The mysterious oil spill in the northeastern coast of Brazil: tracking offshore seawater and the need for improved vessel facilities

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Abstract

A scientific cruise between November 15 and December 18, 2019 aboard R/V Vital de Oliveira collected offshore seawater samples at 59 stations between the states of Ceará and Bahia. The objective was to identify hydrocarbon levels potentially associated with the mysterious oil spill that reached the northeastern coast of Brazil. Median concentrations of aliphatic hydrocarbons (AHs, 0.79 µg L⁻¹) and polycyclic aromatic hydrocarbons (PAHs, 5.39 ng L⁻¹) do not indicate contamination by crude oil and are comparable to baseline levels previously found in other areas of the Brazilian continental margin. The detailed composition of both groups of hydrocarbons revealed that some samples were contaminated during sampling and/or handling on-board. The data set presented herein highlights the difficulty in tracking small oil patches spread over a huge ocean area and, more importantly, the need for improving protocols of national research vessels used to collect seawater samples for trace organic analyses.

Descriptors: Oceanic waters, Oil spill, North-eastern Brazil, Polycyclic aromatic hydrocarbons, Baseline.

INTRODUCTION

Since August 2019, over 3,000 km of the northeastern and part of the southeastern coastlines of Brazil have been recurrently and randomly contaminated by crude oil. This has been referred to as the ‘mysterious oil spill’ (Escobar, 2019). The name was conceived because oil residues with the same chemical composition were found in several places over the region (Lourenço et al., 2020), and are compatible with the heavy crude oil from a Venezuelan reservoir (de Oliveira et al., 2020). However, the party responsible for the spill (tanker accident, illegal dumping, old shipwreck leaking, etc.) is yet to be identified (Soares et al., 2020a). The accident was the largest oil spill in extension and duration in Brazil and even in the tropical South Atlantic (Soares et al., 2020b), representing a real threat to vulnerable coastal communities, public health, economic activities, coastal ecosystems, and marine biodiversity in northeastern Brazil (Magris and Giarrizzo, 2020). In addition to the actions taken by civil society to
clean up impacted areas immediately upon the first oil appearance – the coordination of which was conducted by Brazil’s federal government after a significant period of inaction (Brum et al., 2020; Soares et al., 2020b) –, the severity and magnitude of the impact began to be revealed in the aftermath of the disaster (e.g., Nasri Sissini et al., 2020; Câmara et al., 2021; Magalhães et al., 2021). Research efforts have been made and will continue in the long term, notwithstanding limitations caused by the Covid-19 pandemic (Magalhães et al., 2021).

One of the major challenges faced during the spill was the identification of its onset and dispersal before reaching the coastline. This occurred in part because the oil was transported in subsurface waters due to its high density and was thus not visible until near the coast (Lourenço et al., 2020). In addition, the oil was transported over thousands of kilometers across the continental margin, induced by the northern (North Brazil Undercurrent) and southern (Brazil Current) pathways after the bifurcation of the southern branch of the Southern Equatorial Current (Schott et al. 2005, Rodrigues et al. 2007, Silva et al. 2009), and then to the shoreline by coastal drift, waves, and tidal currents (Soares et al., 2020a).

To track oil slicks or patches spreading on a large-scale at the surface of open ocean waters from northeastern (NE) Brazil, the Group of Evaluation and Monitoring (Grupo de Acompanhamento e Avaliação - GAA), coordinated by the Brazilian Navy with members from academia and governmental agencies, designed a research cruise aboard R/V Vital de Oliveira to collect samples for investigation of several oceanographic parameters, including chemical analysis. The cruise was a collaborative effort between universities (UFPE, PUC-Rio), National Institute for Space Research (INPE), and the Brazilian navy. Herein we report data of dispersed and dissolved hydrocarbons (aliphatic and polycyclic aromatic compounds) determined in 59 sub-surface samples collected in neritic and oceanic waters between the states of Ceará (3° S) and Bahia (14° S) between November 14 and December 11, 2019 (Figure 1). The primary goal was to identify hydrocarbon contamination levels potentially caused by the spill. Issues on sampling and extraction of samples on-board were also addressed. Finally, recommendations are made to improve Brazilian capacity for responding to similar events in the future.

**METHODS**

**SAMPLING AND ON-BOARD SAMPLE PROCESSING**

Water samples were collected between November 15 and December 18, 2019 at 8 m below the sea surface, given numerical modeling suggesting that spilled oil had been transported at 5-15 m below the sea surface (Brazilian navy, unpublished data). A total of 59 stations were carried out following three sampling arrays, as shown in Figure 1. At each station, four liters of seawater were collected using an amber glass bottle, pre-cleaned with dichloromethane, submerged closed and opened below the surface using a cable attached to the bottle cap.

Upon recovery of the bottle and transport to the ship’s laboratory, samples were not filtered to analyze total hydrocarbons (dissolved + dispersed) in seawater. Internal standards (80 μg of hexadecene and 70 μg of eicosene for aliphatic hydrocarbons, and 100 ng of deuterated naphthalene, acenaphthene, phenanthrene, and chrysene for aromatic hydrocarbons) were added to the bottle prior to liquid-liquid extraction with 20 mL of n-hexane (pesticide grade). After one minute of agitation, the organic extract was separated from seawater using a customized glassware apparatus (Figure 1S). The organic extracts were then stored in an on-board freezer (–20 °C) and transported to a land-based laboratory at low temperature (<4 °C). A field blank was carried out on-board for assessing contamination from the ship’s laboratory.

**DETERMINATION OF ALIPHATIC AND AROMATIC HYDROCARBONS**

In the laboratory, the bulk extract was concentrated under vacuum to 0.5 mL and then by a gentle stream of purified N₂. As the extracts were collected from open ocean waters, no further purification or separation between the aliphatic and aromatic fractions were considered. Deuterated tetracosane and p-terphenyl were added to the final extracts for calculating recovery of aliphatic and aromatic internal standards, respectively. The aliphatic hydrocarbons were analyzed by gas chromatography with flame ionization detection equipment (Focus Thermo GC-FID), fitted with a DB-5 (30 m × 0.25 mm × 0.25 μm) capillary column, injector set at 290 °C and detector at 310 °C. The temperature program started at 45 °C for 0.5 min,
The analysis of polycyclic aromatic hydrocarbons (PAHs) followed the EPA-8270D method. A gas chromatography coupled to a mass spectrometer (Thermo Trace-DSQ GC-MS system), equipped with a capillary column (J&W DB5-ms, 30 m x 0.25 mm x 0.25 μm), was used. The oven temperature program was: begin at 50 °C with hold for 5 min, 50 °C min⁻¹ up to 80 °C, 6 °C min⁻¹ up to 280 °C with hold for 20 min, and 12 °C min⁻¹ up to 305 °C with a final hold of 10 min. Data acquisition was performed in the selected ion monitoring (SIM) mode, considering typical ions (m/z) for PAH analysis (Mauad et al., 2015). Quantification of PAHs was based on a nine-point (0.05, 0.50, 1.0, 2.0, 5.0, 10, 20 and 50 μg mL⁻¹) calibration curve, accepted with a correlation coefficient (R²) better than 0.99, made up of n-alkanes from C₁₀ to C₄₀, pristane, and phytane. The presence of an unresolved complex mixture (UCM) (Gough and Rowland, 1990) was also monitored. The limits of detection and quantification for aliphatic compounds were 0.0005 and 0.01 μg L⁻¹, respectively (details below). All results of aliphatics were reported considering a 100% recovery, based on the mass of the internal standards added prior to extraction. The recoveries of hexadecene and eicosane were calculated using an external calibration curve, considered satisfactory within the range of 60-120%. In addition, selected samples were also run in a GC-MS system for confirmatory analysis (see Results and Discussion).
details below). The PAH concentrations are reported considering a 100% recovery of the internal standard, added before extraction. The recovery of the deuterated standard was calculated based on an external calibration curve, considered acceptable between the range of 40-100%. A total of 37 PAHs were identified and quantified. Their names and acronyms can be found in detail in the Supplementary Material.

Quality assurance and control of the hydrocarbon analyses involved the following: evaluation of field and laboratory blanks; precision (± 20% or better for AH and PAHs), and accuracy (recovery between 60-120% of the expected concentration) were estimated based on replicate analyses (n=5) of spiked seawater; the recovery of the standards added before extraction should be between 60-120% for AH and between 40-100% for PAHs; and daily calibration checks of the chromatographic system by the injection of one standard included in the AH and PAHs calibration curves. In addition, the limit of detection was calculated using the formula LD = t_{n-1, 1-α} × S, where t correspond to the Student distribution factor at n-1 degree of freedom and α of 0.05 (95% confident level) and S is the standard-deviation of replicate analyses (n=5) of AH and PAHs spiked blanks (INMETRO, 2016). The limit of quantification was considered as the first point of the calibration curve for both AH and PAHs, divided by the median volume of water extracted.

RESULTS AND DISCUSSION

LEVELS AND DISTRIBUTION OF HYDROCARBONS IN SEA WATER

Table 1 shows a summary of concentrations (mean, median, standard deviation, and range) of total aliphatics hydrocarbons (AHs - n-alkanes, pristane, phytane, UCM, and resolved peaks) and polycyclic aromatic hydrocarbons (PAHs - 37 compounds from 2-6 fused rings, including parental and alkylated homologues). Detailed information about the distribution of AHs and PAHs can be found in the Supplementary Material. Major features in the Table 1 data are the difference between average and median concentrations of both AHs (2.96 vs. 0.79 µg L⁻¹, respectively) and PAHs (104 vs. 5.39 ng L⁻¹, respectively), and the range of concentrations for both parameters (AHs: < 0.005 – 22.5 µg L⁻¹; PAHs: < 0.07 – 2,983 ng L⁻¹). This is due to several samples that exhibited high concentrations of either AHs or PAHs, revealing skewness and lack of normality (Anderson-Darling, n = 59, A > 8.6, p < 0.0001) in the distribution of hydrocarbons in seawater. However, only two samples (#23 and #42 – data in the Supplementary Material) exhibited high concentrations of both AHs and PAHs. Such elevated concentrations of hydrocarbons would be expected for evidencing crude oil in the water.

The usual approach to evaluate contaminant data sets such as that displayed in Table 1 would be comparison of concentrations among regions with similar properties and anthropogenic influence. However, there are limitations to this approach in the case of hydrocarbons. One reason is the distinct number of compounds considered by each analytical protocol, particularly in the case of PAHs, which hinder the comparison of “total concentrations.” In addition, results of hydrocarbons obtained by distinct analytical techniques such as gravimetry, infrared spectrophotometry, and chromatography (e.g., Ahad et al., 2020), among others, may produce data sets that are not directly comparable because different instruments quantify different hydrocarbons. Moreover, analysis of samples can be performed in filtered (dissolved and particulate concentrations determined separately) or unfiltered (dissolved and particulate together) waters, also limiting comparison of concentrations obtained from different sample pre-treatments (Nizzetto et al., 2008; Lohmann et al., 2009; Berrojalbiz et al., 2011; González-Gaya et al., 2019).

Because of these many factors limiting the comparison of AH and PAH data sets, a table listing typical concentrations in various study areas will not be considered herein. Instead, only a selection of previous studies in the Brazilian
continental margin – not related to oil spills but also considering hydrocarbon analyses in non-filtered seawater samples and GC-MS or GC-FID methods – and others conducted after major oil spills in oceanic waters will be mentioned. Regarding PAHs, major contaminants of environmental concern among hydrocarbons (Schwarzenbach et al., 2006), the similarity between data obtained here and baseline studies carried out in sectors of the Brazilian continental margin is noteworthy. For example, total PAHs (37 compounds, dissolved plus dispersed) in the Campos basin exhibited median concentrations varying between 2-4 ng L\(^{-1}\) (Wagener et al., 2017), whereas median total PAHs in the Potiguar basin ranged between 6-24 ng L\(^{-1}\) (Wagener et al., 2006). These values are similar to the median of total PAHs found here (5.39 ng L\(^{-1}\)). A reference to waters affected by a large oil spill is the release of oil between April and July 2010 after the explosion of Deepwater Horizon in the Gulf of Mexico. Boehm et al. (2016) reported data of 50 PAHs from over 5,000 water samples collected at several depths in the water column and farther than 37 km from the rig. Median concentrations of total PAHs from the surface down to 10 m was 69 ng L\(^{-1}\), a value limited to the distance of less than 2 km from the rig. This is an order of magnitude higher than the median concentration found in our study carried out in open waters off northeastern Brazil. At distances between 2-10 km from Deepwater Horizon, Boehm et al. (2016) reported 32 ng L\(^{-1}\) for median total PAHs. These authors also reported concentrations above 1000 ng L\(^{-1}\) in 20% of samples collected during the spill (at a distance of up 20 km from the rig). In our study, only 3% of samples were above this level for total PAHs.

For AHs, data available for comparison is more limited because these compounds draw less attention, as they are less toxic than PAHs. In the Campos basin, for instance, total AHs are below 15.6 µg L\(^{-1}\) in over 80% of samples (Wagener et al., 2017). In comparison, we found 95% of samples had concentrations below this benchmark in this study. In the Ceará basin, total AHs ranged between 1.45–2.38 µg L\(^{-1}\) (Wagener et al., 2006). These values are similar to the mean (2.76 µg L\(^{-1}\)) and median (0.79 µg L\(^{-1}\)) reported herein, although the comparison is not straightforward.

At a first glance, the differences of at least one or two orders of magnitude in the measurements of central tendency and dispersion of AHs and PAHs obtained here, as well as the comparison with other data in the literature, could be interpreted as resulting from the presence of oil residues in stations with high concentrations of both AHs and PAHs. In fact, chemical analyses of oil samples stranded across the northeastern shoreline of Brazil showed the presence of AHs and PAHs (Lourenço et al., 2020). However, this is a simple approach and must not be presumed to be proof of the presence of oil slicks/patches at sea. In general, spatial distribution of higher levels of aliphatic and aromatic hydrocarbons in seawater is not coincident in the same stations. AHs exhibited higher concentrations in one station in the northern sector (#11; 20.7 µg L\(^{-1}\)), in a group of four stations off the states of Pernambuco and Alagoas (#22, #23, #24 and #26; 12.0 – 17.8 µg L\(^{-1}\)), and in one station in the southern sector (#42; 22.5 µg L\(^{-1}\)) (see Figures 1 and 2). In contrast, PAHs revealed high concentrations in one station off Pernambuco (#23, 675 ng L\(^{-1}\)) and two stations in the southern sector (#42 and #46; 1,117 - 2,983 ng L\(^{-1}\)) (see Figures 1 and 3). Additionally, AH profiles detected in seawater (Figure 4b) are not typical of either fresh or weathered oil. Nor are they similar to profiles reported from oil stranded across the shoreline (Lourenço et al., 2020). This is strikingly notable in the case of the two stations (#23 and #42), where higher concentrations of both AHs and PAHs were detected in seawater. Therefore, these findings do not corroborate the presence of oil residues derived from the mysterious oil spill in the samples analyzed, suggesting alternative sources. Considerations on the detailed composition of AHs and PAHs will give more insights into this subject, as discussed below.

**Source assignment of AHs and PAHs**

The detailed composition of AHs and PAHs has provided in-depth insight into sources of hydrocarbons to aquatic systems, be they natural, petrogenic, or pyrolytic (Colombo et al., 1989; Aboul-Kassim and Simoneit, 1996; Readman et al., 2002; Yunker et al., 2002b; Jiang et al., 2009; among others). Nevertheless, in many cases, source assignment and apportionment is challenging due to factors such as the presence of complex mixtures of compounds in the sample, compositional changes due to weathering, and the misuse of established techniques (Boehm et al., 2018).
Figure 2. Concentration of aliphatic hydrocarbons (color palette, in μg L⁻¹) in surface water across the northeastern coast of Brazil. Black dots denote sampling stations. Legend for identifying Brazilian states: CE = Ceará; RN = Rio Grande do Norte; PB = Paraíba; PE = Pernambuco; AL = Alagoas; SE = Sergipe; BA = Bahia.

Figure 3. Concentration of polycyclic aromatic hydrocarbons (color palette, in ng L⁻¹) in surface water across the northeastern coast of Brazil. Black dots denote sampling stations. Legend for identifying Brazilian states: CE = Ceará; RN = Rio Grande do Norte; PB = Paraíba; PE = Pernambuco; AL = Alagoas; SE = Sergipe; BA = Bahia.
In this study, aliphatic hydrocarbons occurred in the range of 1-10 µg L⁻¹ in circa 40% of samples, whereas the concentration ranges < 0.01 µg L⁻¹, 0.01-0.1 µg L⁻¹, and 0.1-1.0 µg L⁻¹ were observed in circa 10-20% of samples, and only a few samples had aliphatic hydrocarbons in the range 10-20 µg L⁻¹ or higher (Figure 4a). In all concentration ranges, the alkanes n-C₂₉, n-C₃₂, n-C₃₉, n-C₂₅, n-C₃₆, and n-C₁₉ (in order of decreasing average concentration) were prevalent with minor contribution of other alkanes and isoprenoids (Figure 4b). When derived from recent biosynthesis, alkanes are marked by saturated and linear chains with odd-over-even carbon predominance, where long (> C₂₅), intermediate (C₂₁ to C₂₅), and short-chains (< C₁₉) are indicative of terrestrial higher plants, submerged macrophytes, and plankton, respectively (Eglinton and Hamilton, 1967; Cranwell, 1982; Ficken et al., 2000). On the other hand, n-alkanes in petroleum range from C₂₀

Figure 4. Distribution of aliphatic hydrocarbons (AHs) in surface water across the northeastern coast of Brazil: (a) frequency of occurrence (%) of total AHs based on concentration ranges (< 0.01 µg L⁻¹ is the limit of quantification); and (b) concentration histograms of n-alkanes and isoprenoids according to each concentration range (gray column on the right). The highest values are caused by contamination during sampling/handling; see text for details.
to C_{40}, with no odd-to-even predominance (Aboul-Kassim and Simoneitt, 1995; Peters et al., 2005). Based on these characteristics, several proxies are proposed to infer the relative input of either biogenic or petrogenic n-alkanes to aquatic systems, including the carbon preference index (Bray and Evans, 1961) and the terrestrial-to-aquatic ratio (Meyers, 1997). None of these ratios could be successfully calculated because the n-alkane distributions displayed in Figure 4b are not consistent with biogenic and/or petrogenic sources, a feature which may be ascribed to the low alkane concentrations in most of the water samples.

In order to further investigate the apparently unusual distribution of n-alkanes shown in Figure 4b, selected samples with higher concentrations of total n-alkanes were injected in the GC/MS system (see Material and Methods section) to confirm the identity of compounds. In 28 of 59 samples analyzed, randomly pertaining to low and high concentration ranges (see Figure 4a), the mass spectra showed a prevalence of m/z 281, 355, and 429 (Figure 5a), whereas an n-alkane standard exhibits m/z 57, 71, 85, and 99 as the most abundant ions (Figure 5b). The former ions are typical of a siloxane-based product, according to the instrument’s NIST library of mass spectra. Moreover, the field blank also showed the same siloxane-derived mass spectra, while the same pattern did not appear in the laboratory blank (data not shown). Based on this evidence, it is possible to infer that the aliphatic fraction of seawater

![Figure 5](image_url)
extracts was contaminated with a siloxane-based product used in the research vessel, although the exact source of contamination could not be identified. Consequently, AH concentrations reported here must be considered with caution, as they are biased by contamination during sampling and/or handling on-board.

The rationale for assignment of PAHs to petrogenic or pyrolytic sources is based on their thermal stability. At low temperatures such as those observed during petroleum formation (< 100-150 °C), PAHs with 2-3 rings are prevalent and alkylated compounds are more abundant than their parental homologues. At higher temperatures (> 1000 °C) such as those found in combustion processes (engines, burning of organic materials, etc.), 4-6 ring PAHs are prevalent, with less abundance of alkylated homologues (see Wang et al., 1999; Yunker et al., 2002a; Tobiszewski and Namieśnik, 2012 for a complete overview on the use of diagnostic ratios). In this study, the PAH distribution is marked by high frequency of occurrence (~40%) within the 0.05-10 ng L⁻¹ concentration range, followed by still significant frequencies (10-20%) in the ranges 10-100 and 100-1,000 ng L⁻¹ (Figure 6a). In all concentration ranges, naphthalene and its alkylated homologues are predominant. In the range 10-100 ng L⁻¹, the alkylated homologues of anthracene and phenanthrene are also observed, although the parental homologues are lacking, while the presence of fluoranthene and pyrene is detected in the 0.05-10 ng L⁻¹ range (Figure 6b). In oceanic waters around the globe, more than 50% of PAHs are comprised of naphthalene, acenaphthylene, acenaphthene, fluorene, and its alkylated homologues, i.e., 2- and 3-ring PAHs (González-Gaya et al., 2019). Although a similar distribution is also recorded herein (Figure 7), the occurrence of individual PAHs is too biased to naphthalene and its alkylated homologues. Moreover, neither the well-known ‘bell-shaped’ profile (higher C2 homologue in comparison to C0, C1, C3 and C4 homologues) of petrogenic PAHs nor the typical decreasing profile (C0 > C1 > C2 > C3 > C4) of pyrogenic PAHs (Boehm et al., 2018) was observed. Thus, source assignment to one of these two origins is not straightforward in the collected samples. Moreover, the field blank also has the same PAH profile of most samples (Figure 7). The evidence provided by the PAHs distribution suggest contamination during sampling and/or handling on-board, as already discussed above for AHs. Potential sources of contamination are different in each case, since the PAH extracts seem to be contaminated by naphthalene and its homologues, which are ubiquitous volatile compounds and common contaminants in petroleum hydrocarbon studies (Boehm et al., 2007).

CONCLUSION

Overall, the median concentrations of hydrocarbons detected in offshore seawater of the northeastern coast of Brazil during the mysterious oil spill event are comparable to baseline levels observed in previous studies across the Brazilian margin, particularly in the case of PAHs. No remarkable crude oil fingerprint was identified in seawater samples, demonstrating the high level of difficulty in finding signals of small oil patches spread over a huge ocean area. Compelling evidence of contamination during sampling and/or sample extraction on-board, particularly in the aliphatic hydrocarbons fraction, must be an alert for improving both analytical protocols and vessel facilities, including the R/V Vital de Oliveira and other Brazilian research vessels. Considering activities of the oil industry across the Brazilian margin, there is an urgent need for vessel facilities capable of sampling seawater for trace organic analysis without compromising the quality of analytical results.

We recommend that Teflon-lined sampling bottles with an automatic open/close device (e.g., Go-Flo) be attached to a hydrocable free of oil/silicone-based coatings. The vessel laboratory must also be equipped with a fume hood for exhausting organic volatiles from its indoor atmosphere, ensuring a clean environment for sample extraction. Analytical protocols must be more rigorous for avoiding contamination during sampling and handling on-board, since a ship has several sources of smoke and organic vapors. With this, the Brazilian oceanographic community would be able to advance towards providing consistent responses in future oil spills in Brazilian waters, leading cruises for accomplishing goals of international oceanographic programs.

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Figure 6. Distribution of polycyclic aromatic hydrocarbons (PAHs) in surface water across the northeastern coast of Brazil: (a) frequency of occurrence (%) of total PAHs based on concentration ranges (< 0.05 ng L⁻¹ is the limit of quantification); and (b) concentration histograms according to each concentration range (gray column on the right). The highest values are caused by contamination during sampling/handling; see text for details.

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AUTHOR CONTRIBUTIONS

R.S.C.: investigation; data curation; writing - original draft; writing - review and editing;
E.Z.-L.: conceptualization; investigation; writing - review & editing;
C.G.M.: investigation, data curation; writing - review and editing;
M.A.: conceptualization, supervision; writing - review and editing;
Figure 7. Distribution of PAHs according to the number of fused rings both in percentage (upper panel) and concentrations (lower panel).

P.N.: conceptualization; supervision; writing - review and editing;
G.T.Y.: conceptualization, investigation, writing - original draft; writing - review and editing.

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