



INFLUENCE OF A WEATHER EVENT ON THE TRAJECTORY AND DEGRADATION LEVELS 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 [1]. 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 beaches and mangroves. These fragments, when they reach the coast are called tarballs [2].

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 [3]. 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. 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 Região dos Lagos. 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 for the separation of the fractions of saturated, aromatic, and polar compounds. The *n*-alkane, pristane and phytane concentrations were measured in the saturated fraction by GC-FID, using 5 α -androstane as an internal standard. The saturated biomarkers, tricyclic and pentacyclic terpanes (*m/z* 191) and steranes (*m/z* 217) were subjected by GC/MS analyzes. The compiled data of meteorological conditions, observed in the oil production region of the Campos Basin, at the time of the real spill, were acquired by consulting the website of the National Institute of Meteorology (INMET).

RESULTS AND DISCUSSION

Results showed that the concentrations of lighter *n*-alkanes (*n*-C₁₇ to *n*-C₂₂) and isoprenoids in the samples from Arraial do Cabo are higher than those observed for the tarball samples collected in Armação de Búzios. Based on these residual concentrations, it was possible to calculate the weathering index of the samples collected on both beaches (Fig.1). 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. The increase in the weathering index was also observed in oil samples collected from a simulated spill in the first five days of exposure [4]. The saturated biomarker diagnostic ratios results showed little difference for the percentage values of C₂₉ steranes (S+R) and for the ratio of C₃₀ Hopane/C₂₇ $\alpha\alpha\alpha$ (S+R). However, for the samples from Arraial do Cabo, the average 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