



Oil impact on the environment and aquatic organisms on the coasts of the states of Alagoas and Sergipe, Brazil - A preliminary evaluation

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ABSTRACT

The oil spill off the coast of the Brazilian Northeast region is one of the most significant global events regarding contamination and environmental impact in recent years. This work evaluates the effects of oil spills on the Northeast coasts between Alagoas and Sergipe states from October 2019 to January 2020. Analysis of some sampling points of seawater revealed the presence of Hg, Cd, Pb, and Cu in levels above the maximum concentration limits established by the Brazilian legislation. For water quality parameters, phosphorus, nitrite, and turbidity showed statistically different values. However, the chromatographic profiles of oil obtained from different beaches were quite similar. Seawater, fishes, and *massunins* (bivalve) presented the main polycyclic aromatic hydrocarbons: naphthalene, phenanthrene, fluoranthene, fluorene, and acenaphthalene. Therefore, the concentration of organic and inorganic contaminants determined in different environmental locations served as a subsidy to assess the effect of the preliminary oil spill on the Brazilian coast.

1. Introduction

In the year 2019, the most significant environmental disaster in Brazilian coastal waters was recorded worldwide. However, the mysterious oil spills on Brazilian beaches still produce their effects on a smaller scale, such as seafood contamination causing damage to the region's economy (Leduc et al., 2020). The spill may have occurred in the area covered by the south-equatorial current, which is located between 500 and 700 km off the northeast coast of Brazil. Initially, several hypotheses were conceived to explain the origin of the contamination, such as Venezuelan or other oil spills or leaks from ships that sank during

World War II (Soares et al., 2020a, 2020b).

The disaster management is more challenging than for a typical oil spill because the dense crude oil is not observed on the ocean surface; it only appears when it washes up on coastal zones such as sandy beaches and intertidal reefs. Furthermore, since this oil is more dense and rigid, its perception by satellite images is impracticable, and containment systems were not very efficient, decreasing its predictability and causing high environmental impacts (Brazil, 2020).

From August 2019 to January 2020, more than 5000 tons of oil were removed from the beaches' sand, swamps, and coral reefs, from the State of Maranhão (upper north coast of Brazil) to the shores of southeastern

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states, affecting about 1000 locations (Soares et al., 2020a, 2020b; Brazil, 2020). However, the Brazilian Northeast was the most affected area, with oil slicks affecting all the states in the region, including the states of Alagoas and Sergipe. The oil may have reached the northeast coast via the Guyana current, and the Brazilian current spread the oil.

Alagoas and Sergipe states have a coastline of 228 and 163 km, respectively. Alagoas stands out with the Mundaú-Manguaba lagoon complex, which is considered one of the essential lagoon systems in the country, producing an estimated 6773 tons of the bivalve sururu (*Mytella charruana*) (Coutinho et al., 2014), which is very much used in the traditional culinary. Besides, the Coral Coast, located in the North seaside of Alagoas, is a federally protected area covering 135 km of coastline, with 413,563 ha of terrestrial and marine regions (Steiner et al., 2015). In turn, the State of Sergipe hosts an extensive mangrove area, with more than 25,000 ha (Almeida and Barbieri, 2008), and the largest nursery of olive turtle (*Lepidochelys olivacea*) in Brazil, located in the area of the Biological Reserve of Santa Isabel (Oliveira et al., 2014). Thus, these are the areas of high environmental importance. Due to the wealth of aquatic ecosystems, alterations caused by the oil spill can last for years, with immeasurable effects on the coral reefs and in abundant swamp areas in the region, which could damage coastal biodiversity, job generation, and income related to tourism and fishing (de Paula et al., 2018).

Marine-protected areas and tropical ecosystems are currently affected by chemical pollution. These areas are necessary for nutrient cycling, animal reproduction and nurseries, recreation, and cultural endeavors (Costanza et al., 2014). According to Lourenço et al. (2020), some oil quantities may still be trapped in coastal and shallow marine sediments. Thus, energetic meteorological events can suspend oil back into the water column, carrying it towards the coast.

This work evaluates the effects of crude oil on the Brazilian coast, mainly on the Northeast region, to trace a profile of the environmental impact caused due to the contaminants present in this ecosystem. Among the coordinated activities highlighted in this work are the collection of water, crude oil, sand, and specimens, bioprospecting through diving in coral environments, and socioeconomic data collection. The spectrometry analytical techniques were performed such as graphite furnace atomic absorption spectrometry (GF AAS), cold vapor atomic fluorescence spectroscopy (CV AFS), hydride generation atomic fluorescence spectrometry (HG AFS), and gas chromatography coupled with mass spectrometry (GC-MS), among others techniques to assess physicochemical parameters, the presence of potentially toxic elements, fatty oil contents, and the presence of hydrocarbons in animal species to determine the effects on organisms and the environment. The results allowed us to understand how the oil spill, in an uncontrolled way, can impact society and nature.

2. Experimental

2.1. Reagents and solutions

All chemicals used were of analytical grade (Merck or Sigma-Aldrich) and prepared with ultrapure water with a specific resistivity of 18.2 M Ω \times cm, from a Master System MS2000 purification system (Gehaka, Brazil).

The elements Hg, As, Cd, Pb, Cr, Cu, Zn, and Ni standard solutions were prepared by serial dilutions of a 1000 mg L⁻¹ stock solution. Diluted nitric and hydrochloric acids were used to prepare the standard solutions. In addition, a solution of Pd(NO₃)₂ at 5.0 μ g L⁻¹ was used as a chemical modifier after dilution from the stock solution (5 mg L⁻¹). The reagents and solutions used in determinations by CV AFS and HG AFS are described in Table S1 (Supplementary material).

2.2. Instrumentation

Microwave-assisted digestion of samples was performed using a

microwave (Ethos One, Milestone, Italy). The measurements were carried out using a Shimadzu AA 6800 atomic absorption spectrometer equipped with an ASC-6100 autosampler. Pyrolytic graphite-coated graphite tubes with transversal heating were used for all experiments. Integrated absorbance values were used exclusively for signal evaluation and a deuterium lamp for background correction. The analytical lines (nm) used were: 228.8 (Cd), 283.3 (Pb), 357.9 (Cr), 324.8 (Cu), 213.9 (Zn), and 232.0 (Ni), all with a spectral bandpass of 0.7 nm. Ultrapure argon (99.999%) (White Martins, www.praxair.com.br) was used as the carrier gas. The autosampler was configured to introduce 20 μ L of the sample and 5.0 μ L of the chemical modifier into the graphite furnace for measurements. A cold vapor and hydride generation atomic fluorescence spectrophotometers (Millennium Merlin and Excalibur, PSA Analytical, U.K.) were used to measure total mercury and arsenic contents with high-intensity hollow cathode lamps (Hg: 253.7 nm, and As: 194.7 nm) and a drying system. Hg⁰ vapor was generated through chemical reduction of inorganic mercury with SnCl₂·2H₂O and transported into a gas-liquid separator by an argon flow (0.25 L min⁻¹). Arsine (AsH₃) was generated from the chemical reduction of As(III) with NaBH₄ in an acidic medium (HCl) and transported to the gas-liquid separator by an argon flow (0.25 L min⁻¹). Carrier gas humidity was removed by a Perma Purer® device, reducing interference by quenching with a dryer gas. Ultrapure synthetic air (Linde gas, Brazil) was employed as a dryer purge gas (2.5 L min⁻¹).

2.3. Seawater samples from Alagoas

All seawater samples were obtained from ten different locations in Alagoas, always at high tide during the periods from October 2019 to January 2020: four beaches on the north coast, Maragogi (P01, 9.045278 S, 35.236528 W), Japaratinga (P02, 9.088806 S, 35.256389 W) São Miguel dos Milagres (P03, 9.266917 S, 35.35151 W), and Ipioca (P04, 9.498472 S, 35.573639 W); one beach in Maceió, capital of the State of Alagoas (P05, Sete Coqueiros beach, 9.663900 S, 35.703200 W, urban beach in the central area of Alagoas state coast, which had minimum contact with oil, and hence can be considered a negative reference point); and five beaches on the south coast, Francês – in the Marechal Deodoro municipality, (P06, 9.770861 S, 35.839991 W), Barra de São Miguel (P07, 9.838886 S, 35.88868 W), the estuary of Coruripe river/Barreiras beach, Coruripe municipality (P08, 10.161553 S, 36.15859 W), Toco beach, Feliz Deserto municipality (P09 10.299444 S, 36.290806 W), and Pontal do Peba beach, Piaçabuçu municipality (P10, 10.339139 S, 10.339139 W) (Fig. 1).

2.4. Seawater samples from Sergipe

Samples were also collected from nine different locations in Sergipe: Saco beach (P20, 11.2545361 S, 37.2028364 W), Men de Sá island (P19, 11.728502 S, 37.923450 W), Viral beach (P18, 11.615609 S, 37.134597 W), Artist's beach (P17, 10.5710853 S, 37.31628 W), Sementeira Park (P16, 10.5631647 S, 37.31397 W), Japaratinga River (P15, 10.3722429 S, 36.3947707 W), Ponta of Mangues (P14, 10.3452420 S, 36.3628141 W), Santa Isabel Reserve (P13, 10.4432801 S, 36.5148535 W), São Francisco River (P12, 10.2511546 S, 36.3344526 W), and the mouth of the São Francisco River (P11, 10.2922023 S, 36.2451894 W) (Fig. 1).

2.5. Sampling procedures

The collection included forty seawater samples with three replicates each, ten samples of crude oil, thirty-five fish samples of the Gerreidae family - mojarra species, *Diapterus rhombeus*, and seventy bivalves samples (massunin, *Anomalocardia brasiliiana*). The crude oil, seawater, fish, and bivalves samples were collected from the Alagoas and Sergipe (Brazil) coasts (Fig. 1) between October 2019 and January 2020.

Seawater samples (250 mL) for total metal and metalloid analysis were collected in polyethylene and glass containers, previously

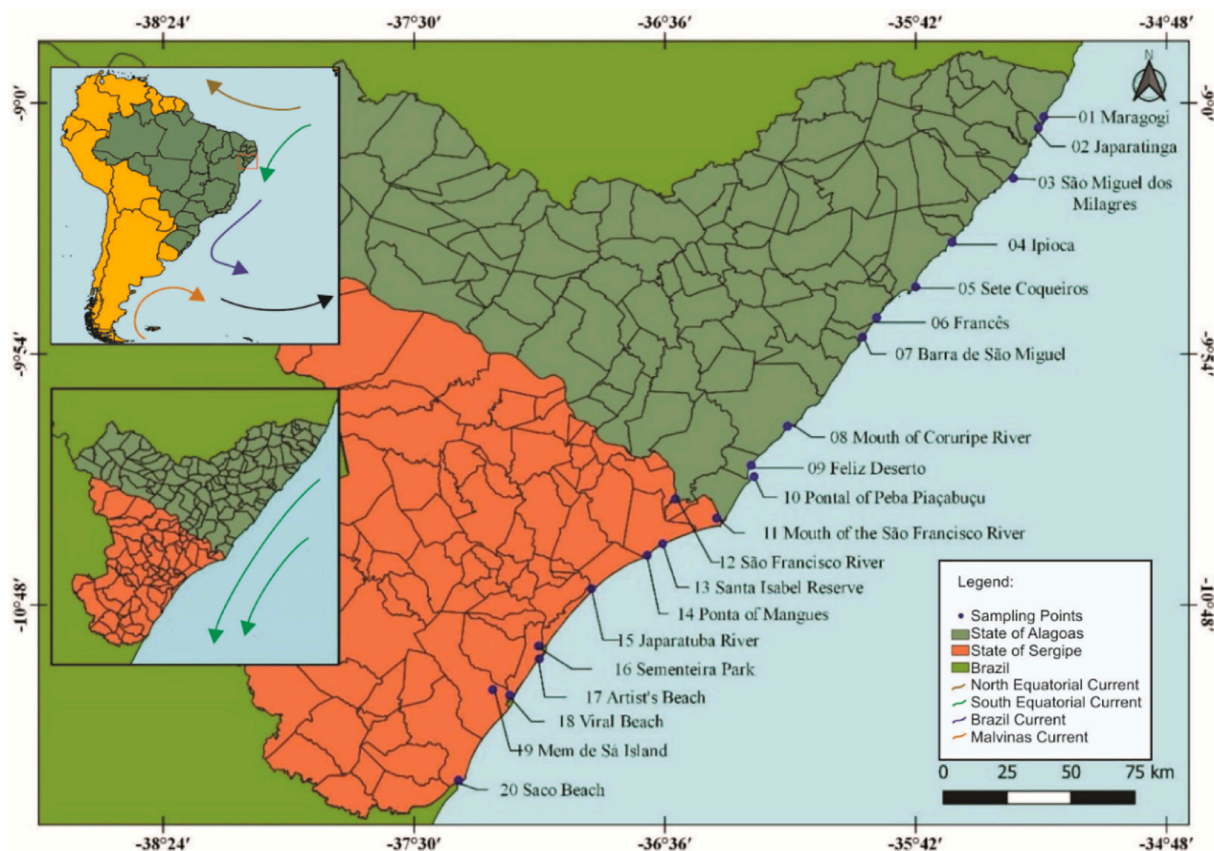


Fig. 1. Location of sampling sites in Alagoas and Sergipe States, Brazil. The internal graphics refer to the main ocean currents present in the sampling region.

decontaminated, containing 5 mL of 65% HNO_3 (m/m) for sample conservation. Before the analysis, the seawater samples were filtered using a 0.45 μm cellulose acetate membrane. Sampling points considered locations where crude oil was found in the beach water or sand, except for P05.

The crude oil samples were collected with stainless steel spatulas, separated from the sand (when necessary), and placed in glass containers. Finally, seawater and crude oil samples were stored at 4 °C, and, to analyze physicochemical parameters, seawater samples were collected and preserved in bottles (500 mL) at 8 °C.

Fish livers were removed to determine the enzymatic analysis of catalase (CAT). Each organ was homogenized at 1:10 (w/v) with phosphate buffer 0.1 M (pH 7.5). The organs were weighed and wrapped in foil, frozen in liquid nitrogen (VOLTA 5), and stored in an ultra-freezer at -80 °C (Thermo Scientific).

2.6. Procedures for metal and metalloid determinations in seawater samples

In GF AAS analysis, analytical curves were constructed (Cd, Pb, Cu, and Zn: 1.0 - 10 $\mu\text{g L}^{-1}$; and Cr and Ni: 0.1 - 10 $\mu\text{g L}^{-1}$) using standard solutions, and HNO_3 was used for matrix compatibilization. The experimental conditions for Hg (CV AFS) and As (HG AFS) determinations are described in Table S1 (Supplementary material) while the main figures of merit for determining metals and metalloid are presented in Table S2.

2.7. Digestion of crude oil total metal and metalloid determinations

The digestion procedure of the crude oil samples was carried out in a closed and pressurized microwave digestion system, equipped with 10 rotors (SK-10) and sensors for temperature and pressure control.

Digestions were performed in triplicate ($n = 3$) for each sample, including the analytical blank. For each crude oil sample, 250 mg was introduced into the reaction vessels; later, 7.0 mL of 65% HNO_3 (m/m) and 1.0 mL of 30% H_2O_2 (m/m) were added at pre-digestion stage lasting 1 h. The heating program conditions are described in Table S3, according to the recommendations of Camera et al. (2015) and Mello et al. (2012), with adaptations. The digested samples were diluted to 25 mL with ultrapure water, and residual acidity was determined by acid-base titration using NaOH standard solution (0.0901 M) and phenolphthalein 1% (m/v) as a visual indicator. The compatibility of the acidity of the medium was carried out with HNO_3 5 M.

2.8. Physico-chemical parameters of seawater analyses

The water quality parameters analyzed were sulfate (mg L^{-1}), total ammonia-nitrogen (mg L^{-1}), phosphate (mg L^{-1}), dissolved oxygen (mg L^{-1}), salinity (PSU), pH, nitrite (mg L^{-1}), total iron (mg L^{-1}), aluminum (mg L^{-1}), total dissolved solids (TDS, μcm^{-1}), and turbidity (NTU). The physicochemical parameters were determined using well-established spectrophotometric assays, micro-Kjeldahl determination of nitrogen (Ma and Zuazaga, 1942), multiparameter probe (YSI, USA), and HANNA (HI9829).

2.9. Quantification analysis – Total oil and grease (TOG)

To measure and quantify the concentration of oil and grease in the waters, described by environmental agencies such as Total Oil and Grease (TOG), a Horiba® model OCMA-350 oil analyzer was used. This technique represents a quick and direct approach commonly used in the literature (Klemz et al., 2020). The measurements were based on the absorption in the infrared in the range of 3.4 - 3.6 μm . For TOG extraction from the PW sample, the poly-trichlorofluoroethylene solvent

(S-316, Horiba®) was used in a 1:1 solvent to sample ratio, according to the Instruction manual HORIBA OCMA-350). For greater reliability, the equipment was calibrated using B-heavy oil as a standard reference having a concentration of 200 mg L⁻¹. From these analyses, it was possible to determine significant quantities of oils present in the waters, reaching concentrations of 31.6 mg L⁻¹ of contamination and correlating with the perspective of CONAMA resolution no 393/2007.

2.10. Gas chromatography and mass spectrometry (GC-MS)

2.10.1. Organic crude oil general composition

The organic composition of general crude oil from 5 beaches in Alagoas (P01, P02, P08, P09, P10) was chosen to compare along the coast. In addition, an adaptation of the SARA methodology, responsible for separating oil fractions, was performed to give the name to the method (saturated, aromatic, resins, and asphaltene). This fractionation and the subsequent analysis of the SARA fractions are of great importance in the characterization of oil. However, the currently used method, ASTM D2007-93, uses the classical open column chromatography procedure, making the analysis irreproducible and expensive.

2.10.2. Extraction and quantification of polycyclic aromatic hydrocarbons (PAH), aliphatic hydrocarbons (HA), and BTEX

Seawater samples were processed for PAH and HA determinations using liquid-liquid extraction, a procedure recommended by the United States Environmental Protection Agency – EPA 3510C (US-EPA, 1996) while BTEX (Benzene, Toluene, Ethylbenzene, *m-p*-xylene, *o*-xylene) followed methodology developed and validated by Gebara et al. (2013). In fish and oysters samples, the PAH was extracted by the MSPD method (Matrix Solid-Phase Dispersion), according to the methodology described by Pensado et al. (2005). The limit of quantification (LOQ) for the determination of PAH and BTEX in seawater was 2.0 ng L⁻¹. For fish samples, the LOQ was 1.0 ng g⁻¹ for PAH quantification, while in oysters it was 0.2 ng g⁻¹. Finally, for the quantification of BTEX in biological samples, the LOQ was 0.1 ng kg⁻¹.

Instrumental analysis, using gas chromatography coupled to mass spectrometry (GC-MS: M.S. Agilent model 5975; G.C. Agilent model 7820 A), followed the conditions of the DB-5 ms MSD chromatographic column (30 m, 0.25 mm of *i.d.*, and 0.25 μm of the film), temperature program 40 °C for 3 min, 7 °C min⁻¹ up to 305 °C for 10 min, carrier gas Helium at 1.0 mL min⁻¹ and injection volume of 1.0 μL. The analyses were performed in linear scanning (SCAN) and the (SIM) mode for aromatic compounds using a range of 57 *m/z*.

2.11. Liver extract preparation and catalase activity

Liver crude extracts were suspended in 20 mM potassium phosphate buffer (pH 7.4, Triton X100 0.1% (m/v), and NaCl 150 mM, 1:20 dilution) and further homogenized in a Potter-Elvehjem glass homogenizer. Catalase activity in the liver extract was analyzed spectrophotometrically at 240 nm (wavelength of maximum absorption of hydrogen peroxide) using H₂O₂ as a substrate (Moraes et al., 2007). Finally, one-Unit (U) of CAT activity was calculated in terms of μmol H₂O₂ consumed min⁻¹.

2.12. Statistical analyses

The data were submitted to the analysis of variance homogeneity with the Shapiro-Wilk test. Parametric data submitted to analysis of variance (ANOVA) followed by Tukey's test. Statistical analyses of enzyme activity were performed using GrapPAHd Prism software (version 6.0, GrapPAHd Software Inc., San Diego, CA, USA).

2.13. Quality assurance and quality control (QA/QC)

QA and QC strictly monitored all analytical procedures. The selected

metals and metalloid standards were purchased from the Specscol® (Brazil) with traceability to the National Institute of Standards and Technology (NIST, USA). Results from blanks demonstrated that the analysis process was free of contamination, as well as the reagents and procedures employed. The procedures applied to determine metals and metalloids are free of matrix effect (oil and seawater) since the recovery assays for the determined elements remained in the range of 80 to 120% (Tables 1 and 2). All the samples analyzed (P01 to P10, metal and metalloid determinations) were randomly selected as parallel samples for repeatability checking. The main parameters from figures of merit are described in Table S2 (relative standard deviations (RSD), LOD, LOQ, among others).

The water analysis regarding the physicochemical parameters was determined by applying spectrophotometric assays from Merck's Spectroquant® system, which supports the safe analysis with easy-to-use test kits and certificates, ensuring that results are measured correctly. Nitrogen determination was based on the micro-Kjeldahl procedure (method TKN). This wet oxidation procedure consists of complete nitrogen sample conversion to N-NH₄⁺, determined spectrophotometry in medium acid (after ammonia distillation). Multiparameter probe (YSI) was used to check the instrument casing periodically looseness of connections (Table S4). The calibration certificate is always required when determining field measurement values. The multiparameter probe HANNA (HI9829) was certificated, calibrated, and tested using standards and reference instruments, the accuracy of which is traceable to the National Institute of Standards (NIST) in the USA or internationally acceptable national physical standards. The procedures and calibration system have been performed according to the manufacturer's instructions and the requirements of ISO 9001, respectively. All the samples analyzed were randomly selected as parallel samples for repeatability checking.

For the analysis of Polycyclic Aromatic Hydrocarbons (PAH), aliphatic hydrocarbons, and BTEX standards were purchased from Sigma Aldrich (USA), and analytical curves were constructed. In each solution of the analytical curve for PAH analysis, deuterated internal standards were also present (naphthalene-*d*8, acenaphthene-*d*10, phenanthrene-*d*10, chrysene-*d*12, and perylene-*d*12), each at a fixed concentration of 30 ng mL⁻¹. A blank in each batch of analyzed samples (*n* = 10) was also analyzed for quality control.

3. Results and discussion

3.1. Crude oil and seawater: Metals, metalloids, and physicochemical parameters

The analysis of crude oil samples collected from different locations with high deposition incidence (P01, P02, and P03, Fig. 1) was performed to assess the profile of the mineral composition (Table 1). In this previous evaluation, the elements Hg (94 - 134 μg kg⁻¹), As (54 - 90 μg

Table 1
Metals and metalloids (*n* = 3) in crude oil samples from the Alagoas coasts (Brazil).

Sampling points	Total concentrations (μg kg ⁻¹)						
	Hg	As	Cd	Pb	Cr	Cu	Zn
P01	104 ± 11	72 ± 9	151 ± 13	149 ± 19	48 ± 3	28 ± 1	175 ± 5
	134 ± 16	90 ± 1	230 ± 10	120 ± 11	48 ± 3	26 ± 2	159 ± 5
P02	94 ± 7	54 ± 8	204 ± 18	336 ± 28	44 ± 4	39 ± 2	235 ± 9
	88 ± 5	91 ± 7	85 ± 4	105 ± 8	101 ± 3	108 ± 6	98 ± 4
Recovery (%) ^a							

^a Recovery assays (*n* = 3) were performed from the following concentrations for each element: Hg and As (25 μg kg⁻¹), while Cd, Pb, Cr, Cu, and Zn (50 μg kg⁻¹).

Table 2
Metals and metalloids ($n = 3$) in seawater from the Alagoas coasts (Brazil) in October 2019.

Sampling points	Total concentrations ($\mu\text{g L}^{-1}$)							
	Hg	As	Cd	Pb	Cr	Cu	Zn	Ni
P01	0.303 \pm 0.025	0.72 \pm 0.03	3.88 \pm 0.10	7.92 \pm 0.24	2.70 \pm 0.10	4.46 \pm 0.04	28.4 \pm 1.9	< 0.10
P02	< 0.05	3.98 \pm 0.14	5.34 \pm 0.07	8.64 \pm 0.51	2.94 \pm 0.51	5.61 \pm 0.13	67.7 \pm 2.3	< 0.10
P03	< 0.05	0.46 \pm 0.02	3.36 \pm 0.06	10.23 \pm 0.42	0.46 \pm 0.20	3.91 \pm 0.10	19.9 \pm 5.3	< 0.10
P04	< 0.05	2.49 \pm 0.07	2.78 \pm 0.09	8.78 \pm 0.45	4.73 \pm 1.18	4.04 \pm 0.09	24.9 \pm 4.6	< 0.10
P05	2.28 \pm 0.024	0.52 \pm 0.04	5.76 \pm 0.11	10.69 \pm 0.32	10.0 \pm 2.0	4.20 \pm 0.05	62.3 \pm 2.5	< 0.10
P06	0.117 \pm 0.007	0.57 \pm 0.05	4.75 \pm 0.12	9.83 \pm 0.23	< 0.10	1.33 \pm 0.07	2.00 \pm 0.20	< 0.10
P07	0.199 \pm 0.001	0.21 \pm 0.01	6.31 \pm 0.14	8.17 \pm 0.31	< 0.10	5.20 \pm 0.05	22.1 \pm 3.8	< 0.10
P08	0.254 \pm 0.011	0.47 \pm 0.06	2.19 \pm 0.08	7.38 \pm 0.47	< 0.10	3.83 \pm 0.06	29.4 \pm 5.4	< 0.10
P09	0.225 \pm 0.004	0.49 \pm 0.07	1.89 \pm 0.05	7.24 \pm 0.26	0.16 \pm 0.10	4.32 \pm 0.05	23.1 \pm 4.6	< 0.10
P10	0.388 \pm 0.006	0.35 \pm 0.02	5.52 \pm 0.10	1.62 \pm 0.08	< 0.10	5.75 \pm 0.12	9.92 \pm 1.62	< 0.10
Recovery (%) ^a	82 \pm 7	86 \pm 4	91 \pm 6	109 \pm 11	95 \pm 8	112 \pm 10	94 \pm 7	106 \pm 8
Maximum limit ^b	0.2	10	5	10	50	5	90	25

^a Recovery assays ($n = 3$) were performed from the following concentrations for each element: Hg and As ($1 \mu\text{g L}^{-1}$), while Cd, Pb, Cr, Cu, Zn, and Ni ($5 \mu\text{g L}^{-1}$).

^b Reference values according to CONAMA resolution no 357/2005 (Brazil) for saltwater.

kg^{-1}), Cd ($151 - 204 \mu\text{g kg}^{-1}$), Pb ($120 - 336 \mu\text{g kg}^{-1}$), and Zn ($159 - 235 \mu\text{g kg}^{-1}$) had the highest concentrations in the crude oil samples, compared to Cr ($44 - 48 \mu\text{g kg}^{-1}$) and Cu ($26 - 39 \mu\text{g kg}^{-1}$). However, the variation in the concentration level between crude oil samples for each element can be associated with the time of exposure and environmental degradation of the analyzed fraction; still, samples P01 and P02 showed greater similarity. However, all three samples had similar results for Cr. The results obtained are consistent with a concentration in similar matrices and fractions derived from petroleum (Camera et al., 2015; Hardaway et al., 2004; Luz et al., 2013; Walkner et al., 2017).

The seawater samples (P01 - P10, Fig. 1) were analyzed to determine the total contents of the following elements: Hg, As, Cd, Pb, Cr, Cu, Zn, and Ni (Table 2). According to the maximum limit of concentration of metals and metalloids in saltwater established by the National Environment Council of Brazil (CONAMA) (Brazil, 2005), the elements As, Cr, Zn, and Ni presented concentrations below the maximum reference values in all samples. Nevertheless, for metals Hg ($< 0.05 - 2.28 \mu\text{g L}^{-1}$), Cd ($1.89 - 6.31 \mu\text{g L}^{-1}$), Pb ($1.62 - 10.69 \mu\text{g L}^{-1}$), and Cu ($1.33 - 5.75 \mu\text{g L}^{-1}$), there were sampling points above the maximum concentration limit established by the national legislation. The evaluated region, referring to the different sampling points on the coast of Alagoas, presented a limitation due to the lack of previous results concerning the concentrations of these elements since there is no history of environmental monitoring in this region. Thus, it is not yet possible to infer whether the values above the legislation for the elements Hg, Cd, Pb, and Cu are related to the environmental contamination of crude oil due to the lack of information from the period before the oil spill. Finally, it is observed that, in general, the levels of metals and metalloid determined in seawater samples are lower than in the water samples impacted or used in the crude oil treatment process (Afzal et al., 2019; Erakhrumen, 2015; Hardi et al., 2019; Owamah, 2013).

Table 3
Metals and metalloids ($n = 3$) in seawater from the Alagoas coasts (Brazil) after the contamination (January 2020).

Sampling points	Total concentrations ($\mu\text{g L}^{-1}$)							
	Hg	As	Cd	Pb	Cr	Cu	Zn	Ni
P01	0.756 \pm 0.021	45.46 \pm 3.33	2.79 \pm 0.77	10.95 \pm 1.46	3.81 \pm 1.18	12.45 \pm 1.55	25.50 \pm 3.12	5.17 \pm 1.31
P02	0.150 \pm 0.007	21.60 \pm 1.08	2.92 \pm 0.51	7.95 \pm 0.86	2.26 \pm 2.50	23.76 \pm 2.24	1.55 \pm 0.52	12.53 \pm 0.82
P03	0.101 \pm 0.010	16.05 \pm 1.92	4.21 \pm 0.33	8.75 \pm 1.14	1.48 \pm 1.37	10.15 \pm 1.91	19.25 \pm 2.81	10.8 \pm 1.64
P04	0.242 \pm 0.040	0.73 \pm 0.03	3.41 \pm 0.88	2.45 \pm 0.32	0.23 \pm 0.16	2.07 \pm 0.33	< 1.0	7.51 \pm 0.58
P05	0.998 \pm 0.166	1.22 \pm 0.011	4.54 \pm 1.05	14.32 \pm 2.25	0.29 \pm 0.34	9.41 \pm 2.57	15.52 \pm 4.21	9.34 \pm 0.92
P06	0.885 \pm 0.188	0.48 \pm 0.03	3.30 \pm 0.90	5.41 \pm 0.71	7.14 \pm 1.81	6.21 \pm 1.12	13.02 \pm 1.46	2.53 \pm 0.75
P07	0.154 \pm 0.011	0.51 \pm 0.08	4.81 \pm 0.80	4.05 \pm 0.50	23.33 \pm 2.36	5.48 \pm 1.25	9.25 \pm 2.29	8.84 \pm 1.05
P08	0.133 \pm 0.013	0.52 \pm 0.08	3.25 \pm 0.32	6.51 \pm 0.81	40.49 \pm 5.38	4.31 \pm 0.78	8.11 \pm 2.13	6.32 \pm 0.42
P09	0.099 \pm 0.005	0.91 \pm 0.11	3.31 \pm 0.66	2.35 \pm 0.69	53.20 \pm 1.74	9.19 \pm 2.25	< 1.0	3.12 \pm 0.28
P10	0.258 \pm 0.024	1.13 \pm 0.14	5.11 \pm 0.38	1.47 \pm 0.36	< 0.10	7.11 \pm 2.15	11.75 \pm 3.18	4.83 \pm 0.17
Maximum limit ^a	0.2	10	5	10	50	5	90	25

^a Reference values according to CONAMA resolution no 357/2005 (Brazil) for saltwater.

dos Milagres beach (P03) and Barra de São Miguel beach (P07), presented the lower values (Tukey test, $p < 0.05$). We can observe that nitrite, phosphorus, and turbidity obtained significant differences ($p < 0.05$) concerning the months (Fig. 2), and in some cases, relative to the collection areas.

Seawater physicochemical parameters in November 2019 presented higher levels compared to data in October 2019 and January 2020. Maragogi and Japaratinga beaches were the most affected, with a higher amount of crude oil, while Ipioca and São Miguel dos Milagres beaches showed the lowest impact. The results from Chen et al. (2017) indicated that the indices of polycyclic aromatics hydrocarbon (PAH), ammonia, turbidity, and nutrient concentrations increased but decreased during an oil spill event due to the action of microorganisms. According to the maximum limit in saltwater established by the World Health Organization (WHO) (2003) and CONAMA (Brazil, 2005), total phosphorus and nitrite values are 0.062 and 0.07 mg L^{-1} , respectively. In this study, the two nutrients levels on the three months analyzed were: 0.60 ± 0.33 and $1.02 \pm 0.56 \text{ mg L}^{-1}$, therefore much above the established limits.

3.2. Quantification analysis of total oil and grease (TOG)

From the data obtained (Table 4), variable contamination levels in the collected water samples were observed. In this analysis, the direct relationship between the pH and the level of contamination (TOG values) was absent since the samples with similar pH were obtained at different TOG concentrations. In general, TOG analyses present a median value of $15.34 \pm 8.57 \text{ mg L}^{-1}$.

Points P01, P05, P10 had the highest registered concentrations of TOGs among the samples of water collected, exclusively pointing to P05. According to the resolution, this point exceeded the average concentration stipulated by World Health Organization (WHO) (2003) and CONAMA resolution no 393/2007; according to the resolution, it deals with wastewater in oil production in Brazil, with its disposal concentrations of 29.0 mg L^{-1} . Although it is a simple monthly arithmetic average value of oils and greases for production waters, it shows the concentrations present in coastal waters as irregular. Therefore, it can cause several environmental and human health problems since crude oil is a complex mixture that contains various species of proven toxicity, including volatile organic compounds (VOCs), PAH, hydrogen sulfide, and potentially toxic metals. The severity of the exposure occurs by ingestion, absorption through the intact skin, and inhalation. The toxicological risks involved are severe, acute, and chronic, with particular attention to toxic fractions of oil that can lead to death from poisoning, primarily when associated with aromatic compounds (PENA, 2020). Such concentrations must be considered, as we know that the samples are not water from oil production fields.

Finally, regarding the pH analysis, the average pH value was 7.90, and it is within limits established by CONAMA resolution 274/2001 for saline waters (pH between 6.5 and 8.5).

Table 4

Total quantification of oil and grease (TOG) in seawater samples.

Sampling point	Parameter	
	pH	TOG (mg L^{-1})
P01	7.60	20.7
P02	7.48	8.49
P03	7.78	4.86
P04	7.90	5.22
P05	7.57	31.6
P06	7.59	11.7
P07	7.44	13.8
P08	7.78	16.8
P09	7.51	15.7
P10	7.45	24.7

3.3. Gas chromatography–mass spectrometry (GC–MS)

3.3.1. Organic crude oil general composition

The oils from five different seawaters in Alagoas (P01, P02, P08, P09, and P10) were analyzed by GC–MS (Fig. 3). The chromatographic profiles are quite similar (Fig. 3), and the main difference is regarding the area and intensities of the compound. This difference may be associated with physicochemical processes such as evaporation, emulsification, dissolution, and biodegradation, caused by weathering due to the action of winds, water, sun, and tides. Weathering can reduce the number of different compounds classes present in the samples, changing their physicochemical properties (Al-Hawash et al., 2018; Han et al., 2018). This behavior was noticed since the naphthalenes and phenanthrenes in the oil collected on the first day decreased by 82% and 58%, respectively. Table 5 shows the main compounds classes identified, indicating the percentage of the sampling point.

It is possible to observe that most samples' area predominates hydrocarbons, except for the sample P09, in which carboxylic acids were predominant (Table 5). Ethers were identified in small amounts, emphasizing the P02 sample since there was no presence of this functional group. Finally, a relationship was observed between the hydrocarbons and ethers content, with P08 and P09, which present higher ether levels and lower concentrations of hydrocarbons (P01 and P02).

Since the sample compositions were similar, it was decided to analyze the most complex sample (P10) using the GC–MS solution software. It was possible to integrate 329 compounds, of which 83% were considered contaminants. This contamination was mainly due to silica derivatives, algae, shellfish, and plastics in the oil sample. Forty-one compounds were identified, 9 polychromatic hydrocarbons (naphthalene, dibenzothiophene, phenanthrene), 18 aliphatic hydrocarbons (from dodecane to triacontane), 13 aromatic hydrocarbons (benzene, vinyl-benzene), and toluene. Weathering may have been responsible for the non-detection of *o*-xylene, *m*-xylene, and *p*-xylene compounds in the samples. Based on these results, it was possible to identify some toxic, persistent, and highly pollutant compounds (naphthalene,

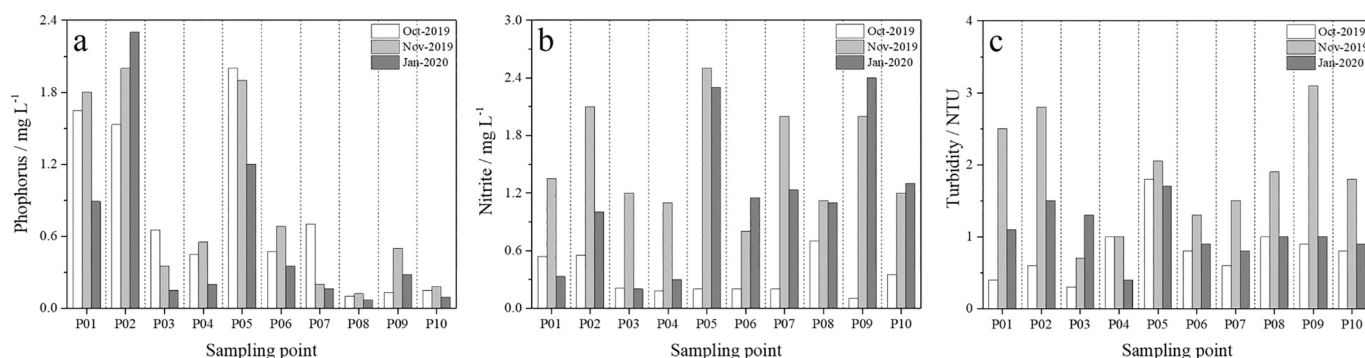


Fig. 2. Total concentrations of (a) phosphorus, (b) nitrite, and (c) turbidity were evaluated in seawater from Alagoas State between October 2019 and January 2020.

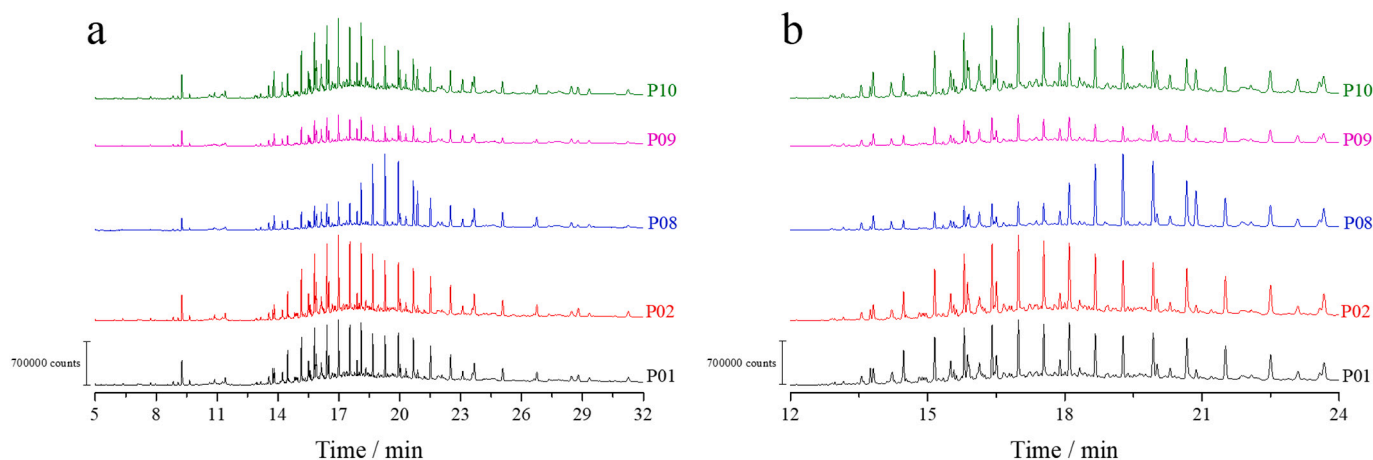


Fig. 3. (a) Chromatographic profiles of the oils collected from the coasts of Alagoas (57 m/z). In (b) are show the respective expansions from 12 to 24 min.

Table 5

Percentage of the area referring to the compounds identified in the main chemical classes.

Samples	Classes (%)		
	Hydrocarbon	Carboxylic acid	Ether
P01	86.8	10.7	2.49
P02	94.9	5.13	N.I.
P08	66.9	25.1	8.00
P09	43.8	46.4	9.78
P10	73.9	22.0	4.06

N.I. = Not identified.

dibenzothiophene, phenanthrene) in different Alagoas coast regions that can cause serious environmental and health problems (Wu et al., 2021). Thus, we are facing an environmental impact that can be related to these oil spills. According to Farrington et al. (2020), in 1969, ~ 600 tons of oil were spilled in Buzzards Bay, Massachusetts. Two years later, hydrocarbons derived from the oil persisted in the swamp and offshore sediments. This fact suggests that the environmental impact caused by these compounds can persist for several years.

Chromatographic analyses of the Sergipe oil were compared with those identified in the oil spill on the Alagoas coast. It was possible to identify mainly hydrocarbons from n -C₁₀ to n -C₂₀, compounds such as eicosane (C₂₀H₄₂) and hexadecane (C₁₆H₃₄), among other hydrocarbons in this range, were found in oils in Alagoas. The oils samples characterized in Sergipe state have a range of hydrocarbons slightly similar to

Table 6

Quantification of polycyclic aromatic hydrocarbons (PAH) in samples of water, fish, and *massunin* from the Alagoas and Sergipe coasts (Brazil).

Sample	Naf	Aftil	Aft	Flu	Fen	Ant	Flut	Pir	B(a) an	Cri	B(b)fl	B(k)fl	B(a) pir	I[1,2,3-cd]	B[ghi] per	D(a,h) a	ΣPAH
Seawater (ng L ⁻¹)																	
P18	49.92	7.95	10.57	12.55	18.33	16.99	12.64	8.71	12.4	12.6	4.03	4.12	2.07	< LOQ	2.84	2.35	178.07
P11	9.94	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	9.94
P12	15.38	n.d.	n.d.	n.d.	2.58	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	17.96
P13	25.11	n.d.	n.d.	n.d.	7.48	< LOQ	3.64	< LOQ	< LOQ	2.24	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	38.47
P14	5.58	n.d.	n.d.	n.d.	3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	8.58
P15	32.51	n.d.	n.d.	n.d.	9.18	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	41.69
P16	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
P17	38.96	13.37	15.79	15.47	20.52	17.87	19.34	18.5	18.87	16.28	14.49	13.34	12.91	12.64	14.36	12.78	275.49
P19	26.01	n.d.	n.d.	n.d.	2.61	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	28.62
P20	29.31	n.d.	n.d.	n.d.	3.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32.46
Massunin (ng L ⁻¹)																	
P09	8.28	4.4	1.05	7.22	7.04	0.95	1.26	2.21	n.d.	< LOQ	n.d.	0.98	< LOQ	n.d.	n.d.	n.d.	33.4
P10	13.99	8.56	n.d.	18.59	22.44	18.55	4.81	8.85	8.93	1.28	0.83	1.23	6.54	n.d.	n.d.	n.d.	114.63
Fish (ng L ⁻¹)																	
P11	4.81	1.64	2.84	1.83	4.72	1.5	8.29	n.d.	1.23	1.76	n.d.	< LOQ	n.d.	n.d.	n.d.	< LOQ	28.62
P12	1.82	1.45	2.99	5.64	3.5	2.52	1.56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	19.47
P15	6.28	2.74	1.66	5.49	1.38	2.71	7.44	4.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	32.06
P16	2.94	1.38	n.d.	3.74	1.51	< LOQ	3.29	1.41	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	14.28
P17	3.18	4.54	2.85	4.18	2.5	2.37	2.29	2.11	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	24.01

n.d.: not detected; < LOQ - less than the limit of quantification.

ΣPAH - total sum of 16 PAH analyzed.

Naf: Naphthalene; Aftil: Acenafitilene; Aft: Acenafitene; Flu: Fluorene; Fen: Phenanthrene; Ant: Anthracene; Flut: Fluoranthene; Pir: Pyrene; B (a) an: Benzo (a) Anthracene; Cri: Chrysene; B (b) fl: Benzo (b) Fluoranthene; B (k) fl: Benzo (k) Fluoranthene; B (a) pir: Benzo (a) Pyrene; I [1,2,3-cd]: Indene (1,2,3-cd) pyrene; B [ghi] per: Benzo (ghi) Perylene; D (a, h) a: Dibenzo (a, h) anthracene (a,h)anthracene.

those found on the Alagoas coast, where the compounds were in the range from *n*-C₁₉ to *n*-C₃₃, which are gammaceran (C₃₀H₅₂) and C₃₃H₅₈ isomers. However, there was no difference between the oils found in the two states, although regional factors such as climate action on oil spilled off the coast of both states and contamination caused by oil degradation on beaches may influence the chemical profile.

3.3.2. Analyses of PAH in samples of seawater, fish, and *massunins* (bivalves)

The PAH determination was made in the 10 seawater samples, 5 fish muscle samples from different points of the Sergipe coast, and 2 *massunins* samples collected from the Alagoas (Table 6). The total PAH concentrations (Σ PAH) per seawater sample collected varied from <0.01 ng L⁻¹ (P16) to 275.49 ng L⁻¹ (P17). Naphthalene was the major contributor to the total concentration of 16 PAH, except in sample P16, where the presence of none of the 16 PAH analyzed was detected.

Phenanthrene was found in all samples except in sample P11. The analysis revealed that 5 samples showed only two PAH, naphthalene and phenanthrene. The total concentrations of PAH (Σ 3-4 rings) ranged from <0.01 ng L⁻¹ to 138.89 ng L⁻¹. Samples P18 and P17 showed the highest total concentrations of PAH of 5 and 6 rings, with values of 15.41 and 80.52 ng L⁻¹. In these regions, a higher proportion of oil was found on the Sergipe coast. These 2 samples also showed the presence of all PAH analyzed.

Total PAH concentrations (Σ PAH) per fish sample ranged from 14.28 (P16) to 32.06 ng g⁻¹ (P15). Fluoranthene was the major contributor to the total concentration of 16 PAH for samples P15 and P11, with 7.44 and 8.29 ng g⁻¹, respectively. Fluorene was the major contributor in the samples of P16 and P12, with values of 3.74 and 5.74 ng g⁻¹, respectively, while acenaphilene presented the highest contributor in the P17, the value being 4.54 ng g⁻¹.

Total PAH concentrations (Σ PAH) per *massunins* sample ranged from 29.88 (P09) to 114.63 ng g⁻¹ (P10). For the P09 sample, the main contributors to the total PAH concentration were naphthalene (8.28 ng g⁻¹), fluorine (7.22 ng g⁻¹), and phenanthrene (7.04 ng g⁻¹), while for the P10 sample, the major contributors were phenanthrene (6.03 ng g⁻¹), naphthalene (4.58 ng g⁻¹), and pyrene (4.52 ng g⁻¹). Phenanthrene was the major contributor for sample P10 (22.44 ng g⁻¹), followed by fluorene (18.59 ng g⁻¹).

BTEX concentrations were below the LOQ (0.1 μ g L⁻¹) in all seawater samples analyzed. Therefore, none of the samples was above the maximum limit (51 μ g L⁻¹) established by the National Environment Council of Brazil (Brazil, 2005).

Cao et al. (2010) reported that PAH contamination in water could be classified in four degrees: micro polluted (10 to 50 ng L⁻¹), slightly polluted (50 to 250 ng L⁻¹), moderately polluted (250 to 1000 ng L⁻¹), and highly polluted (> 1000 ng L⁻¹). In this work, the PAH concentrations showed that most analyzed samples could be classified as micro polluted. However, two samples, which showed all 16 PAH, according to their total concentrations, can be classified as follows: P18 (Σ PAH = 178.07 ng L⁻¹), slightly polluted, and P17 (Σ PAH = 275.49 ng L⁻¹), moderately polluted.

The CONAMA resolution no 357/2005, only determines the maximum concentration, 0.018 μ g L⁻¹, of PAH benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a, h)anthracene and indene(1,2,3-cd)pyrene. In the analyses performed, only benzo(a)anthracene, with a concentration of 18.87 ng L⁻¹ (0.1857 μ g L⁻¹), was found above the established limit in sample P17.

In Brazil, there is no legislation which establishes PAH levels in fish, shellfish, and mollusks. The limits for fish used in this work were established by the National Oceanic and Atmospheric Administration (NOAA), in 1993, due to the disaster caused by the Exxon Valdez spill (NOAA, 1993), in which the following concentrations of PAH, for assessment of contamination in fish samples (wet weight), were set at <10 μ g kg⁻¹ (free of contamination); 10 to 99 μ g kg⁻¹ (minimally

contaminated); 100 to 1000 μ g kg⁻¹ (moderately contaminated) and > 1000 μ g kg⁻¹ (highly contaminated), suggesting that the samples of fish and *massunins* analyzed were minimally contaminated, and P10, can be considered moderately contaminated.

Another classification for fish and oysters analyzed may be based on European standards for fish consumption (EC 1881/2006) (European Community, 2011). This standard has already been updated (EC 835/2011) to remove fresh fish from regulation (European Community, 2011). In the new regulation (EC835/2011), there is the inclusion of the limit of 30 ng g⁻¹ for the sum of four PAH (benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene, and chrysene). Therefore, considering the initial recommendation, the maximum allowed concentration of BaP (benzo(a)pyrene) is 2.0 ng g⁻¹ for fresh fish, crustaceans, and mollusks; it is 5.0 ng g⁻¹. In the samples analyzed, the presence of these compounds was not detected.

It should be noted that these values are for quality control of fish sold on the market under normal conditions, without accidents. This way, considering the amount mentioned above for 4 PAH, only the P11 sample showed a concentration of 2.99 ng g⁻¹, a value well below the limit, so the 5 samples analyzed had the PAH level below the recommended level. Thus, considering the samples of *massunins*, the compound's presence was not detected in the sample P09. Only P10 presented a concentration of BaP (benzo(a)pyrene) of 6.54 ng g⁻¹, a value above the permitted in the legislation. Finally, the sum for 4 PAH, none of the oyster samples analyzed, showed an amount above the limit established by European law. However, despite the results showing little accumulation of the analyzed PAH, we recommend continuous analysis in the affected areas, considering that it was a recent episode. These compounds have accumulative character regarding their concentrations and may increase over time of exposure, increasing the risks of environmental issues.

3.4. Catalase activity in the fish liver

Liver catalase in *D. rhombeus* showed a significant ($p < 0.05$) reduction in samples from the Ipioca beach (P04) (6.50 ± 1.83 U CAT mg⁻¹) compared to Pontal do Peba beach (P10) (11.81 ± 2.37 U CAT mg⁻¹), and Japaratinga beach (P02) with higher value (20.76 ± 5.15 U CAT mg⁻¹). Antioxidant enzyme activities are considered useful markers for oxidative stress (Cheng et al., 2015). Several studies have shown differences in liver catalase of fish exposed to pesticides, and this enzyme has been considered a useful liver marker for damage by toxic substances (Clasen et al., 2018).

The present study showed changes in CAT activity in the liver of *D. rhombeus*, followed by an increase in this enzyme, suggesting a role for catalase in the defense mechanism to reduce oxidative stress. The Japaratinga and Pontal do Peba beaches were the locations most affected by petroleum in Alagoas and are where the individuals present a higher level of catalase activity. The catalase activity changes under polycyclic aromatic hydrocarbons and metals in water (Peters et al., 1994).

4. Conclusion

In this work, it was possible to evaluate the impact caused by the oil spill in the coastal region of Northeastern Brazil between the states of Alagoas and Sergipe. In the analysis of the collected crude oil samples, the elements Hg, As, Cd, Pb, and Zn presented the highest concentrations compared to Cr and Cu. However, the variation in the concentration level between crude oil samples for each element may be associated with exposure and environmental degradation of the analyzed fraction. After the oil spill on the Alagoas coast, the elements Hg, As, Pb, and Cu presented concentration values above those allowed by Brazilian legislation. For oil from five different seawaters in Alagoas, the chromatographic profiles were quite similar, with the main difference being in the area and intensities of the compound. This difference may

be associated with physicochemical processes such as evaporation, emulsification, dissolution, and biodegradation caused by weathering due to winds, water, sun, and tides. Total PAH concentrations per seawater sample ranged from <0.01 to 275.49 ng L⁻¹. Naphthalene was the main contributor to the total concentration of 16 PAH. Phenanthrene was found in all samples except in sample P11. Fluoranthene was the main contributor to the total concentration of 16 PAH for two samples (P15 and P11), while fluorene in samples P16 and P12 and phenanthrene for P10 sample by fluorene. Concentrations of BTEX in all seawater samples analyzed were below the limit established by CONAMA.

Hepatic catalase in *D. rhombeus* showed a reduction in activity in samples from Ipioca beach (P04) compared to samples from Pontal do Peba beach (P10) and Japaratinga beach (P02). The coasts of Alagoas and Sergipe (Brazil) do not have a history of environmental monitoring. The oil-related disaster in the coastal region of northeastern Brazil has impacted nature, the local economy, and the population's health. These residues can remain for a long time in water, sand, and corals, impacting nature, causing health-related problems for the residents of these regions due to the continuous exposure of biota and harming the local economy. Thus, it is necessary to monitor the coast of northeastern Brazil to help local and federal governments take the necessary actions to reduce environmental contamination.

CRedit authorship contribution statement

All authors have seen and approved the final version of the manuscript submitted. **E.C. Soares** (Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision), **M.D. Bispo** (Methodology, Writing – original draft, Writing – review & editing), **V.C. Vasconcelos** (Methodology, Writing – original draft), **J.I. Soletti** (Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization), **S.H. V. Carvalho** (Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization), **M.J. Oliveira** (Methodology, Writing – original draft), **M.C. dos Santos** (Methodology, Writing – original draft), **E.S. Santos Freire** (Methodology, Writing – original draft), **A.S.P. Nogueira** (Methodology, Writing – original draft), **F.A.S. Cunha** (Methodology, Writing – original draft, Writing – review & editing), **R.D.D. Sandes** (Methodology, Writing – original draft), **R.A.R. dos Santos** (Methodology, Writing – original draft), **M.T.S.L. Neta** (Methodology, Investigation, Writing – original draft, Writing – review & editing), **N. Narain** (Methodology, Investigation, Writing – original draft, Writing – review & editing; English verification and corrections), **C.A.B. Garcia** (Methodology, Investigation, Writing – original draft, Writing – review & editing), **S.S.L. da Costa** (Methodology, Investigation, Writing – original draft, Writing – review & editing, Visualization), **J.C.C. Santos** (Methodology, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision).

Declaration of competing interest

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

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Appendix A. Supplementary data

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