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INFLUENCE OF A WEATHER EVENT ON THE TRAJECTORY AND DEGRADATION LEVEL OF TARBALLS SAMPLES FROM AN OIL SPILL OCCURRED IN THE CAMPOS BASIN, RIO DE JANEIRO

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Introduction

The entry of oil into the sea can have different sources: natural exudations, offshore oil E&P activities, transport of oil by pipelines and by tankers, as well as illegal activities involving the washing of tanks with the discharge of oil on the high seas. In addition, catastrophic losses during accidents with oil tankers can be sources of spillage of large volumes of oil at sea. The oil spill causes damage to marine and terrestrial life, human health, natural resources and economic activities such as the fishing industry and tourism (ZHANG et al., 2019).

Oil spilled into the sea undergoes various degradation processes known as weathering. Hydrocarbons with lower molecular weight normally evaporate, and the rest remain on the sea surface and undergo various biological, chemical and physical processes, such as the formation of water-in-oil emulsions. Over a period of time, the oil slick spilled into the sea will disintegrate into smaller fragments, which will eventually be transported via ocean currents to various places, including beaches and mangroves. These fragments, when they reach the coast are called tarballs, characterized by their rounded shape and dark color (SUNEEL et al., 2013).

The occurrence of tarballs on beaches on the coast of Rio de Janeiro is very rare, considering the meteorological and oceanographic conditions normally observed in this region. This is justified by the strong presence of the ocean current, known as the Brazil Current, which flows from North to South to the coast of Uruguay (EVANS & SIGNORINI, 1985). This current normally takes oil spills, resulting from spill accidents in the Campos Basin region, to the southern region of the country. However, between April 2 and 4, 2019, tarballs were found on beaches in the Região dos Lagos, Rio de Janeiro, from a real spill of 122 m³ of oil that occurred after a failure in the oil-water separation system of the P-53 oil production located in the Marlim Leste field, Campos Basin (Fig.1).

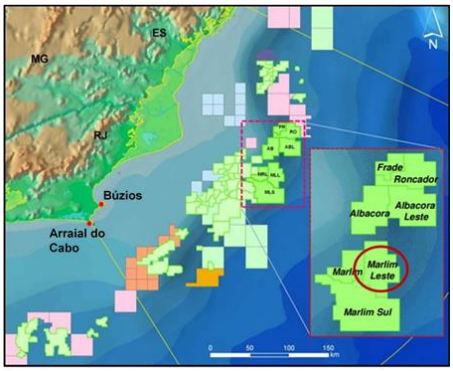

Figure 1. Map of part of the coast of Rio de Janeiro with the locations of the cities of Arraial do Cabo and Armação de Búzios, the Campos Basin and the producing fields, with emphasis on the Marlim Leste field, where the oil spill occurred. 122m³ of oil. *Source: (http://www.anp.gov.br/images).*

The present work aimed to characterize, through the use of diagnostic ratios of oil-saturated biomarker compounds, the degree of weathering of tarball samples that arrived in the Lagos Region. And yet, to evaluate the influence of atypical meteorological events, observed in the oil E&P region of the Campos Basin during the spill period, on the trajectory and time of permanence of the oil spilled in the sea.

Experimental

Six tarball samples were collected from Praia Brava in Armação de Búzios and Prainha, Arraial do Cabo, Região dos Lagos (Rio de Janeiro) to geochemical analyzes. The tarballs samples were submitted to liquid chromatography using previously activated silica gel as stationary phase, for the separation of the fractions of saturated, aromatic,

and polar compounds (NSO). The fraction of saturated hydrocarbons was obtained from the elution with 30 mL of n-hexane, the aromatic hydrocarbons with 30 mL of the mixture n-hexane: dichloromethane (8:2 v/v) and polar hydrocarbons with 30 mL of the mixture dichloromethane: methanol (9:1 v/v). The n-alkane, pristane and phytane concentrations were measured in the saturated fraction by gas chromatography-Flame Ionisation Detector (GC-FID) using α-androstane as an internal standard. The saturated hydrocarbon fractions from the tarball samples were subjected by gas chromatography/mass spectrometry (GC/MS) analyzes. Single Ion Monitoring was used as a mode of analysis for compounds from the tricyclic and pentacyclic terpane (m/z 191) and sterane (m/z 217) families. The compiled data of meteorological conditions, observed in the oil production region of the Campos Basin, at the time of the actual spill, were acquired by consulting the website of the National Institute of Meteorology (INMET).

Results and Discussion

Figure 2 shows the ternary diagram indicating the percentages of the fractions of saturated, aromatic and polar compounds (NSO) obtained after analysis by liquid chromatography of the samples collected on the beaches of Arraial do Cabo and Armação de Búzios. Samples from Arraial do Cabo are located in the region closest to the center of the diagram, indicating a lower degree of weathering when compared to samples from Armação de Búzios, which contain higher percentages of polar compounds (NSO).

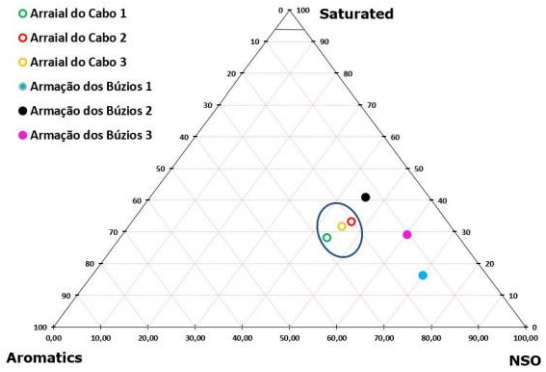

Figure 2. Ternary diagram containing the percentages of saturated, aromatic and polar compounds (NSO) in samples collected in Arraial do Cabo, and in Armação de Búzios.

Figure 3 shows the comparison between the mean residual concentrations of n-alkanes, from n-C17 to n-C31, of Pristano and Fitano from samples collected in Arraial do Cabo and Armação de Búzios. It is observed that the concentrations of lighter n-alkanes (n-C17 to n-C22), of Pristano and Phytane in the samples from Arraial do Cabo are higher than those observed for the tarball samples collected in Armação de Búzios.

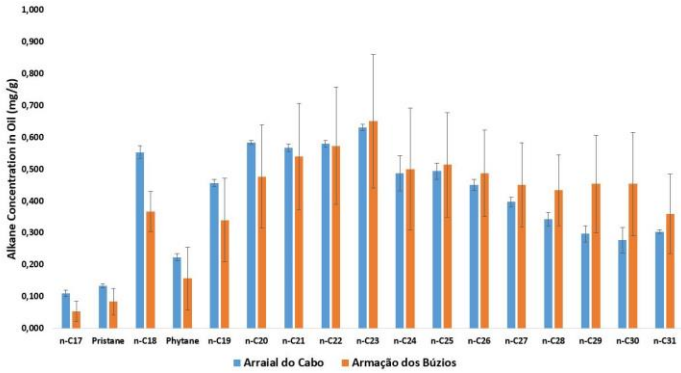

Figure 3. Average values of n-alkanes, pristane and phytane calculated for samples from Arraial do Cabo and Armação de Búzios.

Based on these residual concentrations, it was possible to calculate the weathering index of the samples collected on both beaches (Fig.4). Note that the average referring to the weathering indices for the samples from Armação de Búzios was 1.67 (±0.03) and for the samples collected in Arraial do Cabo was 1.23 (±0.11), and it can be inferred that the samples from Arraial do Cabo were less exposed to weathering agents, that is, they spent less time adrift at sea. Lima et al. (2021) also observed an increase in the weathering index in oil samples collected from a simulated spill in the first five days of exposure.

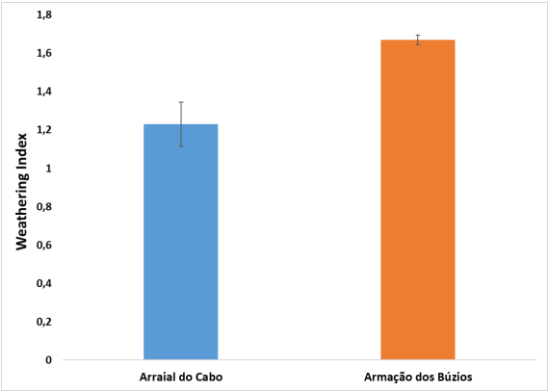

Figure 4. Average values of the weathering index of samples from Arraial do Cabo and Armação de Búzios. Weathering Index = (∑ n-C23-n-C31)/ (∑ n-C17-n-C22), including Pristane and Phytane.

The saturated biomarker compounds identified by GC/MS in the samples collected from both beaches allowed the calculation of the diagnostic ratios of tricyclic Terpanes (Tr21/Tr23), % of C29 steranes (S+R) and of C30 Hopano/Colestano C27 ααα (S +R) (Lima et al., 2021). The results showed little difference for the percentage values of C29 steranes (S+R) and for the ratio of C30

Hopane/C27 αβ (S+R). However, for the samples from Arraial do Cabo, the values were higher for the ratio of Tr21/Tr23 (0.67) when compared to those from Armação de Búzios (0.58), which may indicate that the samples from Arraial do Cabo are more preserved and, consequently, they spent less time exposed to weathering processes after the spill, having reached the beach earlier than those collected on the beach of Armação de Búzios.

According to the ANP bulletin, the spill of 122m3 of oil from the P-53 platform at Campo de Marlim Leste in Campos Basin, RJ, occurred between March 24 and 25, 2019 (ANP, 2020). In Figure 5a, it is possible to observe the map made by the Petroleum and Gas Production Coordination (COPROD/CGMAC/IBAMA) and the satellite image showing the oily feature of the slick with a clockwise trajectory, adrift between the 25th and 26th of March 2019, with an indication of the origin of an oil leak. In the same period of time that the oil slick was adrift in the ocean, tropical storm “Iba” had its highest intensity window recorded between March 24 and 25, 2019. On March 24, the storm reached maximum speed winds of 35 knots (65 km/h) and central pressure estimated at 1008 hPa, rotating clockwise (REIS et al., 2019). In Figure 5b, the satellite image of tropical storm Iba, recorded by the National Institute of Meteorology (INMET) website, is located on the northern limit of the Campos Basin, close to the P-53 platform.

a) b)

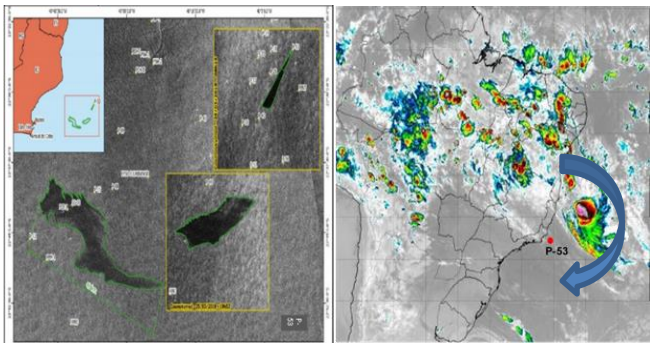

Figure 5. Mapa e fotos de satélite mostrando a feição oleosa da mancha, à deriva entre os dias 25 e 26 de março de 2019, com indicativo de origem de vazamento de óleo (a). Imagem de satélite da tempestade Iba com a indicação do sentido horário dos ventos gerados pela tempestade e a localização aproximada da plataforma P-53 (b).

Conclusions

Concluiu-se que, com o uso de diferentes razões diagnósticas de *n*-alcanos, isoprenóides e de terpanos tricíclicos foi possível detectar que as amostras de tarballs coletadas na Prainha em Arraial do Cabo apresentaram níveis mais baixos de intemperismo, quando comparadas àquelas coletadas na Praia Brava em Armação de Búzios. Conclui-se também que a formação da tempestade tropical Iba, com ventos em sentido horário e velocidade de 65 km/h, no mesmo dia em que se deu o derramamento de 122 m^3 de óleo da plataforma P-53, foi determinante para que a mancha de petróleo tenha atingido o litoral da Região dos Lagos, em rara ocorrência. Além disso, sugerimos que a mudança do sentido Norte-Sul da trajetória da mancha de petróleo, em função de novos e frequentes eventos meteorológicos, observada neste trabalho, deva ser considerada nos modelos matemáticos/computacionais de deslocamento de manchas de petróleo em futuros acidentes que venham a ocorrer nas regiões de E&P de petróleo das bacias de Campos, Santos e do Espírito Santo.

Acknowledgements

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