Sources and depositional patterns of sedimentary organic matter in the Mira Estuary (SW Portugal)

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Salt marshes represent a depositional zone in the transition between terrestrial and marine domains. Organic matter (OM) in these environments is usually composed by a complex mixture of terrestrial and marine residues originated from the decomposition of vegetal, animal and microbial organisms. In May 2010 sediment cores of about 1 m depth were collected on the high-marsh of "Xisto". This salt-marsh is located in the South border of the Mira estuary, close to Vila Nova de MilFontes (SW Portugal). This research intends to evaluate if shifts observed in OM composition are informative about its sources and of possible climatic and environmental events occurred in the area. Sedimentary OM was characterized using complementary techniques including elemental analysis (C, N, S), and Analytical Pyrolysis (Py-GC/MS).

Total organic carbon (TOC) ranged from 5.7 % (0-2 cm) to 1.8 % (40-42 cm). TOC decreased from the surface until 22 cm being consistent with the effects of diagenesis. From 22 to 32 cm and from 52 to 100 cm increased, probably as result of biological accumulation of high marsh biota. From 32 to 52 cm depth, TOC reached minimum values. Similar trends were observed for the total nitrogen (TN) content, which varies from 0.6 % (0-2 cm) to 0.2 % (40-60 cm). The positive correlation between TOC and TN ($r^2 = 0.88$) suggests that N is predominantly fixed in the OM. The atomic C_{org}/N ratio provides valuable information about organic sources. Because of the high peptide content, typical C_{org}/N values for fresh marine biogenic OM vary between 4 and 10, whereas typical ratios for terrigenous OM from vascular plants are usually around 20 and higher due to high contents in cellulose, lignin and tannins. The C_{org}/N ratios in the core ranging from 9.4 (40 cm) to 14.8 (80 cm) indicate a predominantly marine contribution to the sedimentary OM with minor OM terrestrial contributions. The increase of the C/N ratios at deeper sections of the core may indicate a greater input from terrestrial OM, however a preferential degradation of marine OM cannot be ruled out. Total S contents increased in sections deeper than 60 cm (max 3 %, 90-92 cm). Consequently very low C_{org}/S values are found below 60 cm indicating the occurrence of reducing depositions conditions.

Total ion current (TIC) of the pyrolysis chromatograms were dominated by the presence of *n*-alkane/alkene pairs (C_8-C_{32}). The lack of an odd to even predominance in the *n*-alkane series, added to the no predominance of high molecular weight homologues may be related to the presence of distinct sources to the sediment such as marsh vegetation aquatic macrophyta, microalgae or sea grasses indicating a low contribution of terrestrial OM through the core. Polysaccharide derived products were abundant, but presented a noteworthy reduction with depth, probably due to higher degradation rates. Lineal fatty acids (FAs; C_{14}-C_{28}) with a maximum at C_{16} and even-C number predominance were present. Pyrolysis has major limitations in the detection of FAs due to the incompatibility with the apolar columns used in GC and to secondary reactions that occur at elevated temperatures, so they were detected in low relative abundance. These compounds have been assigned to algal and bacterial OM. A homologous series of *n*-alkan-2-ones (methyl ketones) ranging in carbon number C_{11}-C_{29} with a strong odd-to-even predominance was detected in all the sections. Compounds derived from peptides and numerous other compounds, such as benzene derivatives were also detected. Polycyclic Aromatic Hydrocarbons were practically absent in all the sections, reflecting minimum organic pollutants influence in this area.

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