

APPLICATION OF PYROLYSIS-GC/MS FOR THE CHARACTERISATION OF ENVIRONMENTAL CHANGES IN THE SALT MARSHES OF THE TAGUS ESTUARY (PORTUGAL)

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Salt marshes and estuaries are key environments for organic matter (OM) burial, which plays an essential role in the global carbon cycle (López-Capel et al., 2006). Common to these environments is the diversity of OM sources, which is usually composed by a complex mixture of terrestrial and marine residues originated from the decomposition of vegetal, animal and microbial organisms (Hedges and Keil, 1999). Concomitantly, anthropogenic contaminants are transported and deposited.

The proposed research is focused on the assessment of OM inputs changes in the salt marshes of Alfeite, which may be related to environmental changes in the Tagus estuary. The Tagus discharges into the Atlantic Ocean close to Lisbon through a 350 km² mesotidal estuary, being the third largest estuary in Europe. It acts as a depocenter for river-transported sediments, with a sedimentation rate of around 80 cm kyr⁻¹. Run-off and sediment load carried by Tagus river to estuary and towards the continental shelf has been highly modified during last centuries because of a range of anthropogenic activities (including damming, urbanization, deforestation and dredging) and natural events (floodings and tsunamis). Past changes in the marine environment and in the continental hinterland may therefore be recorded in these sediments. Our approach includes the sampling of a set of sediment cores (1m depth) and the characterization of their sections by using elemental (TOC, TN, TS) and stable isotopic analysis ($\delta^{13}\text{C}$), widely used to determine historical changes in sources of OM. Corg/N values within the range 12-18 are representative of a mixed terrestrial-marine derived OM (Meyers and Ishiwatari, 1993). They revealed a complex input of OM, including marine and terrestrial origin. The chronological framework is currently been established by using a combination of techniques (²¹⁰Pb, ¹³⁷Cs and ¹⁴C).

Pyrolysis gas chromatography-mass spectrometry (Py-GC/MS) of bulk and decarbonized sediments were carried out in these materials, owing to their complexity, are difficult to analyse by way of conventional methods.

Pyrograms are dominated by *n*-alkanes, polysaccharides and lignin derived compounds, which are typically found in pyrolysates of estuarine sediments. The lack of an odd-to-even predominance of *n*-alkanes (average CPI 0.99 ± 0.22) points to a significant anthropogenic contribution (Fig 1). The ratios C_{17}/C_{27} and short/long ratio of *n*-alkanes increase down-core, which could indicate an increase in the marine signature. However

confirmation is not possible due to interferences of anthropogenic inputs. The low values of $\Sigma C_{11}-C_{33}/C_{16}$ parameter (≤ 15) could indicate the presence of petroleum pollutants with a possible partial recovery in recent times.

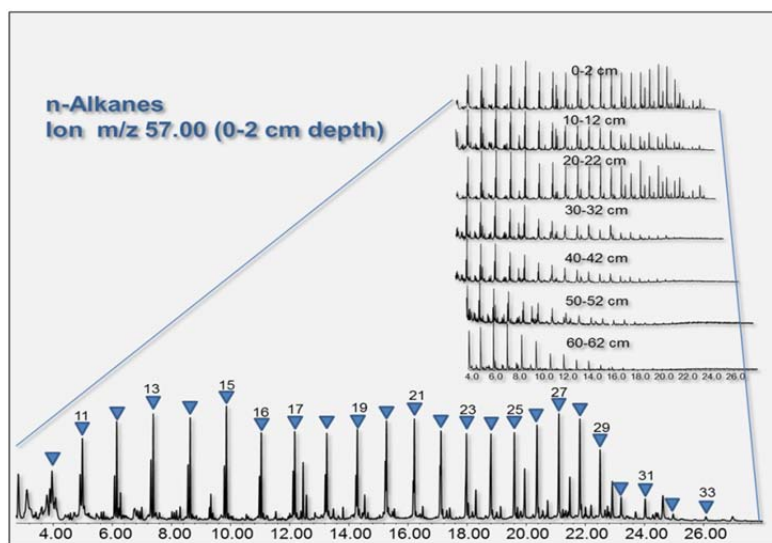


Figure 1. Relative abundances of *n*-alkanes (%) according to Py-GC/MS Selected Ion Chromatogram (m/z 57)

Polycyclic Aromatic Hydrocarbons (PAHs) are present through the sediment profile, they are related to combustion of fossil fuels and release of oil products. The abundance of Linear Alkyl Benzenes in all the sediment sections is indicative of inputs from waste outfalls, surfactants or detergents.

REFERENCES

- López-Capel E., De la Rosa, J.M, González-Pérez, J.A., González-Vila, F.J., Manning, D., 2006. Elucidation of different forms of organic carbon in marine sediments from the Atlantic coast of Spain using thermal analysis coupled to isotope ratio and quadrupole mass spectrometry. *Organic Geochemistry* 37, 1983–1994.
- Hedges, J.I., Keil, R.G., 1999. Organic geochemical perspectives on estuarine processes: sorption reaction and consequences. *Marine Chemistry* 65, 55–65.
- Meyers, P.A., Ishiwatari, R., 1993. Lacustrine organic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediments. *Organic Geochemistry* 20, 867–900.