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).

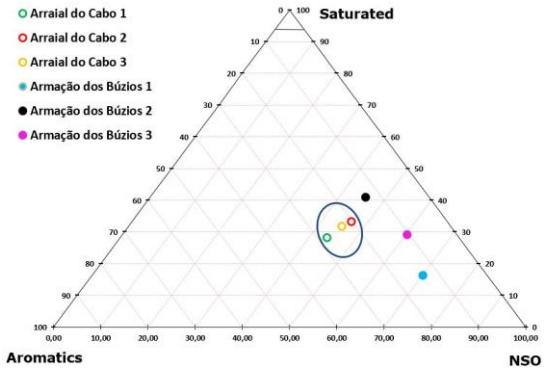

Figure 2. Ternary diagram containing the percentages of saturated, aromatic and polar compounds (NSO) in samples collected in Arraial do Cabo, and in Armação de Búzios.

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.

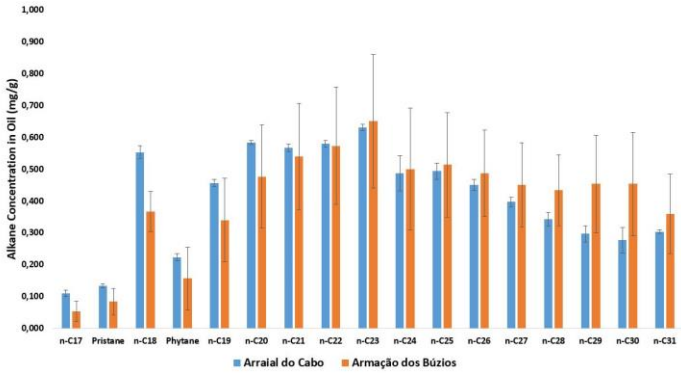

Figure 3. Average values of n-alkanes, pristane and phytane calculated for samples from Arraial do Cabo and Armação de Búzios.

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.

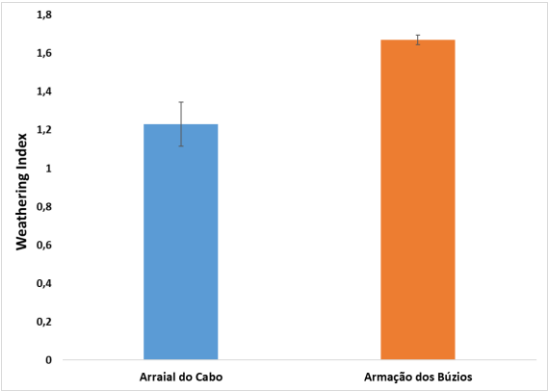

Figure 4. Average values of the weathering index of samples from Arraial do Cabo and Armação de Búzios. Weathering Index = (∑ n-C23-n-C31)/ (∑ n-C17-n-C22), including Pristane and Phytane.

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