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Environmental disaster in the northeast coast of Brazil: Forensic geochemistry in the identification of the source of the oily material



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ABSTRACT

The characterization of petroleum or its products spilled in the environment in relation to its source rocks is an important tool to assist in the resolution of issues of environmental impact and legal responsibility since it clarifies the possible region or the producing country of that type of petroleum. This article analyzes the application of analytical techniques for petroleum geochemistry to identify the type and origin of oily material collected from beaches in Northeast Brazil in 2019. Samples of the oily material collected on the beaches in the states of Bahia and Sergipe were analyzed and for comparison purposes, samples of crude oils produced in Brazil, Middle East, Nigeria and Venezuela were also analyzed. The analytical results showed that the oily material that reached the beaches has geochemical characteristics compatible with those of the Venezuelan oil, indicating it was severely weathered or a product made with heavy oil produced.

The stages of the oil production chain (exploration, production, transport, refining, storage and distribution) can cause oil leaks, for example, oil spills, accidents at refineries, oil tankers and platforms, or during the cleaning of vessel tanks, among others. According to [ITOPF \(2019\)](#) the number of major spills (with the launch of > 700 thousand tons) in the world has been reduced in recent decades due to the development of new control technologies. Even so, there is still a risk that leaks will occur, given that in 2018 alone, 116,000 tons of oil were spilled into marine waters worldwide.

The catastrophe that occurred in the second half of 2019 on the coast of Brazil is an example of recurring events involving the oil spill with a major impact on the environment and the socioeconomic sector. In this accident, 2880 km of area extension were affected with > 200 tons of oily material removed from coastal environments in a period of approximately five months, being considered the largest length of contaminated coast in the world recorded in 30 years ([IBAMA, 2019](#)). These incidents ratify the importance of applying forensic geochemistry in identifying the type and origin of the spilled material and proposing

solutions to problems of environmental crimes.

Anthropic impacts on nature are of incalculable magnitude, this without assessing the environmental cost related to the effect on animal species, plants, microorganisms, and the short and long term damage due to the recalcitrance of some of the heaviest components of oil ([Kanjilal, 2015](#); [Rekadwad and Khobragade, 2015](#); [Turner et al., 2014](#); [Fingas, 2011](#); [Stout and Wang, 2007](#); [Peters et al., 2005](#)). Estuarine and mangrove ecosystems are most affected in the long term after an oil spill, causing damage to biological organisms and requiring the application of more complex remediation techniques ([Rios et al., 2017](#); [Miranda et al., 2016](#); [Moreira et al., 2015](#); [Silva et al., 2014](#); [Goncalves da Silva et al., 2013](#); [Moreira et al., 2013](#); [Ferreira et al., 2011](#); [De Brito et al., 2002](#)).

In spill events, oil can be physically and chemically altered by biotic and abiotic factors called weathering processes ([Yang et al., 2013](#); [Anderson and Hess, 2012](#); [Stout and Wang, 2007](#); [Prince and Clark, 2004](#); [Wang and Fingas, 1995](#)). The weathering of oil in marine environments, or involving water as a means of physical contact, covers

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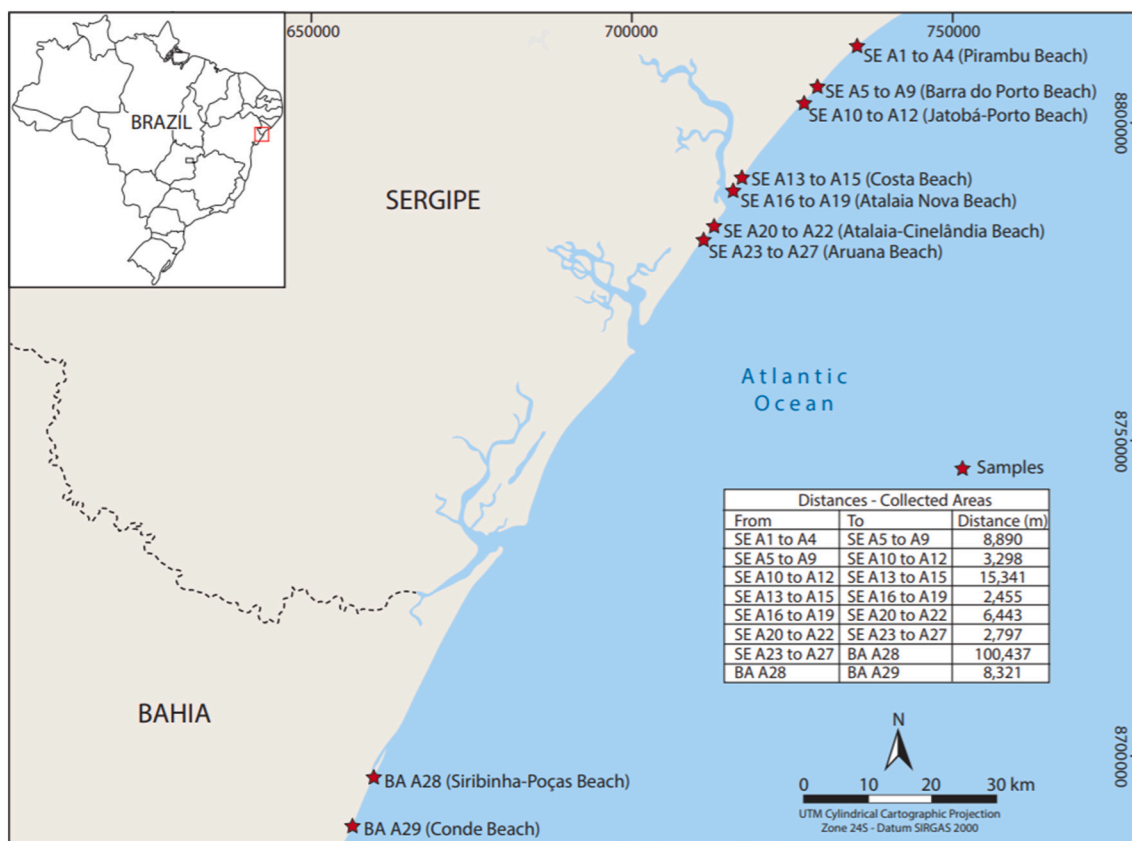


Fig. 1. Location map of oil samples collected on the coast of the states of Sergipe and Bahia.

processes such as adsorption, biodegradation, dispersion (horizontal and vertical), dissolution, emulsion, scattering, evaporation and photo-oxidation (Ho et al., 2015; Reyes et al., 2014; Anderson and Hess, 2012; Fingas, 1996; Price, 1995). These factors modify or degrade petroleum compounds, such as hydrocarbons and other substances that compose them (Al-Majed et al., 2012; Fingas, 2011; Lobão et al., 2010; Andersen et al., 2008; Peters et al., 2005; Philp et al., 2002; Price, 1995; Wang and Fingas, 1995).

Once accidents occur, the identification of the type of spilled oily material and its origin begins, using the results of chromatographic and isotopic analyses. Petroleum biomarkers and stable carbon isotopes are tools that allow defining the origin of each oil, which is unique for each type of oil. Biomarkers are molecular fossils derived from compounds present in living organisms, which undergo little change during the generation process and remain present in oil, helping to establish its origin. Among the most studied are branched alkanes (isoprenoids, such as pristane and phytane), cyclic (terpanes, steranes, etc.) and aromatic compounds (retene, cadalene, methyl phenanthrene, etc.). The isotopic composition of carbon is the result of the physical-chemical conditions of the environment in which the organic matter that gave rise to oil lived (Fingas, 2011; Wang et al., 2009; Peters et al., 2005).

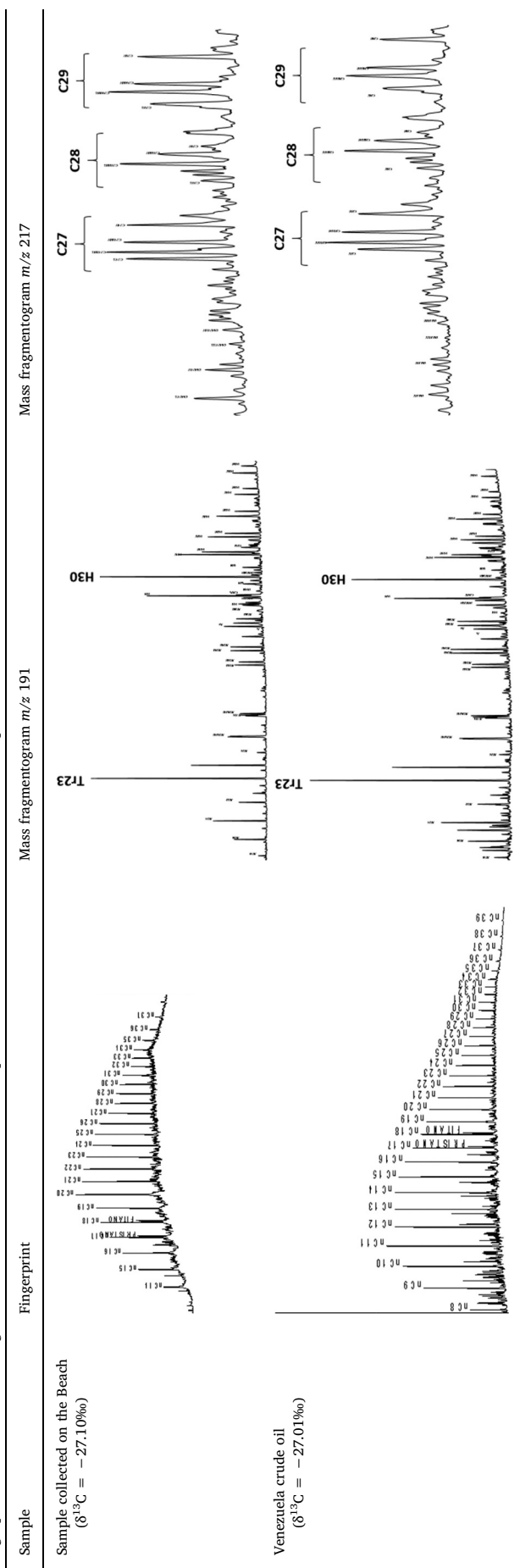
The objective of this study was to identify the geological origin of the oily material that reached the coast of northeastern Brazil, helping to elucidate the environmental responsibility of the disaster and contributing to the emergency actions for its mitigation.

Seven samples were collected on the beaches along the coast of the

State of Sergipe and two samples in the municipality of Conde, the first contaminated coastal region on the coast of the State of Bahia (Fig. 1), under the same protocol conditions. The collected samples had visual physical characteristics (viscosity, color and odor) of oil. All collected material was analyzed by liquid chromatography, gas chromatography, gas chromatography coupled to mass spectrometry and isotopic ratio mass spectrometer at Center of Excellence in Petroleum Geochemistry, Energy and Environment at Geosciences and Physics Institutes, University of Bahia, Brazil.

To identify the possible origin of the oil spilled in the sea, the results were compared with the data from the oil samples of the LEPETRO Oil Bank, which has different types of oil produced in Brazil, which were generated by source rocks of sedimentary paleoenvironments lacustrine fresh water, lacustrine saline water, Albian marine and Turonian marine (Mello et al., 1988) and in the world. Oil samples from the Middle East, Nigeria and Venezuela were selected and analyzed, since the tankers that transport oil from these countries have their routes through the Atlantic Ocean, passing through the northeast region of Brazil, an area of great influence of the Equatorial Marine Current, whose waters are directed to Brazil (Talley et al., 2011).

The first analytical step consisted of the physical separation of the oily material from sand and sea water, using an open chromatographic column (30 × 2 cm) filled with 12 g of sodium sulfate PA (Merck, Darmstadt, Germany), previously calcined in muffle (SP-1200, SPLabor, São Paulo, Brazil) at 400 °C for 4 h. 10 g of sample was added and percolated through the column using 100 mL of dichloromethane

Table 1
Fingerprint and Mass chromatograms m/z 191 and m/z 217 of a sample collected on the coast of Bahia and a sample of crude oil from Venezuela.

(Merck, Darmstadt, Germany). Then it was evaporated on a rotary evaporator (R-201/215, BÜCHI, Flawil, Switzerland) and transferred to a 20 mL vial. For the analysis of the total oil (fingerprint), approximately 20 mg of sample was weighed and dissolved in 0.4 mL of dichloromethane. The analyses were performed in a gas chromatograph with flame ionization detector (GC-FID 7890B, Agilent Technologies, Santa Clara, California, United States) using capillary fused silica column DB-1 (15 m $\times$ 0.25 mm $\times$ 0.25 μm), temperature oven 40 $^{\circ}\text{C}$ for 2 min and heating rate of 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$, remaining for 12 min; injector and detector temperature at 300 $^{\circ}\text{C}$, with helium as carrier gas, at 1 mL/min, constant flow and injection volume 1 μL .

For the analysis of saturated biomarkers, the samples were fractionated using an open column (30 $\times$ 2 cm) filled with 4 g of silica gel (60 mesh size, Merck, Darmstadt, Germany) moistened in n-hexane PA (Merck, Darmstadt, Germany). About 20 mg of sample was eluted using 30 mL of n-hexane to obtain the saturated fraction. This fraction was evaporated in a rotary evaporator (R-201/215, BÜCHI, Flawil, Switzerland) and transferred to a 1.8 mL vial, continuing the evaporation with nitrogen flow until the final volume 250 μL . The saturated fraction was quantified by gas chromatography coupled to a mass spectrometer (GC/MS, Agilent Technologies, Santa Clara, California, United States), using a capillary column of fused silica DB-5 (60 m $\times$ 0.25 mm $\times$ 0.25 μm). Helium was used as carrier gas with a flow of 1 mL/min and a constant pressure of 30 psi. The sample concentration of 0.05 mg sample/1 μL of hexane, injection volume 1 μL , heating from 60 $^{\circ}\text{C}$ to 310 $^{\circ}\text{C}$ with a heating ramp of 2 $^{\circ}\text{C}/\text{min}$. The ions m/z 217 (steranes), m/z 191 (triterpanes) and m/z 259 (tetracyclic polyprenoids and diasteranes) were monitored.

In addition, in partnership with the Laboratory of Stable Isotopes (LISE) of the Nuclear Physics Institute/UFBA, analyses of the isotopic carbon ratio ($\delta^{13}\text{C}$) of the oil samples were made, using 0.05 mg of sample in capsules of tin. The method consisted of dry combustion (1020 $^{\circ}\text{C}$) of the samples under continuous helium flow, with the aid of an elementary analyzer coupled to the isotopic ratio mass spectrometer (Isotope Ratio Mass Spectrometer- IRMS, Delta V, Scientific Term, Waltham, USA). The CO_2 resulting from the combustion of the samples were compared with the CO_2 of the international standard PDB (American limestone Pee Dee Belemnite).

The results were interpreted through the use of the main ratios of the saturated biomarkers and the ratio of the stable carbon isotopes with the aid of the software Excel (Microsoft Office 2016) and Past3 (Paleontological Statistics Version 3.0 - University of Oslo) that allowed the making of graphs and multivariate statistical analysis (HCA).

The samples collected on the beaches presented whole oil gas chromatography profiles (Table 1) with the presence of isoprenoids pristane and phytane, absence of light hydrocarbons (nC_8 - nC_{13}) probably due to evaporation, predominance of long chain paraffin (nC_{14} - nC_{35}) and elevation of the baseline due to the presence of a mixture of unresolved chromatographic compounds (UCM). It is observed that phytane is present in similar abundance to the pristane, suggesting a deposition environment under suboxide conditions. The predominance of paraffin nC_{17} and nC_{18} over pristane and phytane isoprenoids suggests thermal maturity and relative preservation of the material (Lee et al., 2020; Li et al., 2016; Lourenço et al., 2020; Magris and Giarrizzo, 2020; Wang et al., 2013; Peters et al., 2005). Due to the high degree of weathering of the samples collected on the beach, it was not possible to calculate the ratios between the concentrations of compounds normally used to make the correlations between the samples. Therefore, no comparison was made with the results of the analysis of oil samples from the database to determine the origin of the spilled oil using whole oil gas chromatograms. This was done using results of analyses of saturated biomarkers and $\delta^{13}\text{C}$.

The most striking characteristics in the mass chromatogram of the saturated biomarkers referring to the terpanes (m/z 191) of the samples collected on the beaches are: the great abundance of the C23 tricyclic terpane (TR23), high homohopane/hopane ratio ($\text{H}_{29}/\text{H}_{30}$), low

Table 2 $\delta^{13}\text{C}$ ratio and main reasons for biomarkers indicative of the origin of the samples collected on the beach and of different Brazilian and international oils.

Sample	HOP/STER	TRIC/HOP	OL/H30	GAM/H30	TET24/26TRI	21/23TRI	TPP/TPP + DIAS	C27/C29	H35/H34	H29/H30	26/25TRI	$\delta^{13}\text{C}$
Brazil Lacustrine (Freshwater)	15,66	1,83	0,00	0,24	0,12	0,86	0,94	0,38	0,66	0,65	1,07	-31,32
Brazil Lacustrine (Saline Water)	5,04	1,72	0,00	0,14	0,33	1,02	0,51	2,02	0,68	0,65	0,97	-24,52
Brazil Marine (Evaporitic)	1,97	0,47	0,00	0,52	0,18	0,87	0,24	1,13	0,70	0,75	1,65	-26,57
Brazil Marine (Albian)	1,71	0,71	0,00	0,17	0,48	0,71	0,41	0,52	0,72	0,47	1,07	-25,28
Brazil Marine (Turonian)	2,25	0,35	0,00	0,07	0,35	0,67	0,35	0,71	0,65	0,51	1,15	-25,56
Nigeria Oil	9,03	0,12	0,36	0,02	1,25	0,75	0,70	0,71	0,45	0,61	1,43	-27,56
Arabe Oil	5,04	0,24	0,00	0,06	5,38	0,47	0,18	0,82	0,72	0,89	0,92	-26,46
Venezuela Oil	2,67	1,02	0,00	0,08	0,32	0,35	0,83	1,16	0,89	0,74	0,96	-27,02
Beach 1	4,39	0,57	0,00	0,11	0,40	0,30	0,76	0,87	1,11	0,71	0,88	-27,00
Beach 5	3,51	0,97	0,00	0,11	0,26	0,34	0,74	0,93	0,86	0,78	0,62	-27,06
Beach 11	2,78	1,04	0,00	0,12	0,38	0,34	0,72	1,29	0,81	0,79	0,76	-27,08
Beach 13	4,39	0,58	0,00	0,13	0,38	0,30	0,76	0,90	1,10	0,72	0,80	-27,07
Beach 16	3,16	1,10	0,00	0,12	0,45	0,43	0,72	0,95	0,76	0,80	0,49	-27,20
Beach 20	3,70	0,68	0,00	0,11	0,42	0,28	0,76	0,91	0,98	0,74	0,84	-27,13
Beach 23	4,47	0,59	0,00	0,12	0,40	0,29	0,75	0,82	1,10	0,71	0,73	-27,11
Beach 28	3,87	0,61	0,00	0,11	0,42	0,27	0,76	0,92	1,02	0,72	0,71	-27,08
Beach 29	3,76	0,72	0,00	0,12	0,37	0,34	0,75	1,10	0,84	0,73	0,77	-27,02

abundance of gammacerane, and low hopanes/steranes ratio (< 5), indicating origin from marine organic matter. In relation to the mass chromatogram of the m/z 217 ion, the similar proportion between the regular C27 and C29 steranes is notorious, which are higher in relation to C28 and the low abundance of diasteranes (Table 1), suggesting marine source rock rich in carbonates (Fingas, 2011; Wang et al., 2009; Peters et al., 2005).

In the mass chromatogram characteristic of the m/z 259 ion, the predominance of tetracyclic polyprenoids (TPP) over diasteranes (DIA) was found, resulting in a high TPP/TPP DIA ratio (Table 1).

Holba et al. (2003) showed that the abundance of TPP in oil indicates generator rocks of lacustrine origin, considering that the origin of these compounds is related to river and lake algae. The steranes and terpanes characterized the analyzed material as originating from petroleum generated by marine carbonate source rock, due to the low abundance in diasteranes. Therefore, the low TPP/TPP + DIA ratio is due to the low abundance in diasteranes present in the samples. The mass chromatograms of m/z 191 and 217 ions of one of the beach samples were compared with those of the Venezuelan oil sample and it was observed that the profiles are similar (Table 1).

The main reasons for the saturated biomarkers diagnosing the origin of the petroleum and the carbon isotope ratio (Table 2), allowed to compare the results of the samples collected on the beaches with the oil samples from different origins. For better visualization and understanding, the results of the diagnostic reasons were plotted in the form of graphs (Fingas, 2011; Wang et al., 2009).

Fig. 2A shows the correlation between the ratios (TPP/TPP + DIA) and Tricyclic Tr21/Tr23. It is observed that the beach samples are grouped with the Venezuelan oil sample because they have lower Tr21/Tr23 tricyclic ratios since the physicochemical conditions of the Venezuelan sea water may have led to the proliferation of Tr23 cyclical precursor organisms. Similar behavior can be seen in Fig. 2B, where there is a correlation between the tricyclic ratios Tr21/Tr23 and hopanes/steranes, since oils originated from marine organic matter have a

greater abundance of steranes which have an origin related predominantly to algal material (Peters et al., 2005).

The analysis of hierarchical grouping (HCA) of samples using the Manhattan method (single linkage) using the $\delta^{13}\text{C}$ ratios and the main ratios of biomarkers indicative of origin, corroborates the results above (Fig. 3). There is some similarity between the samples of marine petroleum from Brazil with grouping those from the samples collected on the beaches and the petroleum from Venezuela. This is due to the common origin of Brazilian and Venezuelan oils from marine organic matter. However, the evolution of Brazilian sedimentary basins in relation to their deposition phases of marine generating rocks was completely different from the Venezuela basins with differentiated physical-chemical conditions of water, which led to the production of specific petroleum source organic matter for each basin (Lee et al., 2020; Li et al., 2016; Lourenço et al., 2020; Magris and Giarrizzo, 2020; Wang et al., 2013). The results of the geochemical analyses allowed to characterize that the oily material collected in the beaches of the Northeast of Brazil has characteristics that correlate it with oil of Venezuelan origin.

This article used techniques of analysis of petroleum geochemistry and multivariate statistics to identify the origin of the oily material collected on the beaches of Northeast Brazil in 2019, showing its potential use in investigations of Forensic Geochemistry. The analytical results showed that the oily material that reached the beaches, has geochemical characteristics compatible with those of the Venezuelan oil sample, indicating that it is crude oil that has been badly weathered due to the time it remained in the sea, or a product manufactured with heavy oil produced in that country.

CRediT authorship contribution statement

Olívia M.C. de Oliveira: Supervision, Writing - original draft, Formal analysis. **Antônio F. de S. Queiroz:** Supervision, Writing - original draft, Formal analysis. **José R. Cerqueira:** Writing - original

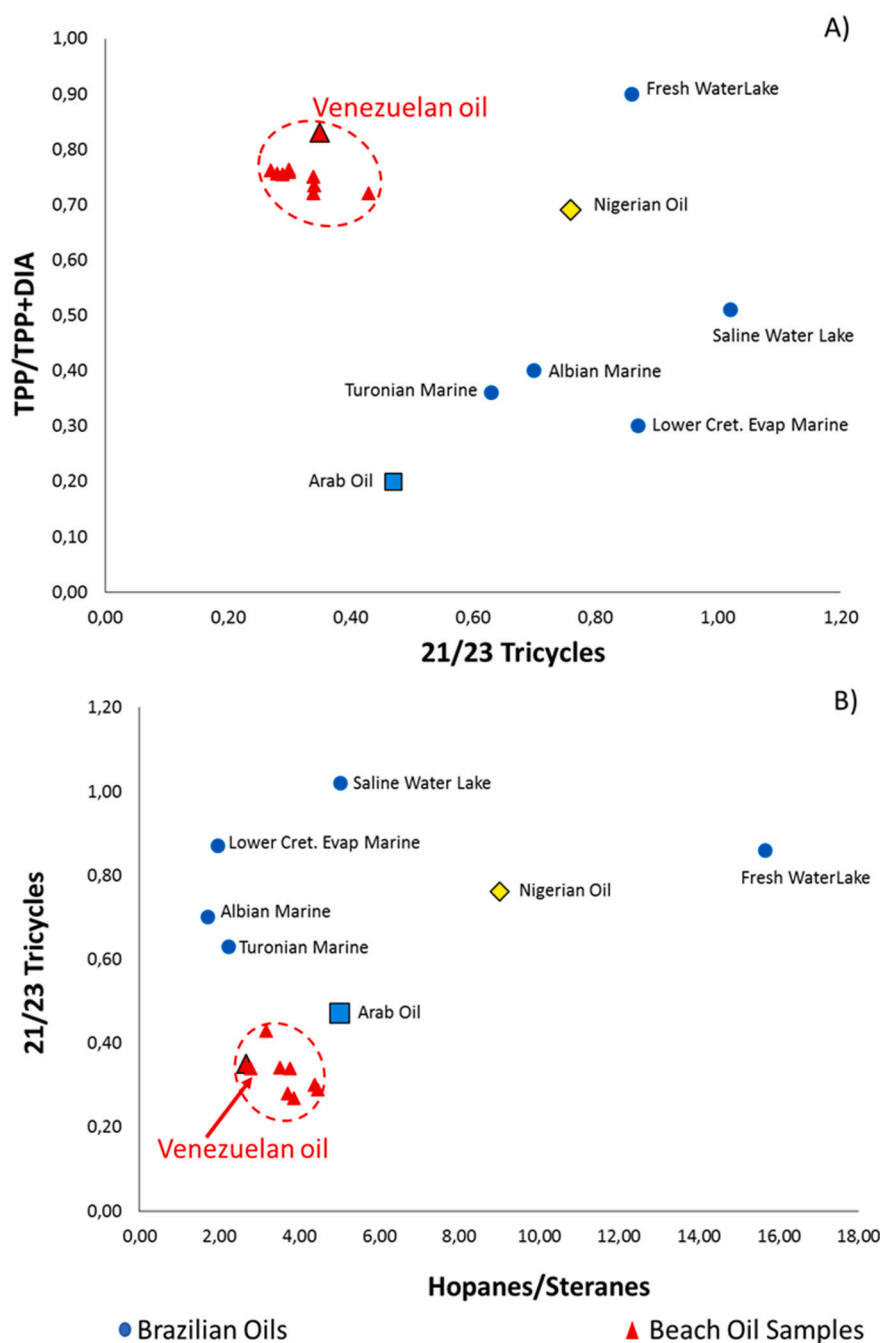


Fig. 2. Correlation between diagnostic reasons. A) TPP/TPP + DIA $\times$ 21/23 Tricyclics and B) 21/23 Tricyclics $\times$ Hopanes/steranes, from samples collected on the beach and from different Brazilian and international oils.

draft, Methodology, Writing - review & editing. **Sarah A.R. Soares:** Writing - original draft, Methodology. **Karina S. Garcia:** Writing - review & editing. **Aristides Pavani Filho:** Writing - review & editing. **Maria de L. da S. Rosa:** Investigation. **Caroline M. Suzart:** Investigation. **Liliane de L. Pinheiro:** Investigation. **Ícaro T.A. Moreira:** Supervision, Data curation, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

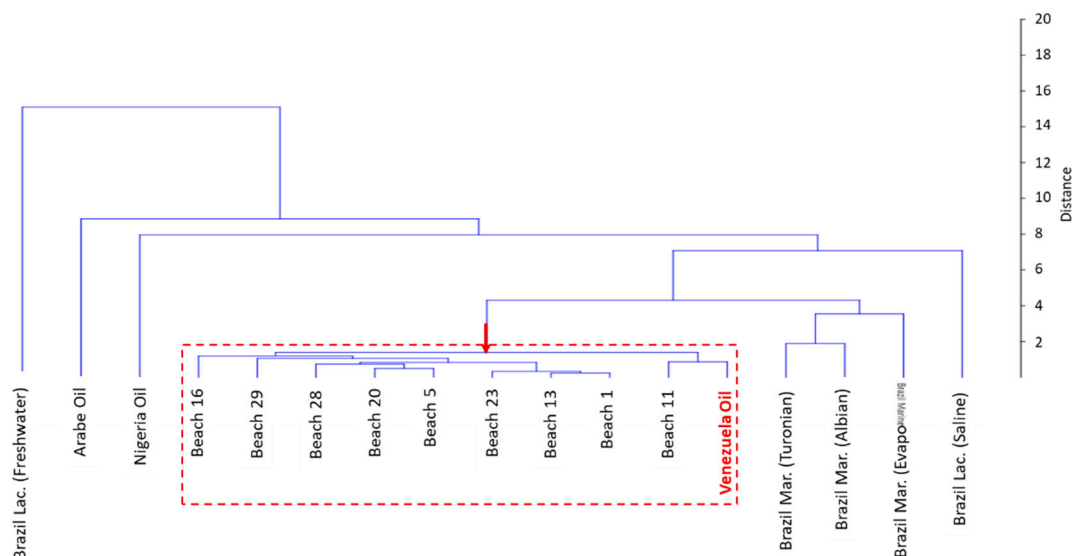


Fig. 3. HCA representation of oil spill and possible sources.

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References

- Al-Majed, A.A., Adebayo, A.R., Hossain, E.M., 2012. A sustainable approach to controlling oil spills. *J. Environ. Manag.* 113, 213–227.
- Andersen, L.E., Melville, F., Jolley, D., 2008. An assessment of an oil spill in Gladstone, Australia – impacts on intertidal areas at one month post-spill. *Mar. Pollut. Bull.* 57, 607–615.
- Anderson, C.J., Hess, T.A., 2012. The effects of oil exposure and weathering on black–needle rush (*Juncus roemerianus*) marshes along the Gulf of Mexico. *Mar. Pollut. Bull.* 64, 2749–2755.
- De Brito, A.P.X., Bruning, I.M.R.D., Moreira, I., 2002. Chlorinated pesticides in mussels from Guanabara Bay, Rio de Janeiro, Brazil. *Mar. Pollut. Bull.* 44 (1), 79–81.
- Ferreira, S.L.C., Lima, D.C., Moreira, I.T.A., Oliveira, O.M.C., 2011. Critical study using experimental design of the determination of lead by high-resolution continuum source hydride generation atomic absorption spectrometry. *J. Anal. At. Spectrom.* 26 (10), 2039–2044.
- Fingas, M., 1996. The evaporation of oil spills: prediction of equations using distillation data. *Spill Science & Technology Bulletin* 3 (4), 191–192.
- Fingas, M., 2011. *Oil Spill Science and Technology. Prevention, Response and Cleanup*. Gulf Professional Publishing, Boston (2011, 1156 pp.).
- Goncalves da Silva, S.F., Bruening, I.M.R.A., Montone, R.C., Taniguchi, S., Cascaes, M.J., Dias, P.S., Lavandier, R.C., Hauser-Davis, R.A., Moreira, I., 2013. Polybrominated diphenyl ethers (PBDES) and polychlorinated biphenyls (PCBS) in mussels and two fish species from the estuary of the Guanabara Bay, Southeastern Brazil. *Bull. Environ. Contam. Toxicol.* 91 (3), 261–266.
- Ho, S.J., Wang, C.Y., Luo, Y.M., 2015. GC–MS analysis of two types of mixed oils, a comparison of composition and weathering patterns. *Mar. Pollut. Bull.* 96 (1–2), 271–278.
- Holba, A.G., Dzou, L.I., Wood, G.D., Ellis, L., Adam, P., Schaeffer, P., Albrecht, P., Greene, T., Hughes, W.B., 2003. Application of tetracyclic polyprenoids as indicators of input from fresh-brackish water environments. *Org. Geochem.* 4 (3), 441–469.
- Instituto Brasileiro do Meio Ambiente e Recursos Naturais Renováveis – IBAMA, 2019. *Manchas de Óleo Litoral do Nordeste*. Access in: 15/11/19. <http://www.ibama.gov.br/manchasdeoleo>.
- International Tanker Owners Pollution Federation – ITOPF, 2019. *Oil tanker spill statistics 2018*. Access in: 20/10/2019. <https://www.itopf.org/knowledge-resources/data-statistics/statistics/>.
- Kanjilal, B., 2015. Enhanced marine oil spill response regime for Southern British Columbia, Canada. *Aquatic Procedia* 3, 74–84.
- Lee, K., Wells, P.G., Gordon, D.C., 2020. Reflecting on an anniversary. The 1970 SS Arrow oil spill in Chedabucto Bay, Nova Scotia, Canada. *Mar. Pollut. Bull.* 157, 111332.
- Li, Pu, Cai, Q., Lin, W., Chen, B., Zhang, B., 2016. Offshore oil spill response practices and emerging challenges. *Mar. Pollut. Bull.* 110 (1), 6–27.
- Lobão, M.M., Cardoso, J.N., Mello, M.R., Brooks, P.W., Lopes, C.C., Lopes, R.S.C., 2010. Identification of source of a marine oil-spill using geochemical and chemometric techniques. *Mar. Pollut. Bull.* 60 (12), 2263–2274.
- Lourenço, R.A., Combi, T., Alexandre, M.R., Sasaki, S.T., Zanardi-Lamardo, E., Yogue, G.T., 2020. Mysterious oil spill along Brazil's northeast and southeast seaboard (2019–2020): trying to find answers and filling data gap. *Mar. Pollut. Bull.* 156, 111219.
- Magris, R.A., Giarrizzo, T., 2020. Mysterious oil spill in the Atlantic Ocean threatens marine biodiversity and local people in Brazil. *Mar. Pollut. Bull.* 153, 110961.
- Mello, M.R., Gaglianone, P.C., Brassel, S.C., Maxwell, J.R., 1988. Geochemical and biological marker assessment of depositional environments using Brazilian offshore oils. *Mar. Pet. Geol.* 5 (3), 205–223.
- Miranda, L.S., Moreira, I.T.A., Oliveira, O.M.C., Santos, C.P., Pinheiro, S.M.M., Oliveira, L.M.L., Martins, A.B.O., Filho, M.S.C., 2016. Oil-suspended particulate material aggregates as a tool in preventing potential ecotoxicological impacts in the Sao Paulo river, Todos os Santos Bay, Bahia, Brazil: influence of salinity and suspended particulate material. *Mar. Pollut. Bull.* 112 (1–2), 91–97.
- Moreira, I.T.A., Oliveira, O.M.C., Triguês, J.A., Queiroz, A.F.S., Barbosa, R.M., Anjos, J.A.S.A., Reyes, C.Y., Silva, C.S., Trindade, M.C.L.F., Rios, M.C., 2013. Evaluation of the effects of metals on biodegradation of total petroleum hydrocarbons. *Microchem. J.* 110, 215–220.
- Moreira, I.T.A., Oliveira, O.M.C., Silva, Carine S., 2015. Chemometrics applied in laboratory study on formation of oil-spm aggregates (OSAs) - a contribution to ecological evaluation. *Microchem. J.* 118, 198–202.
- Peters, K.E., Walters, C.C., Moldowan, J.M., 2005. *The Biomarker Guide, Biomarkers and Isotopes in Petroleum Exploration and Earth History*, 2 ed. v.2 Cambridge University Press (700 pp.).
- Philp, R.P., Allen, J., Kuder, T., 2002. The use of the isotopic composition of individual compounds for correlating spilled oils and refined products in the environment with suspected sources. *Environ. Forensic* 3, 341–384.
- Price, D.G., 1995. Weathering and weathering processes. *Q. J. Eng. Geol. Hydrogeol.* 28, 243–252.
- Prince, R.C., Clark, J.R., 2004. Bioremediation of marine oil spills. In: Vazquez-Duhal, R., Quintero-Ramirez, R. (Eds.), *Studies in Surface Science and Catalysis*, pp. 495–512 chapter 18.
- Rekadwad, B., Khobragade, C.N., 2015. A case study on effects of oil spills and tar-ball pollution on beaches of Goa (India). *Mar. Pollut. Bull.* 100 (1), 567–570.
- Reyes, C.Y., Moreira, I.T.A., Oliveira, D.A.F., Medeiros, N.C., Almeida, M., Wandega, F., Soares, S.A.R., Oliveira, O.M.C.D., 2014. Weathering of petroleum biomarkers: review in tropical marine environment impacts. *Open Access Library Journal* 1 (9), 1–13.
- Rios, M.C., Moreira, I.T.A., Oliveira, O.M.C., Pereira, T.S., de Almeida, M., Trindade, M.C.L.F., Menezes, L., Caldas, A.S., 2017. Capability of Paraguanu estuary (Todos os Santos Bay, Brazil) to form oil-SPM aggregates (OSA) and their ecotoxicological effects on pelagic and benthic organisms. *Mar. Pollut. Bull.* 114 (1), 364–371.
- Silva, C.S., Moreira, I.T.A., de Oliveira, O.M.C., Queiroz, A.F.S., Garcia, K.S., Falcao, B.A., Escobar, N.F.C., Rios, M.C., 2014. Spatial distribution and concentration assessment of total petroleum hydrocarbons in the intertidal zone surface sediment of Todos os Santos Bay, Brazil. *Environ. Monit. Assess.* 186 (2), 1271–1280.
- Stout, S.A., Wang, Z., 2007. Chemical fingerprinting of spilled or discharged petroleum—methods and factors affecting petroleum fingerprints in the environment. *Oil Spill Environmental Forensics* 1, 1–53.
- Talley, L.D., Pickard, G.L., Emery, W.J., Swift, J.H., 2011. *Descriptive Physical Oceanography*, Sixth edition. Academic Press (2011).
- Turner, R.E., Overton, E.B., Meyer, B.M., Miles, M.S., Hooper-Bui, L., 2014. Changes in the concentration and relative abundance of alkanes and PAHs from the Deepwater

- Horizon oiling of coastal marshes. *Mar. Pollut. Bull.* 86 (1–2), 291–297.
- Wang, Z., Fingas, M., 1995. Differentiation of the source of spilled oil and monitoring of the oil weathering process using gas chromatography–mass spectrometry. *J. Chromatogr.* 712 (2), 321–343.
- Wang, Z., Yang, C., Kelly–Hooper, F., Hollebone, B.P., Peng, X., Brown, C.E., Landriault, M., Sun, J., Yang, Z., 2009. Forensic differentiation of biogenic organic compounds from petroleum hydrocarbons in biogenic and petrogenic compounds cross-contaminated soils and sediments. *J. Chromatogr.* 1216, 1174–1191.
- Wang, C., Chen, B., Zhang, B., He, S., Zhao, M., 2013. Fingerprint and weathering characteristics of crude oils after Dalian oil spill, China. *Mar. Pollut. Bull.* 71 (1–2), 64–68.
- Yang, Z., Hollebone, B.P., Wang, Z., Yang, C., Landriault, M., 2013. Effect of storage period on the dominant weathering processes of biodiesel and its blends with diesel in ambient conditions. *Fuel* 104, 342–350.