DISCERNING ORGANIC MATTER INPUTS AND DISTRIBUTION ALONG THE SALINITY GRADIENT OF A LARGE ESTUARY IN THE SW ATLANTIC

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The relative importance and the fate of different sources of OM in estuarine systems may change with shifts in physical mixing, freshwater discharge, tidal amplitude, algal productivity, sediment dispersal and deposition among other factors. As large-scale estuaries account for significant amounts of the global organic carbon buried in the oceans, they are relevant links of global biogeochemical cycles.

The Río de la Plata (RdlP) is a large estuary located on the east coast of South America. Its fluvial drainage area is the second largest basin in this continent and delivers the major freshwater discharge to the SW Atlantic Ocean. The inner estuary has an elevated concentration of suspended sediments that generates a maximum turbidity zone, which usually occurs near the bottom salinity front around the Barra del Indio shoal and is associated to deposition and re-suspension processes. The RdlP is a very productive estuary that represents an area particularly important for the global carbon budget. Here, we considered sterols and n-alcohols to evaluate the relative importance of terrestrial versus marine OM sources in surface sediments along the salinity gradient of the RdlP to assess the influence of the environmental transition on the inputs and distribution of sedimentary OM in this large estuary.

The cruise ARTEMISA1 was carried out in March 2008, during late austral summer on board the R/V Aldebaran from the *Dirección Nacional de Recursos Acuáticos* (DINARA) of Uruguay. A transect of ca. 80 nautical miles with 11 sampling stations (S1 to S11), was followed along the salinity gradient of the RdlP estuary (Figure 1). This transect was selected to cover a wide range of water depth (5 to 30 m), salinity, turbidity and primary production (Burone et al., 2013). Sediment samples were taken with a Smith–McIntyre grab, packed in pre-sterilized aluminium trays (450 °C, 4 h) and stored in the dark at -20 °C until laboratory analysis. About 10 g of dried sediment were Soxhlet extracted for 8 h with hexane/dichloromethane (1:1; v:v). The 5α-androstan-3β-ol was added before extraction as surrogate. Concentrated extracts were fractionated and purified with 15 ml of methanol by column chromatography using 5% deactivated alumina. Sterols were evaporated to dryness and derivatized to form trimethylsilyl ethers using BSTFA with 1% TMCS for 90 min at 65 ºC. The 5α cholestane was used as internal standard for quantification. Identification and quantification were performed by GC/FID and compound confirmation by GC/MS in the SCAN mode.

The salinity front with strong stratified conditions was located between stations 3 and 5. Stations 1 and 2 showed low salinity waters, while from stations 6 to 11 marine conditions prevailed (Figure 1). Total sterols and n-alcohols ranged from 0.39 to 6.13 μg g^{-1} and 0.08 to 5.82 μg g^{-1}, respectively. Overall, the distribution of n-alcohols and sterols was associated to the percentage of fine sediments (silt + clay) that diminish from the inner to the outer estuary

(Figure 1). Long chain (≥ C_{22}) n-alcohols and C_{29} sterols (campesterol, stigmasterol and sitosterol) were the most abundant suggesting a higher influence of terrestrial vegetation relative to marine sources in the RdlP sediments (Figure 1). They showed maximum concentrations in station 3 indicating deposition that may be linked to the maximum turbidity zone (Figure 1). However, high relative contribution of C_{27} sterols (cholesterol, cholestanol and brassicasterol) in stations 4 and 5 in the salinity front may be associated to high plankton productivity in this frontal zone. C_{27} sterols decreased in stations 6 and 7, and gradually increased again towards the outer estuary with marine prevalent conditions.

Lipid biomarker distribution allowed the identification of allochthonous (terrestrial) and autochthonous (marine) inputs of OM with the terrestrial contribution as the predominant one, excepting in the outer estuary. The position of the salinity front and the associated maximum turbidity zone are key control factors of the distribution of these two OM sources, and influence the deposition and/or exportation of continental OM from the RdlP estuary to the SW Atlantic Ocean.

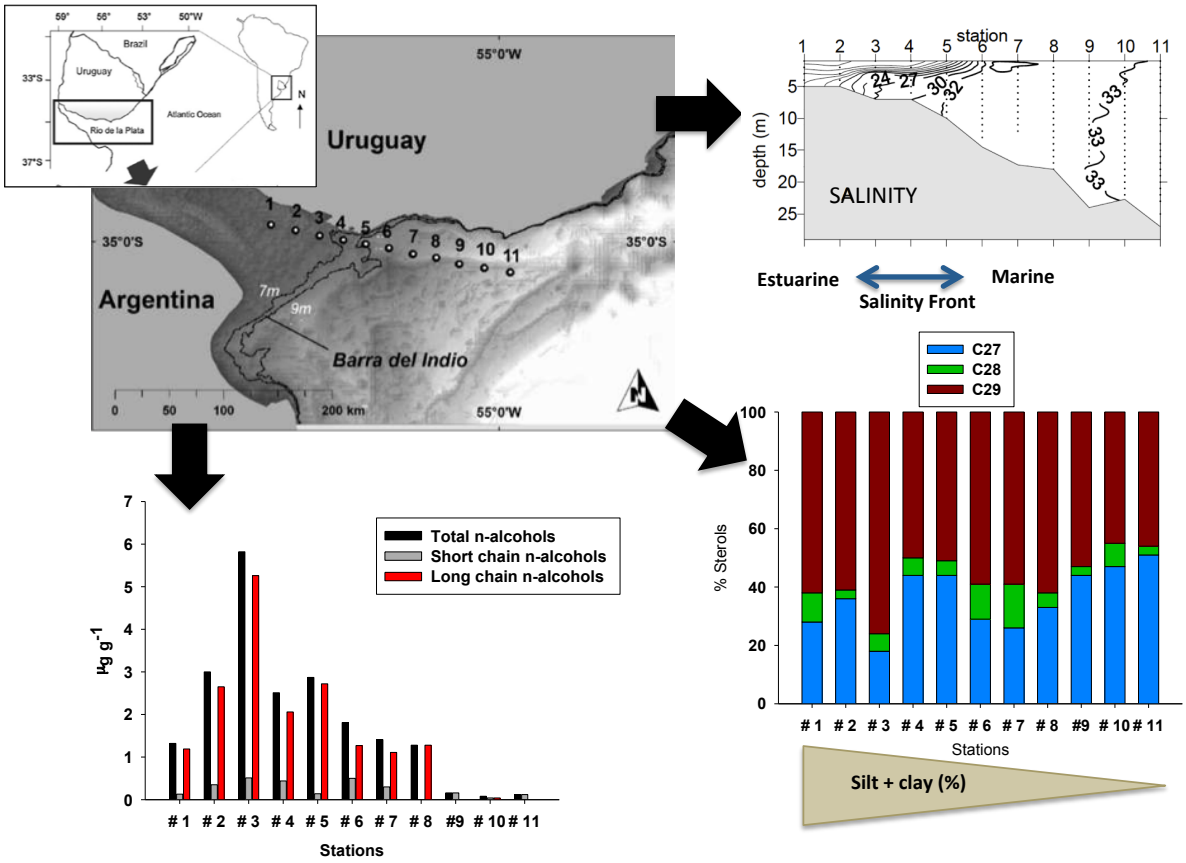

Figure 1 *Map of the study area, salinity profile, relative abundance of C_{27}-C_{29} sterols and concentrations of n-alcohols in the 11 sampling stations.*

Burone, L., Ortega, L., Franco-Fraguas, P., Mahiques, M., García-Rodríguez, F., Venturini, N., Marín, Y., Brugnoli, E., Muniz, P., Bícego, M.C., 2013. A multiproxy study along the transition between the Río de la Plata and the adjacent Southwestern Atlantic inner Shelf to assess the sediment footprint of river vs. marine influence. Continental Shelf Research 55, 141-154.