Experimental
The tarball sample collected at Taipus de Fora beach was crushed and pulverized before oil extraction with dichloromethane solvent using Soxhlet system. The oil obtained was fractionated in asphalten and maltene fractions using n-pentane, and the asphalten was purified in Soxhlet system\(^3\). The tarball asphalten and maltene fractions were dissolved at 0.5 mg mL\(^{-1}\) in toluene:methanol (1:1 v/v) with 0.5% of NH\(_4\)OH prior to LTQ XL Orbitrap analysis.

Results and Discussion
The relative abundance of heteroatom classes in the asphalten and maltene fractions of the tarball sample is presented in Figure 1 and Figure 2, respectively. The compound classes indentified are characterized by the type and the number of heteroatoms. Only the detected heteroatom classes of >1% of the total summed relative abundances are presented (O\(_2\), O\(_3\), O\(_4\), N, NO, NO\(_2\), NO\(_4\), N2O\(_4\) classes). The relative abundance for the N and N2 are also showed, although these classes have low relative abundance (<1%), since these are important for the distinction of potential spill sources according to a previous work\(^4\).

The O\(_2\) and O\(_4\) classes represent acidic compounds, presumably carboxylic and dicarboxylic acids, and it is expected that these classes present higher relative abundance in the tarball sample and the N and N2 classes present least relative abundance, since this sample is severely biodegraded. Among the OO classes, the O\(_1\) class showed the lowest abundance. Alcohols, mainly phenols, which are considered as intermediates in a number of biodegradation pathways of petroleum components, dominate this class\(^5\). These intermediates compounds may be almost completely consumed during further biodegradation. The relative abundance of N1OO classes is high to this sample, which is in agreement with the fact that the compounds in these classes appears to be biodegradation products of N-containing compounds, it being formed, for example to the N1O2 class, from ring opening of hydroxyl dibenzocarbazoles with additional of a carboxyl group\(^5\).
Conclusions

We conclude that the tarball sample has higher abundance of oxygen classes, but the oxygen species are not useful as conserved internal polar markers to identify origin of tarballs. We also estimate that the time after the oil spill that originates the tarball sample is more than 511 days. Other tarball samples from Taipus de Fora beach will be analyzed in a higher resolution and higher mass accuracy analytical techniques to confirm the results obtained in this study, and also to assess potential species (i.e. NS class) as a conserved internal polar markers to indentify the origin of these tarballs.

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References


