that upgraded crudes have 2-MA and other catalytic cracking-related compounds in their composition. Such a possibility, which still has to be better understood, has not been investigated.

Thus, based on the information available and the characteristics of the product, the oil spill on the Brazilian coast was probably caused by a heavy (or extra-heavy) crude oil or an HFO discharge residue whose geographic source was a Venezuelan basin. As described in Lobão et al. (2010), spills involving oils produced in that important producer country (or another producer in its vicinity, with similar oils) do not seem novel in Brazilian waters, as a previous incident in San Marcos Bay (MA) in 2005 shared the same fingerprinting characteristics.

As described by Mudge (2008), some unscrupulous companies or individuals may choose to dispose of their waste in an uncontrolled or illegal manner, causing contamination of the environment. These illegal discharges might be done in secret to avoid detection by the authorities, making their characterization relatively hard. The oil spill more recently registered on the Israeli coast (February 2021) indicates that illegal dumping of residues from ships is still probably causing many of the so called mysterious spills. Regardless of being interpreted as environmental terrorism (Reuters 2021), such incidents show operational or management problems that must be dealt with,

Table II. Normative and informative ratios used to determine the relative difference (%) between samples (CEN 2012b).

DR		SAMPLES																				
		DB01	DB06	DB10	DB13	DB23	DB39	DB61	DB76	DB83	DB94	DB132	DB162	DB192	DB194	DB198	DB205	DB219	B254	DB256	DB268	DB281
NORMATIVE RATIOS	NR-C6-/C7-Benz	0.22	0.28	0.34	0.20	0.41	0.35	0.47	1.14	0.16	0.89	1.25	0.00	0.09	0.23	9.17	0.00	0.00	0.00	0.00	1.52	1.25
	NR-2-E-N/2,6+2,7 DM-N	0.26	0.31	0.28	0.25	0.28	0.26	0.32	0.20	0.19	0.34	0.00	0.00	0.04	0.13	0.26	0.00	0.00	0.00	0.00	0.53	0.20
	NR-BS4/BS5	0.25	0.26	0.24	0.24	0.25	0.25	0.29	0.00	0.20	0.22	0.00	0.59	0.19	0.16	0.00	0.56	0.48	0.27	0.70	0.00	0.00
	NR-Br-Alk-169-3/n-C15	0.02	0.03	0.03	0.02	0.03	0.03	0.03	0.00	0.02	0.03	0.00	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	NR-BS5/BS6	3.48	3.45	3.70	3.26	3.48	3.46	3.35	0.00	3.93	3.89	0.00	1.37	3.93	4.67	0.00	0.94	0.97	3.01	1.11	0.00	0.00
	NR-BS8/BS9	1.22	1.20	1.20	1.17	1.24	1.17	1.28	0.00	1.30	1.02	1.08	0.78	1.37	1.04	0.00	1.03	0.90	1.31	1.32	0.00	0.00
	NR-BS10/Norpri	0.57	0.58	0.56	0.50	0.60	0.58	0.62	0.00	0.50	0.99	0.03	0.00	0.49	0.45	0.34	0.00	0.00	0.00	0.00	0.06	0.04
	NR-n-C17/Pri	5.67	5.22	5.64	5.80	5.76	5.82	5.84	10.24	6.10	5.85	0.56	3.64	4.32	2.49	0.50	0.44	4.74	3.19	0.00	5.92	5.82
	NR-Pri/Phy	0.74	0.77	0.75	0.71	0.74	0.75	0.74	0.73	0.60	0.90	0.89	0.25	0.62	0.84	3.49	3.69	1.43	0.36	0.00	0.58	0.46
	NR-n-C18/Phy	3.98	3.77	4.10	4.06	4.01	4.06	3.92	6.45	4.06	4.47	1.15	1.15	2.95	2.68	3.06	2.93	8.30	1.22	0.00	6.25	4.53
	NR-4-M-Dbt/1-M-Dbt	3.78	3.93	4.05	4.07	3.98	3.87	3.93	6.72	3.89	4.64	0.00	1.56	4.28	4.09	5.16	1.05	0.00	0.00	1.99	3.24	3.33
	NR-Br-Alk-225-3/n-C19	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.00	0.01	0.02	0.02	0.00	0.02	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01
	NR-2-M-Phe/1-M-Phe	2.27	2.36	2.31	2.35	2.31	2.29	2.33	4.02	2.26	2.46	4.15	1.55	2.38	2.31	1.86	6.72	0.00	1.20	0.00	1.96	1.98
	NR-2-M-Fl/4-M-Py	0.12	0.13	0.12	0.13	0.13	0.13	0.12	0.00	0.12	0.12	0.01	0.03	0.13	0.13	0.02	0.01	0.00	0.00	0.01	0.12	0.12
	NR-C15-Benz/C17-Benz	1.26	1.30	1.34	1.40	1.31	1.36	1.38	0.00	1.21	1.54	0.46	0.00	1.23	1.14	0.69	0.00	0.00	0.00	0.00	0.77	0.89
	NR-BaF/4-M-Py	0.35	0.37	0.35	0.34	0.34	0.36	0.34	0.00	0.32	0.24	0.03	0.25	0.15	0.14	0.15	0.02	0.00	0.00	0.01	0.25	0.25
	NR-Retene/ 29bb	0.68	0.70	0.76	0.71	0.64	0.73	0.67	0.00	0.60	4.98	0.00	0.00	0.49	0.00	0.00	0.00	0.00	0.00	0.00	0.45	0.10
	NR-2-M-Py/4-M-Py	0.86	0.94	0.92	0.88	0.92	0.92	0.87	0.29	0.86	1.00	0.22	0.80	0.89	0.88	0.65	0.58	0.39	0.45	0.17	0.91	0.92
	NR-1-M-Py/4-M-Py	0.81	0.86	0.83	0.82	0.85	0.87	0.81	0.07	0.79	0.90	0.21	0.69	0.56	0.61	0.73	0.42	0.28	0.64	0.20	0.82	0.75
	NR-C23Tr/C24Tr	2.26	2.25	2.36	2.38	2.38	2.25	2.24	1.61	2.36	2.23	1.39	1.73	2.28	2.22	1.08	1.45	1.71	2.48	1.30	2.20	1.47
	NR-27bb/29bb	1.22	1.27	1.31	1.23	1.20	1.24	1.24	0.24	1.18	0.94	1.34	0.48	1.18	1.13	0.95	0.39	0.36	0.00	0.38	0.93	1.07
	NR-27Ts/30ab	0.16	0.15	0.14	0.14	0.15	0.14	0.13	0.20	0.15	0.16	0.22	0.13	0.14	0.15	0.07	0.14	0.18	0.45	0.17	0.14	0.15
	NR-SC26/ RC26+SC27 TA	0.27	0.27	0.29	0.28	0.29	0.28	0.29	0.00	0.27	0.30	0.23	0.36	0.28	0.27	0.42	0.34	0.14	0.34	0.32	0.28	0.46
	NR-27Tm/30ab	0.29	0.29	0.27	0.28	0.28	0.28	0.27	0.14	0.28	0.38	0.15	0.14	0.27	0.28	0.17	0.12	0.19	0.88	0.21	0.37	0.21
	NR-28ab/30ab	0.14	0.16	0.14	0.15	0.14	0.15	0.14	0.03	0.15	0.06	0.00	0.01	0.16	0.16	0.05	0.00	0.00	1.16	0.03	0.00	0.03
	NR-SC28/RC26 + SC27 TA	0.49	0.50	0.48	0.48	0.50	0.48	0.49	0.00	0.49	0.00	0.00	0.00	0.52	0.30	0.00	0.00	0.00	0.49	0.85	0.65	0.67
	NR-29ab/30ab	0.73	0.72	0.71	0.73	0.73	0.71	0.68	0.55	0.70	0.74	0.53	0.49	0.77	0.70	0.57	0.45	0.67	1.69	0.65	1.07	0.66
	NR-30O/30ab	0.08	0.08	0.07	0.08	0.08	0.08	0.08	0.02	0.08	0.20	0.00	0.00	0.08	0.09	0.00	0.00	0.04	0.23	0.70	0.04	0.09
	NR-RC28/RC26+SC27 TA	0.15	0.16	0.17	0.16	0.18	0.17	0.18	0.41	0.16	0.08	0.09	0.31	0.16	0.15	0.78	0.19	0.18	0.21	0.29	0.13	0.17
	NR-31abS/30ab	0.53	0.53	0.54	0.54	0.52	0.53	0.51	0.33	0.54	0.39	0.31	0.28	0.53	0.52	0.40	0.20	0.39	0.50	0.29	0.45	0.40
	NR-30G/30ab	0.15	0.13	0.13	0.13	0.13	0.13	0.12	0.25	0.13	0.10	0.10	0.31	0.13	0.14	0.21	0.43	0.25	2.35	0.03	0.07	0.13

Table II. Continuation.

DR		SAMPLES																				
		DB01	DB06	DB10	DB13	DB23	DB39	DB61	DB76	DB83	DB94	DB132	DB162	DB192	DB194	DB198	DB205	DB219	B254	DB256	DB268	DB281
INFORMATIVE RATIOS	C7-/C10-Benz	0.39	0.50	0.53	0.29	0.62	0.59	0.81	0.55	0.34	1.97	0.00	0.00	0.14	0.08	0.76	0.00	0.00	0.00	0.00	0.02	0.02
	BS3/BS5	0.27	0.29	0.29	0.28	0.32	0.31	0.31	0.00	0.23	0.34	0.00	1.52	0.21	0.14	0.00	0.99	1.32	0.54	0.85	0.00	0.00
	1,6-DM-N/1,3+1,7-DM-N	0.87	0.88	0.90	0.91	0.88	0.89	0.88	0.90	0.95	0.82	0.82	1.02	0.86	1.04	1.04	1.04	0.00	0.00	0.00	0.94	0.80
	ANY/ 1,2-DM-N	0.14	0.15	0.15	0.15	0.15	0.15	0.15	0.00	0.09	0.15	0.00	6.59	0.24	0.19	0.29	4.18	0.00	0.00	0.00	72.73	16.64
	1,3,7 TM-N/1,3,6-TM-N	24.30	24.65	23.36	23.58	22.57	22.76	24.12	0.00	0.75	26.36	0.00	0.00	0.76	0.57	0.00	0.00	0.00	0.00	0.00	0.67	1.00
	BS8/BS10	0.13	0.14	0.21	0.15	0.17	0.19	0.21	0.00	0.09	0.19	0.59	0.53	0.10	0.08	0.00	0.80	0.63	0.10	0.51	0.00	0.00
	1-E-Phe/1,7-DM-Phe	1.46	1.52	1.42	1.44	1.49	1.52	1.50	0.00	1.45	1.69	0.00	0.00	1.28	1.28	0.58	0.00	0.00	0.00	0.00	1.33	1.20
	C21Tr/C23Tr	0.38	0.39	0.37	0.37	0.38	0.37	0.38	0.22	0.37	0.75	0.54	0.56	0.37	0.36	0.51	0.76	0.45	0.14	0.55	0.51	0.60
	C28(22S)/30ab	0.17	0.17	0.16	0.17	0.16	0.17	0.16	0.02	0.17	0.06	0.12	0.03	0.16	0.16	0.02	0.04	0.01	0.46	0.01	0.04	0.09
	BaPy/BePy	0.60	0.61	0.61	0.55	0.62	0.61	0.61	0.05	0.59	0.92	0.00	0.44	0.32	0.32	0.14	0.25	0.10	0.36	0.19	0.68	0.41
	29aaS/29aaR	1.21	1.23	1.23	1.21	1.16	1.23	1.20	1.40	1.15	1.32	1.16	1.01	1.06	1.12	1.02	2.20	1.36	0.00	0.86	1.12	0.93

Legend: C6-Benz - hexyl-benzene; C7-Benz - heptyl-benzene; 2-E-N - 2-ethyl-naphthalene; 2,6+2,7-DM-N - 2,6+2,7-dimethyl-naphthalene; Br-alk 169-3 - Branched alkane 169-3; BS4 - bicyclic sesquiterpane 4; BS5 - bicyclic sesquiterpane 5; BS6 - bicyclic sesquiterpane 6; n-C15 – pentadecane; BS8 - bicyclic sesquiterpane 8; BS9 - bicyclic sesquiterpane 9; BS10 - bicyclic sesquiterpane 10; Norpri - Norpristane (2,6,10-trimethylpentadecane); C10-Benz - decyl-benzene; n-C17 – heptadecane; Pri – Pristane (2,6,10,14-tetramethylpentadecane); n-C18 – octadecane; Phy – Phytane (2,6,10,14 tetramethylhexadecane); 4-M-Dbt - 4-methyl-dibenzothiophene; Br-alk 225-3 - Branched alkane 225-3; n-C19 – nonadecane; 1-M-Dbt - 1-methyl-dibenzothiophene; 2-M-Phe - 2-methyl-phenanthrene; 1-M-Phe - 1-methyl-phenanthrene; 2-M-Fl - 2-methyl-fluoranthene; C15-Benz - pentadecyl-benzene; BaF - benzo(a)-fluorene; Retene - 1-methyl-7-isopropyl-phenantrene; 2-M-Py - 2-methyl-pyrene; 4-M-Py - 4-methyl-pyrene; 1-M-Py - 1-methyl-pyrene; C23Tr - C23 tricyclic terpane; C24Tr - C24 tricyclic terpane; C17-Benz - heptadecyl-benzene; 27bbR+S - 5α (H),14β(H),17β(H), 20(R+S)-cholestane; 27Ts - 18α(H)-22,29,30-trisnorneohopane; SC26TA - C26,20S-triaromatic sterane; 27Tm - 17α(H)-22,29,30-trisnorhopane; RC26TA+SC27 TA - (C26,20R + C27,20S) triaromatic sterane; 29bbR+S - 24-ethyl-5α(H),14β (H),17β(H), 20(R+S) cholestane; 28ab - 17α(H), 21β(H)-28,30-bisnorhopane; SC28TA - C28,20S-triaromatic sterane; 29ab - 17α(H), 21β(H)-30-norhopane; 30º - 18α(H)-oleanane; 30ab - 17α(H), 21β(H)-hopane (hopane); RC28TA - C28,20R-triaromatic sterane; 31abS - 17α(H), 21β(H), 22(S)-homohopane; 30G – gammacerane; 1,3+1,7-DM-N - 1,3+1,7-dimethyl-naphthalene; 1,6-DM-N - 1,6-dimethyl-naphthalene; BS3 - bicyclic sesquiterpane 3; 1,2-DM-N - 1,2 -dimethyl-naphthalene; 1,3,7-TM-N - 1,3,7-trimethyl-naphthalene; 1,3,6-TM-N - 1,3,6-trimethyl-naphthalene; 1-E-Phe - 1-ethyl-phenanthrene; 1,7 DM-Phe - 1,7-dimethyl-phenanthrene; C21Tr - C21 tricyclic terpane; C28 (22S) - C28 tricyclic terpane; BePy - benzo (e) pyrene ; BaPy - benzo (a) pyrene ; 29aaS - 24-ethyl-5α(H),14α(H),17α(H), 20S- cholestane; 29aaR - 24-ethyl-5α(H),14α(H),17α(H), 20R- cholestane.

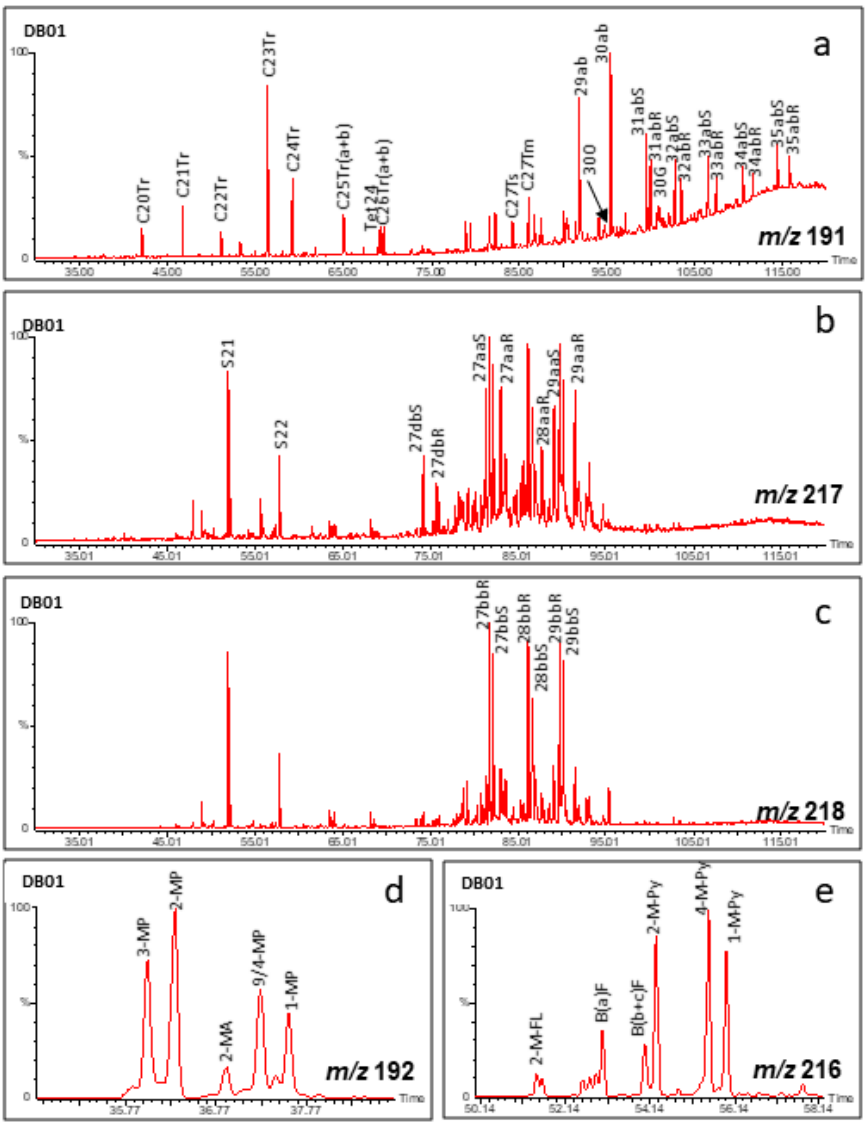

Figure 2. Mass chromatograms of the spilled oil (ions m/z 191, 192, 216, 217 and 218).

as they represent noncompliance with MARPOL's Convention rules.

Out of the 21 samples considered in this study, 10 share the same chromatographic profile (GC-FID and GC-MS) and were chosen to represent all those samples collected in view of the observed spillage. Each of that samples was collected in a different location, being previously analyzed during the response actions, when the coverage of the incident was determined by Brazilian Maritime Authority agents, indicating that the same oil reached from Cururupu (MA) to São João da Barra (RJ). In the current study, spilled oil is represented by samples DB01, DB06, DB10, DB13, DB23, DB39, DB61, DB83, DB192, and DB194. As can be observed in Figure 3, samples DB01 and DB06 (both chosen to represent the samples of the main incident in this study) shared very similar chromatographic profiles based on the GC-FID analysis (Fig. 3a and 3b). The same can be observed in Fig. 3 (c and d) and Fig. 3 (e and f), where tricyclic, tetracyclic, and pentacyclic terpanes are represented in *m/z* 191 and ββ steranes are represented in *m/z* 218. Fig. 3g

shows the PW-plot for both samples, indicating that there was no significant difference related to conservative compounds (preservation of the unaffected compounds was close to 100%). This information is confirmed in Fig. 3 (h and i), where CD between normative and informative DRs was under 14% for almost all DRs calculated for both samples. Also, according to Fig. 3 (h and i), apart from the labile compounds probably affected by weathering, such as lower molecular weight *n*-alkanes, monoaromatics (e.g., BTEX), bicyclic sesquiterpanes, and lower molecular weight PAHs (Uhler et al. 2016), there are no significant differences between the relative abundances of the analytes on these oils, which means that both samples are from the same source. The same characteristics were also observed for samples DB10, DB13, DB23, DB39, DB61, DB83, DB192, and DB194 (not presented), which showed that the same oil had reached all the affected areas from which these samples were collected by Maritime Authority agents. Samples DB192 and DB194 (both collected in the state of Rio de Janeiro in November 2019) were also identified as belonging to the main spill from oil biomarker profiles, although some DRs do not comply with CEN (2012b) matching criteria. These samples were collected almost three months after the first occurrences, and these slight differences in some DRs were probably due to weathering effects, which affected compounds more prone to degradation (Wenger & Isaksen 2002). All

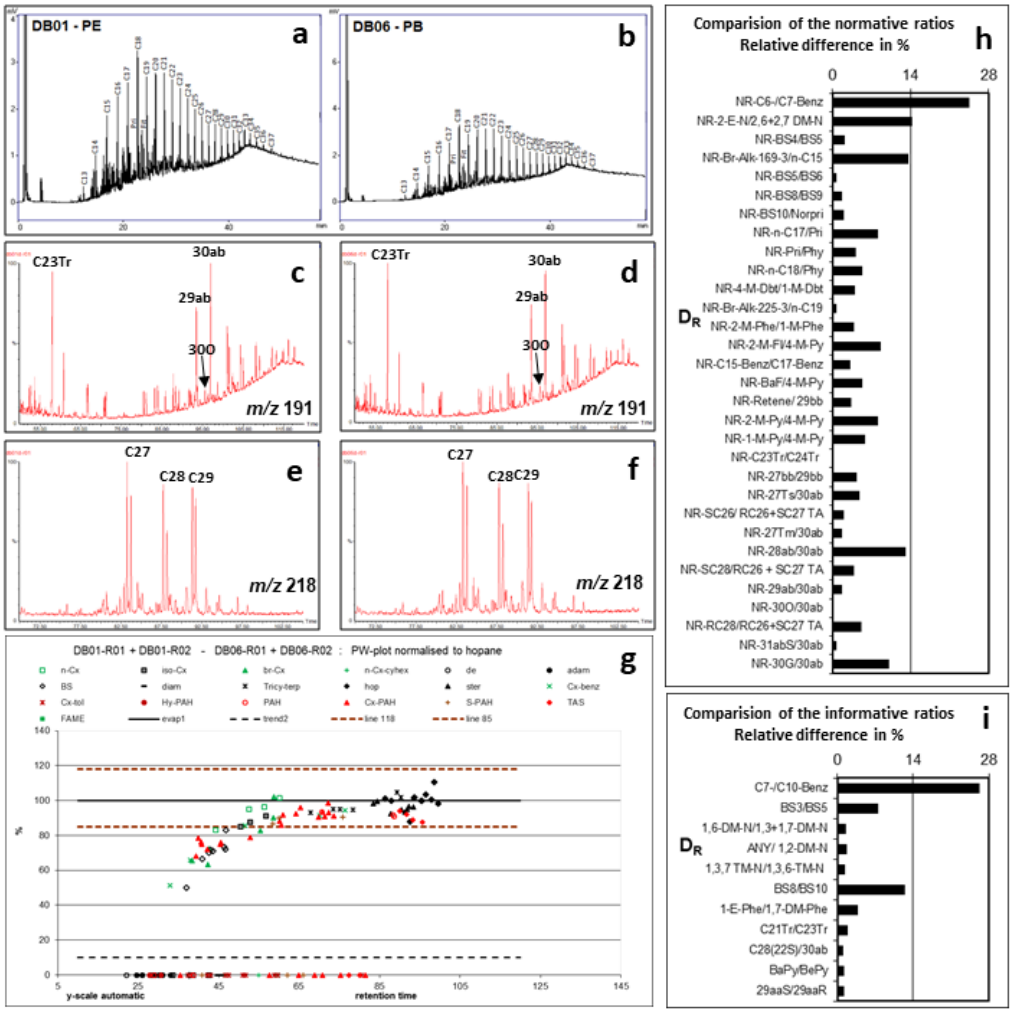

Figure 3. Combined results between samples DB01 and DB06, indicating that both samples are from the same source (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C23 Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; 30O – Oleanane; C30ab - 17α(H),21β(H)-hopane; C27 – C27αββ steranes (R+S); C28 – C28αββ steranes (R+S); C29 – C29αββ steranes (R+S).

of these samples were grouped together in the cluster analysis, evidencing, due to their similarity, that they belong to the same oil (see Section "Integrated view using multivariate data analysis" ahead).

Other detected spills

During the incident, spilled oil spread from Cururupu (MA) to São João da Barra (RJ), although oil residues were also detected in more southern locations in the states of Rio de Janeiro and São Paulo (Fig. 1), also including the oceanic islands of Fernando de Noronha, as previously described. In the following images, the chemical profiles of these samples (right chromatograms) were compared with the first sample collected during the incident (left chromatograms, reference oil). Chromatographic analysis indicated different products at variable weathering levels, suggesting both older and more recent occurrences not related to the main incident.

Sample DB76 – Bahia

The "Whole Oil" chromatographic profile of the DB76 sample, collected in the state of Bahia (inside the affected area), indicates a highly weathered oily material (GC-FID) when compared to the main incident spilled oil (Fig. 4a and 4b), characterized by the significant loss of light molecular weight n-alkanes, with preservation and proportional enrichment of high molecular weight n-alkanes, due to an unknown time exposure to weathering. This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclic terpanes and a prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 4c to 4f). Its high degree of weathering suggests that the sample might have been exposed to the environment for a longer time, perhaps a few years, although is not possible to determine its age (how long the oil has been exposed to weathering at sea or when it was discarded by the polluting ship). The relatively high abundance of Gammacerane (30G/30ab equal to 0.25, Table II), also seen in some crude oils from the Sergipe/Alagoas, Potiguar and Ceará basins in Brazil (Mello et al. 1988), suggest a possibly national oil, although Gammacerane is also present in high concentrations (up to 50% in relation to C_{30} αβ-hopane) in the African Angola Cabinda and Gabon crude oils (Wang et al. 2006).

The PW-plot (Fig. 4g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 4h and 4i), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB94 – Bahia

The "Whole Oil" profile of the DB94 sample, collected in the state of Bahia (inside the affected area), indicates an unrelated discharge of a medium cut oil product (GC-FID) when compared to the main incident spilled oil (Fig. 5a and 5b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclic terpanes, a higher abundance of Oleanane (DR 30O/30ab present a value of 0.20 instead of 0.07-0.08 for the samples from the main incident) and the prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 5c to 5f). Such a higher abundance of Oleanane, as presented in Table II, not only evidences that both oils are from different products but also — according to the characteristics described for Brazilian oils in Mello et al. (1988) — rules out a national source for the oil represented by the sample DB94.

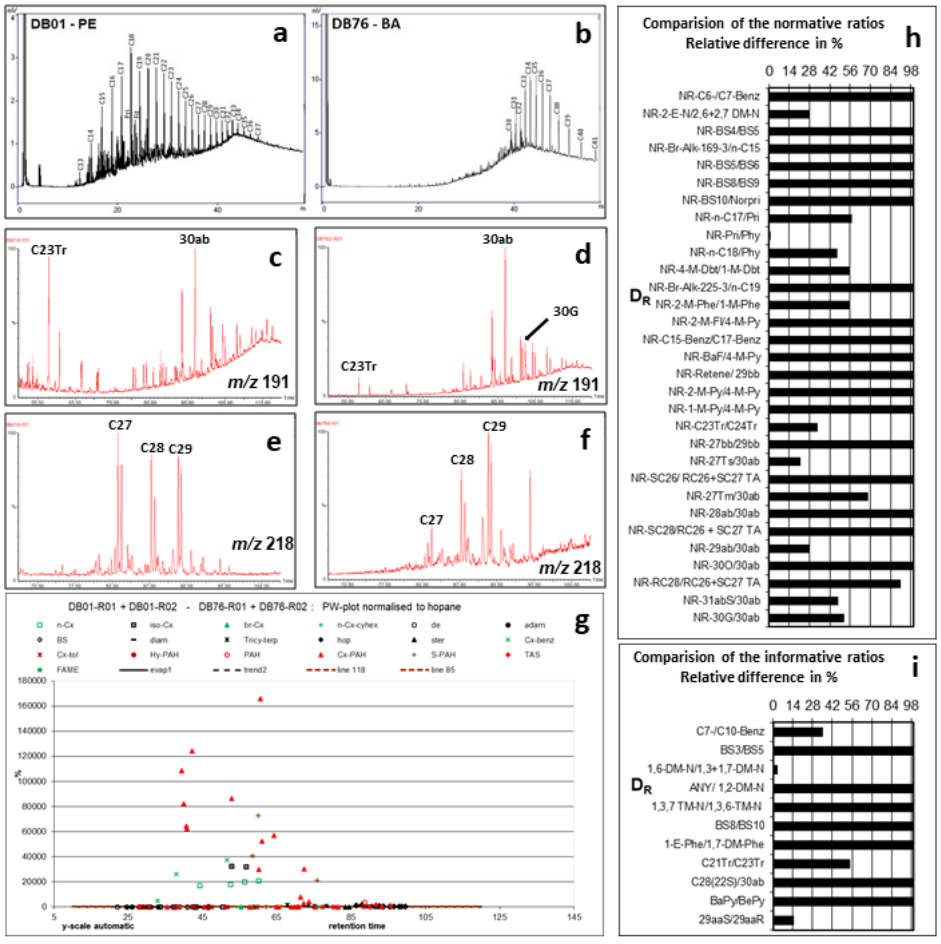

Figure 4. Combined results between samples DB01 and DB76, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C23 Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30G – Gammacerane; C27 – C27αββ steranes (R+S); C28 – C28αββ steranes (R+S); C29 – C29αββ steranes (R+S).

The PW-plot (Fig. 5g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 5h and 5i). Most DRs were outside the 14% CD threshold defined by CEN (2012b), confirming that this sample is originated in some other discharge, unrelated to the incident on the Brazilian coast in 2019.

Sample DB132 – Espírito Santo

The "Whole Oil" profile of the DB132 sample, collected in the state of Espírito Santo (inside the affected area), indicates an unrelated and possibly older discharge of a heavy fuel oil or a medium weathered crude oil, with significant loss of n-alkanes smaller than n-C_{17} (GC-FID) when compared to the main incident spilled oil (Fig. 6a and 6b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclic terpanes (including C_{23}Tr) and prevalence of C_{28} steranes over C_{27} and C_{29} steranes (Fig. 6c to 6f).

The PW-plot (Fig. 6g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 6h and 6i),

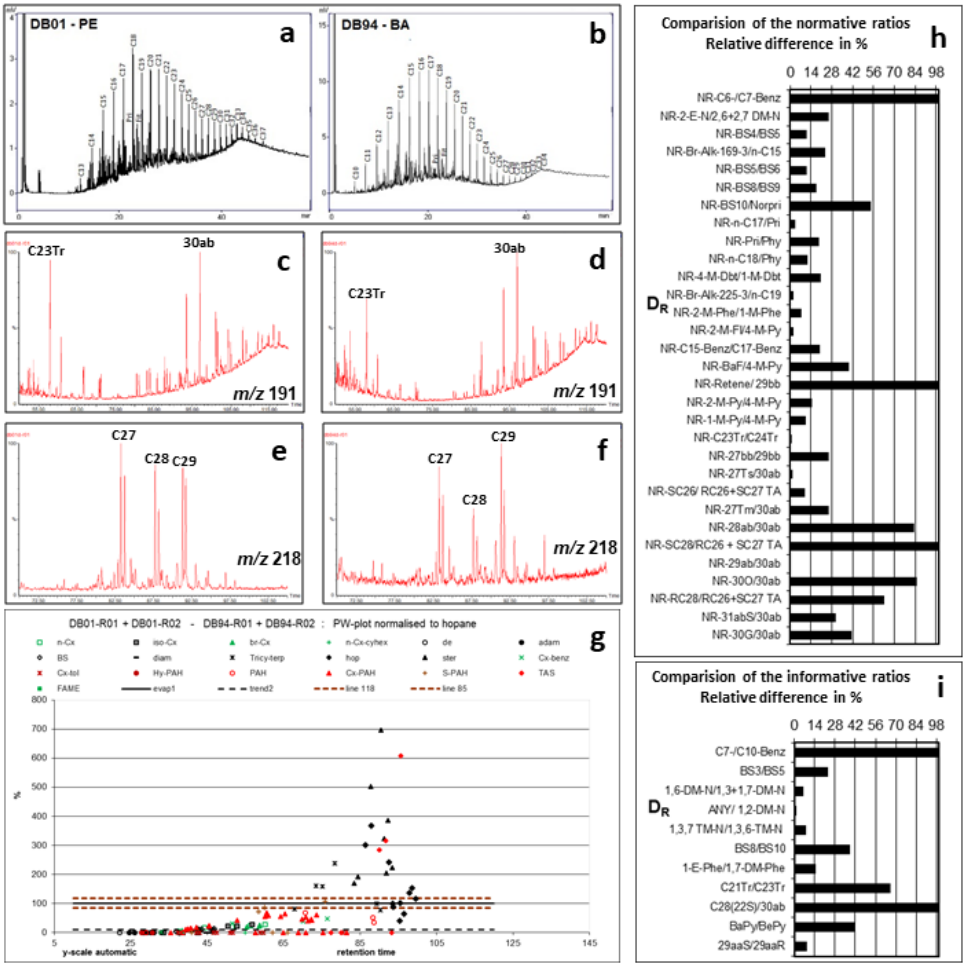

Figure 5. Combined results between samples DB01 and DB94, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB162 – São Paulo

The "Whole Oil" profile of the DB162 sample, collected in the state of São Paulo (outside the affected area), indicates an unrelated and highly weathered oily material (GC-FID) when compared to the main incident spilled oil (Fig. 7a and 7b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclics (including C23Tr) and prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 7c to 7f). Again, there is also a relatively high abundance of Gammacerane (30G/30ab equal to 0.31 instead of 0.13 for the samples from the main incident, Table II), similar to described for DB76 sample.

The PW-plot (Fig. 7g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 7H and 7I), with almost all DR outside the 14% CD threshold defined by CEN (2012b), confirming that this sample is originated in some other discharge, unrelated to the main incident.

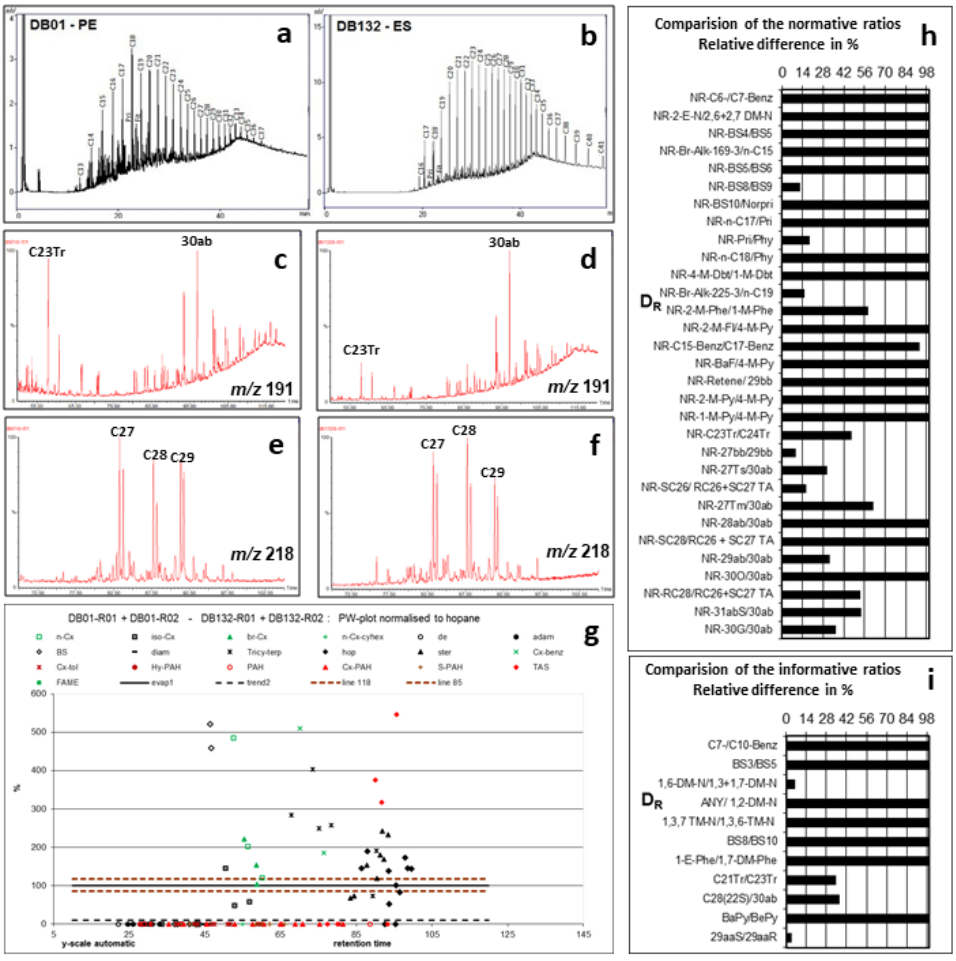

Figure 6. Combined results between samples DB01 and DB132, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

Sample DB198 – Rio de Janeiro

The "Whole Oil" profile of the DB198 sample, collected in the state of Rio de Janeiro (inside the affected area), indicates an unrelated and heavily weathered product (GC-FID) — suggestive of an apparently older discharge — when compared to the main incident spilled oil (Fig. 8a and 8b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclics (including C23Tr) and prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 8c to 8f).

The PW-plot (Fig. 8g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 8h and 8i), with almost all DR outside the 14% CD threshold defined by CEN (2012b), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB205 – Rio de Janeiro

The "Whole Oil" profile of the DB205 sample, collected in the state of Rio de Janeiro (outside the affected area), indicates an unrelated and highly weathered oily material (GC-FID) when compared to the main incident spilled oil (Fig. 9B and 9b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclics (including C23Tr) and prevalence

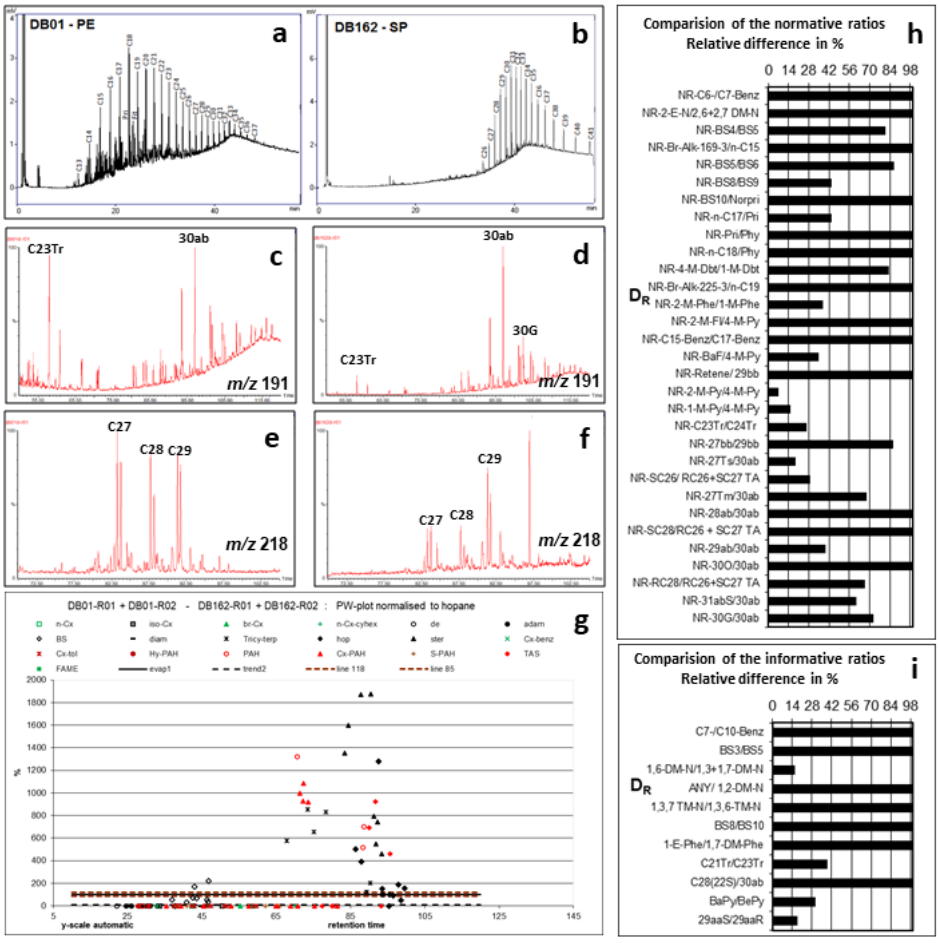

Figure 7. Combined results between samples DB01 and DB162, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30G – Gammacerane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

of C_{29} steranes over C_{28} and C_{27} steranes (Fig. 9c to 9f). Again, there is also a relatively high abundance of Gammacerane (30G/30ab equal to 0.43 instead of 0.13 for the samples from the main incident, Table II), similar to described for DB76 sample.

The PW-plot (Fig. 9g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 9h and 9i), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB219 – Rio de Janeiro

The "Whole Oil" profile of the DB219 sample, collected in the state of Rio de Janeiro (outside the affected area), indicates an unrelated and highly weathered oily material (GC-FID) when compared to the main incident spilled oil (Fig. 10a and 10b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as lower abundance of tricyclics (including C23Tr) and prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 10c to 10f). Again, there is also a relatively high abundance of Gammacerane (30G/30ab equal to 0.25 instead of 0.13 for the samples from the main incident, Table II), similar to described for DB76 sample.

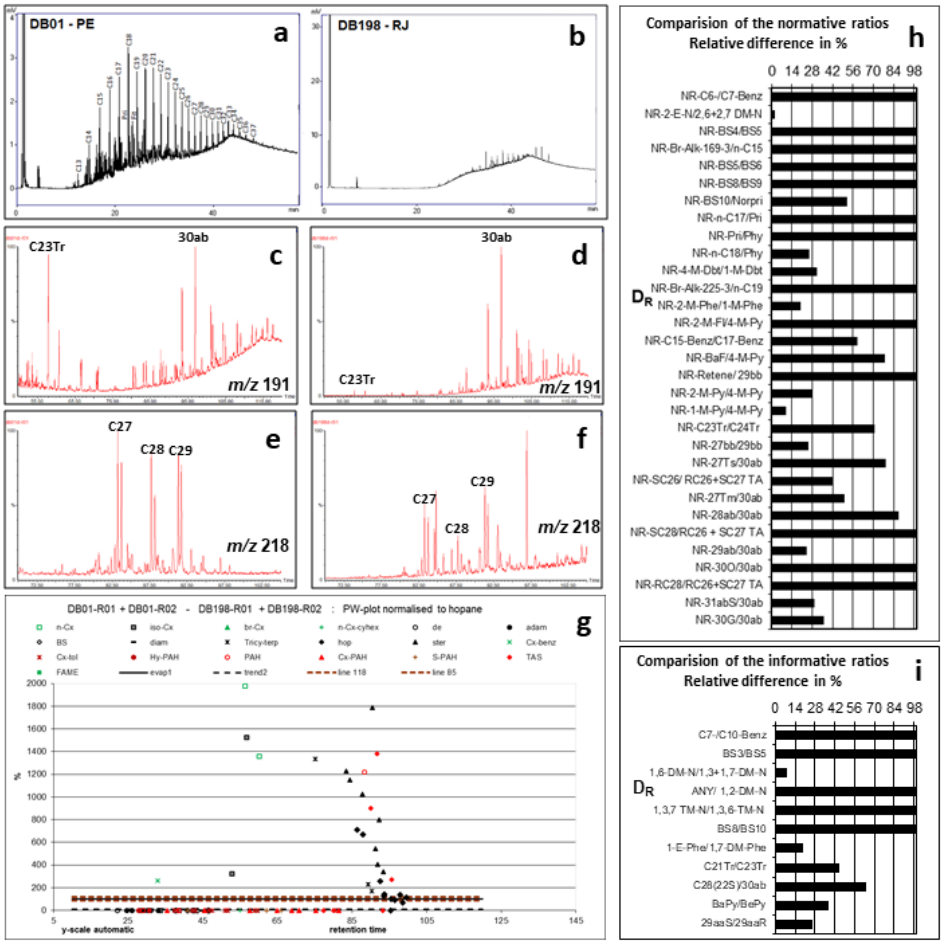

Figure 8. Combined results between samples DB01 and DB198, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

The PW-plot (Fig. 10g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 10h and 10i), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB254 – Rio Grande do Norte

The "Whole Oil" profile of the DB254 sample, collected in the state of Rio Grande do Norte (inside the affected area), indicates an unrelated and highly weathered oily material (GC-FID) when compared to the main incident spilled oil (Fig. 11a and 11b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as prevalence of C_{29} steranes over C_{28} and C_{27} steranes (hardly detected) or the abundance of Gammacerane observed in this sample (Fig. 11c to 11f). The high abundance of Gammacerane (30G/30ab equal to 2.35 instead of 0.13 for the samples from the main incident, Table II), whose geochemical characteristics were previously described for DB76 sample, suggests a possibly national oil as source for these residues. However, the higher abundance of 29ab over 30ab in *m/z* 191 (29ab/30ab present a value of 1.69 instead of values close to 0.73 for samples from the main incident) resemble a signature similar to that of Kuwait crude oil described

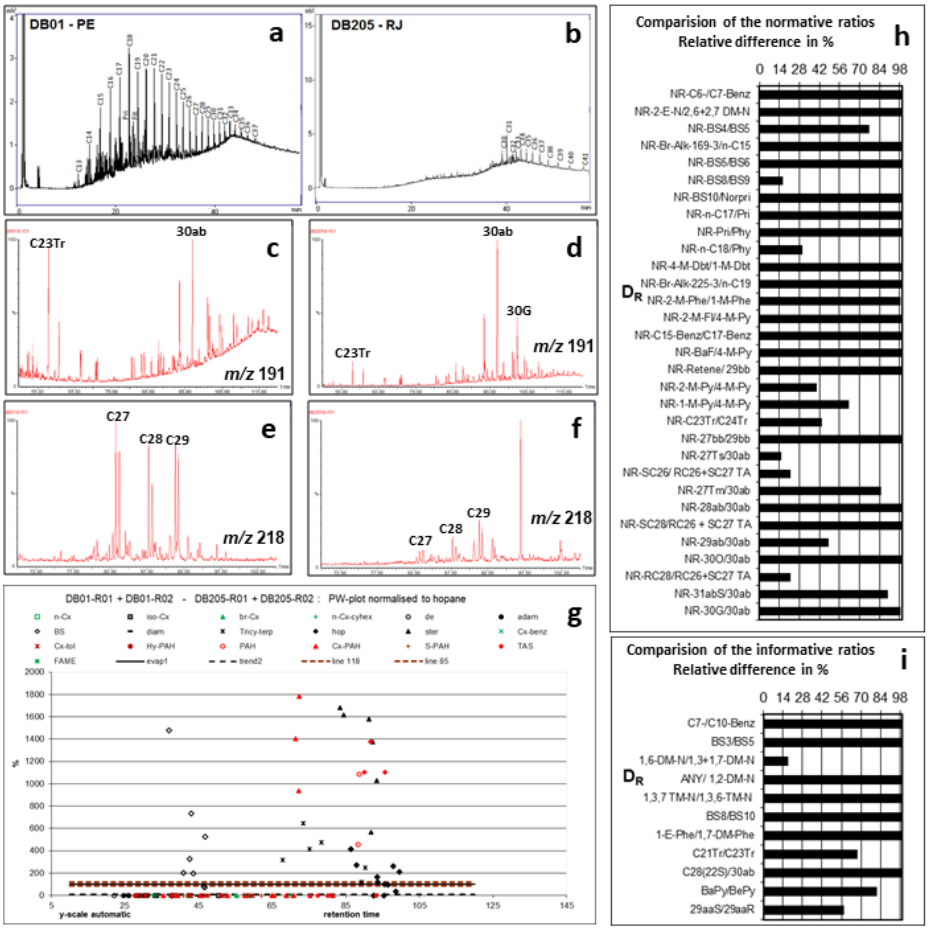

Figure 9. Combined results between samples DB01 and DB205, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30G – Gammacerane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

by Wang et al. (2006). Perhaps, due to the high weathering state of the oil residues analyzed, some of these characteristics have been altered to a point that hinder any speculation of its geographical origin.

The PW-plot (Fig. 11g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 11h and 11i), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB256 – Pernambuco (Fernando de Noronha Island)

The "Whole Oil" profile of the DB256 sample, collected in the state of Pernambuco (Fernando de Noronha Island) (outside the affected area), indicates an unrelated and very weathered product (GC-FID) when compared to the main incident spilled oil (Fig. 12a and 12b). This sample also has biomarker profiles that differ significantly from the oil found in the main incident, such as low abundance of tricyclics (including C23Tr), much higher abundance of Oleanane and prevalence of C_{29} steranes over C_{27} and C_{28} steranes (Fig. 12c to 12f). Such higher abundance of Oleanane, as presented in Table II, where the DR 30O/30ab present a value of 0.70, resemble characteristics that are very similar to

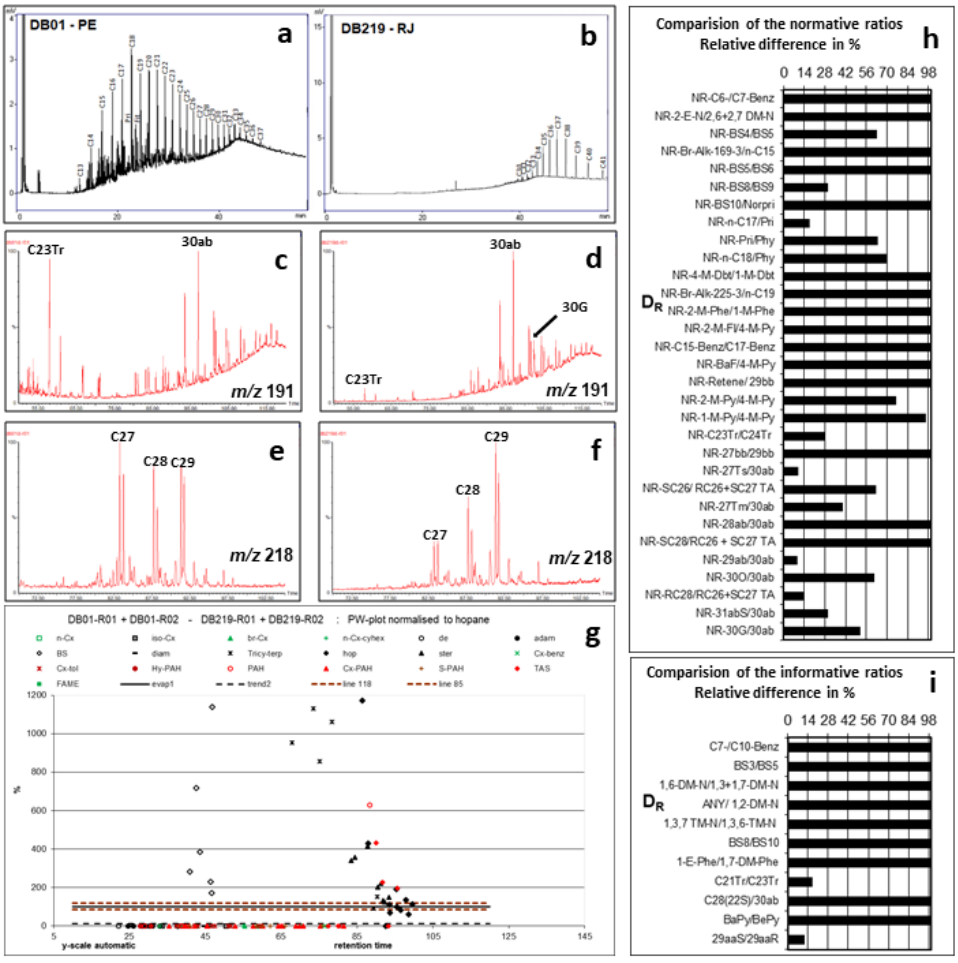

Figure 10. Combined results between samples DB01 and DB219, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30G – Gammacerane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

those from the Tertiary Niger Delta petroleum system. The Niger Delta is located in the southern Nigeria margin of the Gulf of Guinea. Terrigenous oils from that region present some specific characteristics as high Oleanane index, prevalence of C_{29} over C_{28} and C_{27} steranes and high Pri/Phy DRs (Samuel et al. 2009).

The PW-plot (Fig. 12g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples evidence significant differences in both the normative and informative DRs (Fig. 12h and 12i), confirming that this sample is originated in some other discharge, unrelated to the main incident.

Sample DB268 – Ceará

The "Whole Oil" profile of the DB268 sample, collected in the state of Ceará (inside the affected area), indicated an unrelated and supposedly more weathered oil discharge (due to the weathering degree from GC-FID profile, with significant loss of n-alkanes smaller than n-C_{16}) when compared to the main incident spilled oil (Fig. 13a and 13b). This sample had biomarker profiles that differed significantly from the oil found in the main incident, such as lower abundance of tricyclics (including C_{23}Tr), prevalence of 17α(H),21β(H)-norhopane

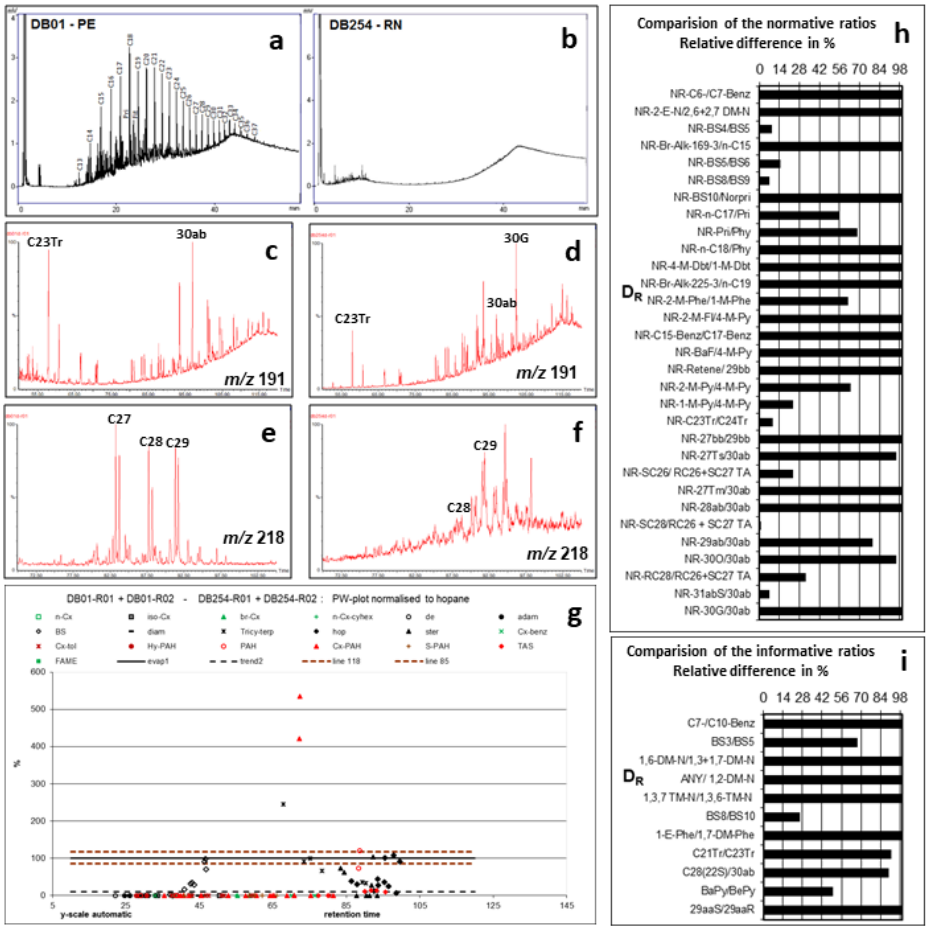

Figure 11. Combined results between samples DB01 and DB254, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30G – Gammacerane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

(29ab) over 17α(H),21β(H)-hopane (30ab), and prevalence C_{29} steranes over C_{27} and C_{28} steranes (Fig. 13c to 13f, Table II). Unlike the other samples that did not match with the main incident, the material did not degrade on beaches, having arrived in Caetanos de Cima beach, São Bento de Amontada (CE), on December 30, 2019. The higher abundance of 29ab over 30ab in *m/z* 191 (29ab/30ab present a value of 1.07 instead of values close to 0.73 for samples from the main incident) resemble a signature similar to that of Kuwait crude oil described by Wang et al. (2006).

The PW-plot (Fig. 13g) indicates significant differences between both samples, not explained by weathering, as an additional evidence that these samples do not match each other. Comparison between the DRs of both samples showed significant differences in both the normative and informative DRs (Fig. 13h, and 13i), indicating that this sample was originated in some other discharge, unrelated to the main incident.

Sample DB281 – Paraíba

The "Whole Oil" profile of the DB281 sample, collected in the state of Paraíba (inside the affected area) almost five months after the first occurrence of oil in the Brazilian coast, indicated an unrelated and more weathered oil discharge (with significant loss of n-alkanes smaller than n-C_{16}) when compared to the main incident spilled oil (Fig. 14a and 14b). This sample had biomarker profiles that differed from the oil found in the main incident, such as a lower abundance of

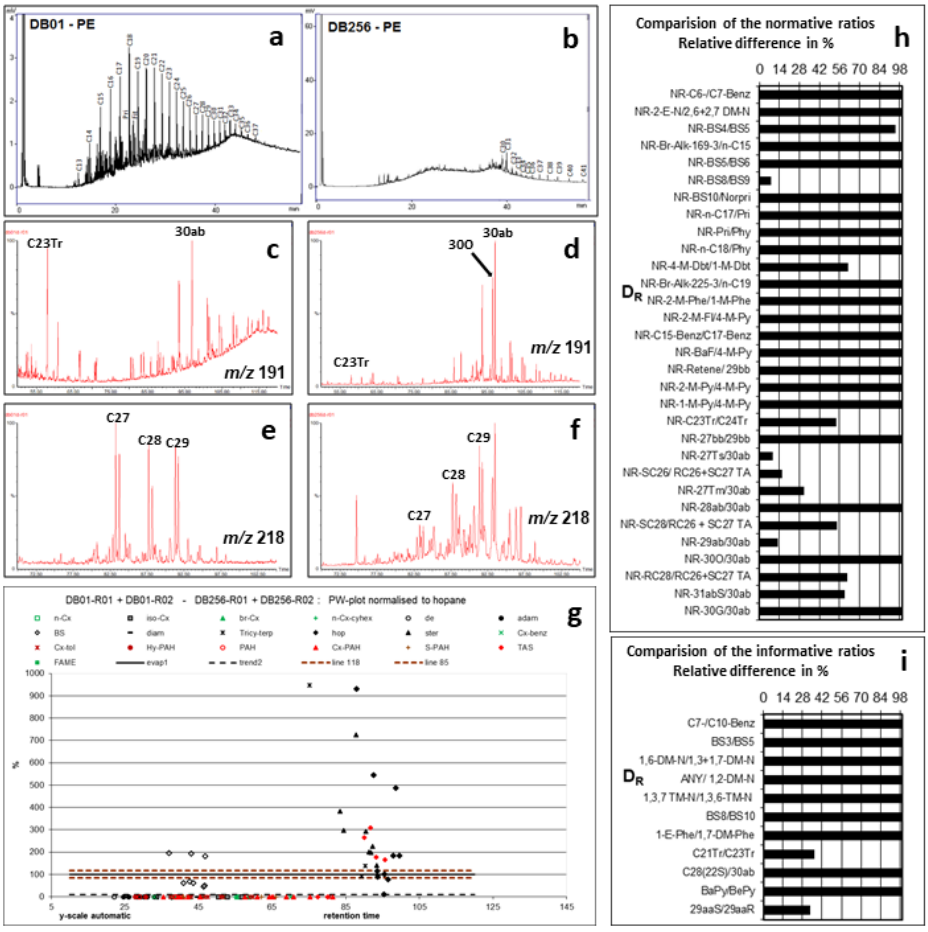

Figure 12. Combined results between samples DB01 and DB256, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; 30O – Oleanane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

tricyclics (including C_{23}Tr), despite sharing some similarities with terpanes and the ββ steranes profiles (Fig. 14c to 14f). Such similarities might suggest the same oil from the main incident in a more advanced weathering degree.

The PW-plot (Fig. 14g) indicates that, despite many compounds differ significantly from the reference sample (DB01), part of the conservative compounds (those more resistant to the effects of weathering) presented preservation close to 100%. Also, comparison between the DRs of both samples, according to the criteria described in CEN (2012b), showed significant differences in both the normative and informative DRs (Fig. 14h, and 14i), despite some significant DRs match with those from the originally observed incident, including the normative ratios (NR) 30O/30ab, 29ab/30ab and 30G/30ab. However, as most of the DRs were outside the 14% CD threshold defined by CEN (2012b) methodology, this oil did not match with the samples from the main incident. Such methodology was developed to establish standardized procedures in order to proceed with the forensic fingerprinting of oil spills, usually in short-term events. It is possible that this methodology has not been tested for the conditions of the incident reported here, in which highly weathered samples, exposed to the environment for an unknown time, in a region with a tropical climate (high temperatures, incidence of wind and other factors that can speed up the effects of weathering) may have its chromatographic profile altered to, at some point, preventing the unequivocal identification

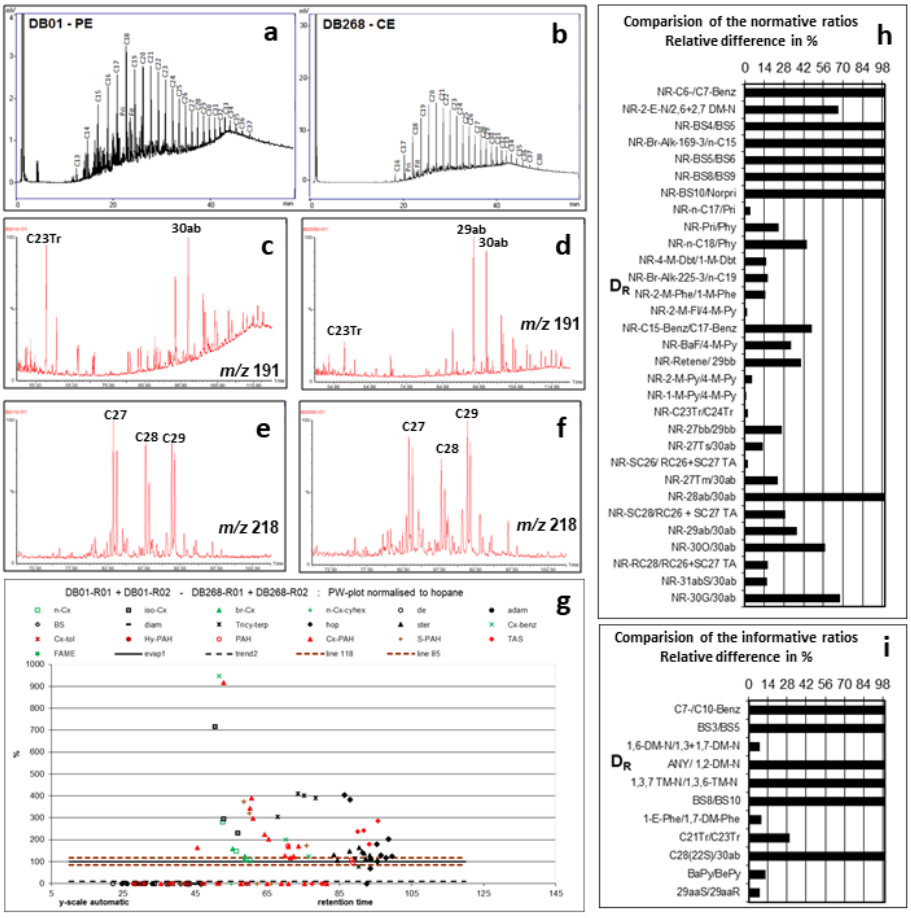

Figure 13. Combined results between samples DB01 and DB268, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

of its origin. Thus, as previously mentioned, is expected to report an experiment specifically designed to elucidate possible false negatives related to weathering, which might be the case of DB281 sample.

Integrated view using multivariate data analysis

According to Fig. 15, almost all samples from the main incident (DB01, DB06, DB10, DB13, DB23, DB39, DB61 and DB83) were grouped together showing similarity indices higher than 0.90. Samples DB192 and DB194 (both collected in the state of Rio de Janeiro in November 2019), also identified as belonging to the main spill by the chemical profiles of oil biomarkers, are very similar to each other (similarity indices higher than 0.90) although they have presented slightly lower similarity with the other samples (close to 0.80). These samples, although coincident, have some DRs that do not meet the CD matching criteria (CEN, 2012b) when compared to the first samples from the incident, probably due to its weathering, as mentioned earlier.

All other samples presented similarity indices that clearly indicate non-match with respect to the main spill samples, evidencing the chronic character of such kind of discharge in Brazilian coastal waters. Samples DB76, DB162, DB205, DB219 and DB254, all of them that do not match with the main spill, presented high relative content of Gammacerane when compared to the other samples (despite their relatively differences between them). The cluster analysis

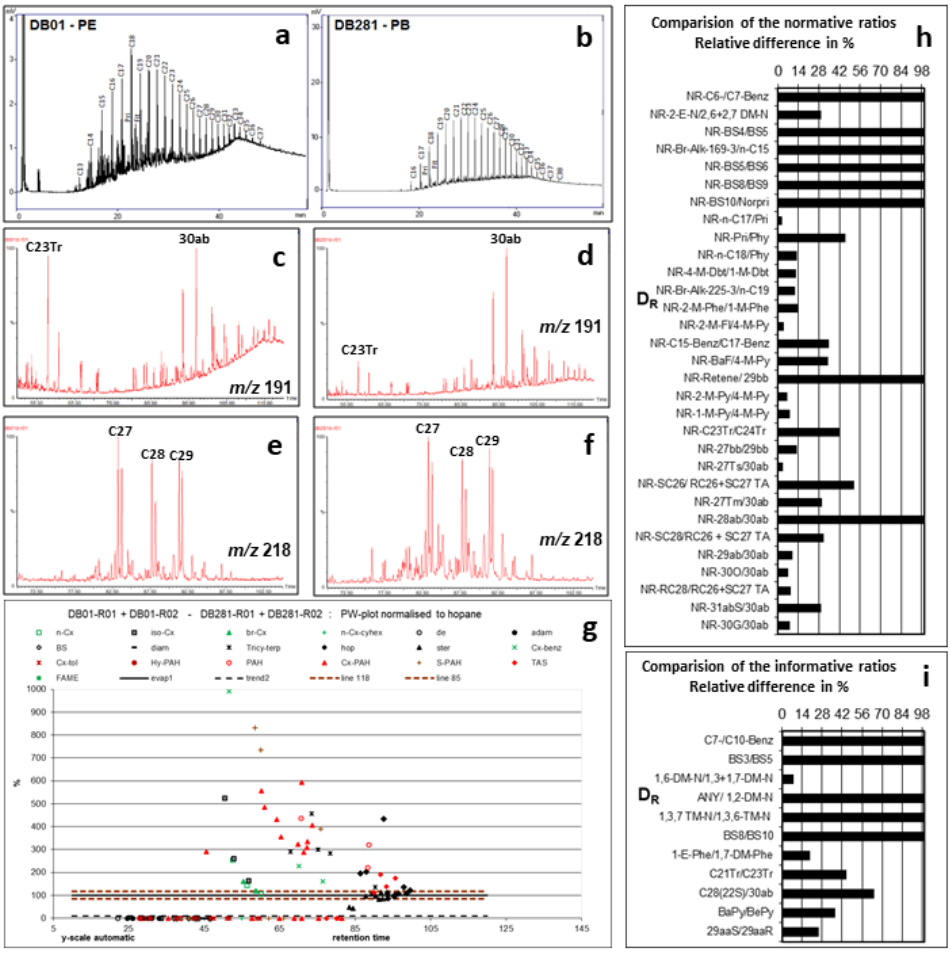

Figure 14. Combined results between samples DB01 and DB281, indicating that both samples are from different sources (DRs and compound names as described in CEN, 2012b). Legend: C23Tr – C_{23} Tricyclic terpane; C29ab - 17α(H),21β(H)-norhopane; C30ab - 17α(H),21β(H)-hopane; C27 – C_{27}αββ steranes (R+S); C28 – C_{28}αββ steranes (R+S); C29 – C_{29}αββ steranes (R+S).

showed that these samples are not related to each other, in view of the low rank of the similarity indices observed in their relative comparison, which indicates that other DRs (see Table II) are also different between these samples. For the set of samples considered, the highest similarity indice is observed between samples DB162 and DB205 (lower than 0.60), making it possible to exclude a possible common origin (which could suggest the same discharge of oily residues).

CONCLUSIONS

The results of the analyses confirmed that a same Venezuelan oil reached a length of coastline higher than 3,000 kilometers in 2019, from Cururupu (MA) to São João da Barra (RJ), Brazil. The results also evidenced the occurrence of unrelated oily discharges, both in the affected region and in areas unaffected by the main incident, as in Ilha Bela (SP). Such unexpected occurrences, which suggest chronic events, were detected due to the huge repercussions resulting from the spill when the response teams carried out an active search in all the regions of the coast where oily residues were registered at that time. From these residues, found even in regions far from the coast, such as the archipelago of Fernando de Noronha, it is possible to infer that irregular and recurrent oily discharges are being carried out by ships in open seas. Eventually, such discharges can reach the coast, causing extensive damage to the environment; hence,

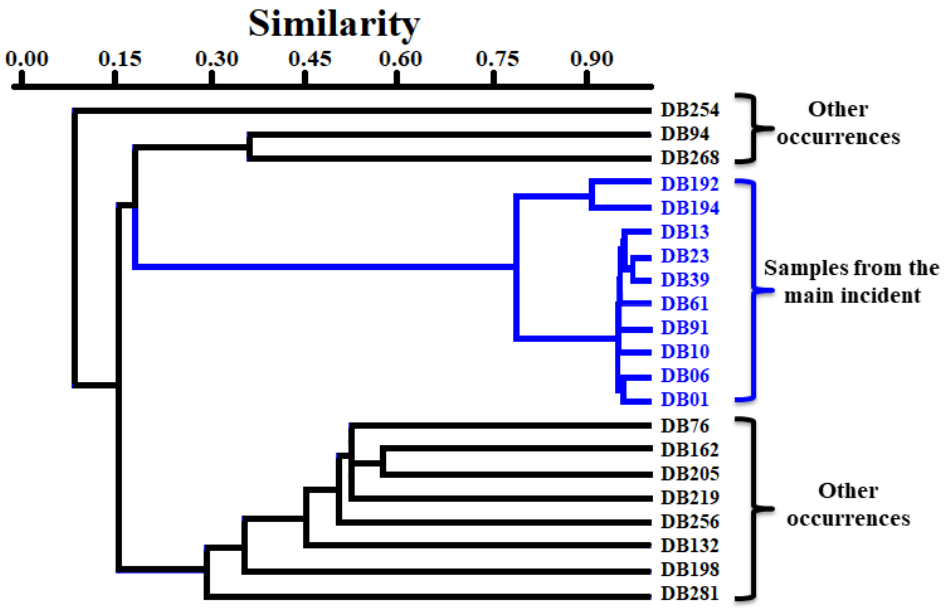

Figure 15. Cluster Analysis showing relations for all considered samples.

authorities must deal with this problem to avoid even more serious environmental damage in the future.

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