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A multiproxy study along the transition between the Río de la Plata and the adjacent South Atlantic Shelf

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Although continental shelves comprise only about 7.5 % of the total ocean bottom they represent the most important marine sink for fine-grained, land derived material in modern systems. Only 7–10% of the fluvial input is proposed to reach the deep sea (Nittrouer *et al.*, 2008). Shelves are also areas of major relevance for the global carbon budget due to their enhanced surface-water productivity. Consequently, they are important habitat for marine organisms including fishery resources. On a region scale, climatic conditions as well as hydrological and oceanic regimes are the principal responsible for sediment supply and its sedimentation.

Rivers add to the complexity of continental margin processes through their discharge of freshwater and solutes. Rivers are also the dominant suppliers of particulate material from land to sea (globally ~85–95% is fluvial sediment (Syvitski *et al.*, 2003). The largest rivers create extensive deposits near their mouths (e.g. Amazon, Ganges–Brahmaputra, Mississippi), but the combined discharges of moderate and small rivers dominate global sediment supply (Nittrouer *et al*., 2008) and, therefore, are important to the creation of continental margin stratigraphy.

Thus, fully characterize source-to-sink movement of terrigenous sediment is essential to decipher the sedimentary record. The recognition of different environments (riverine, estuarine and marine zones) and sediment depositional conditions allows the inference of climatic cycles through the Late Quaternary.

In these environments different proxies could be used for providing information on the average physicochemical conditions. Among these, proxies of terrigenous input (Al and Ti, Fe/Ca and Ti/Ca ratios, origin of organic matter ($\delta^{13}C$, $\delta^{15}N$ and C/N ratio, productivity (C_{org}, N_t, $CaCO_3$, P and Ca, Ba content, Al/Ti , Fe/Al, Ba/Al and Ba/Ti ratios; environmental

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energy (grain-size, mean diameter and sorting, and benthic foraminifera assemblages distribution as a record of the main features of the environment, can been used.
The Río de la Plata estuary, drains the second largest basin of the South American continent and constitutes the main point source of freshwater in the South Atlantic. This system entails a highly productive area acting as a CO_2 sink spot, especially during spring and summer.
The aim of this work is to characterize the environment along the environmental gradient of Río de la Plata- adjacent South Atlantic Shelf based on a multi-proxy analysis of surface sediment samples.
The Río de la Plata (Lat. 35° 00` - 36° 10` S, Long. 55° 00´ – 58° 10 W) located on the Southeast South America, covers an area of 36 x 10^3 km^2 . These river main tributaries are the Paraná and Uruguay rivers, with an annual average discharges of 16,000 and 6,000 m^3/s, respectively. It is a large-scale estuary characterized by a salt-wedge regime; semidiurnal tide with low tidal amplitude ranging from 0.4 m to 1 m; a broad and permanent connection to the sea, and high susceptibility to atmospheric forcing, due to its large extension and shallow water depth (Acha *et al*., 2008, and references therein). The position of the turbidity maximum is highly variable according to tide, river discharge and wind. The Rio de la Plata is a funnel-shaped coastal plain tidal river with a semi enclosed shelf area at the mouth and a river paleovalley on the northern coast that favours its discharge and the transport of sediment to the adjacent continental shelf (López Laborde and Nagy, 1999). The area evolved during the Late Quaternary throughout several stages related to different positions of sea level which are represented by the succession of estuarine, fluvial and coastal sedimentary environments (Cavallotto *et al*., 2004).
A transect with 11 sampling stations (S1 to S11) was made along the salinity gradient occurring in the outer region of the Río de la Plata. The cruise was carried out during late austral summer (3 – 9, March) 2008 onboard R.V. Aldebaran (DINARA). The distance between stations was 10 nautical miles (Fig.1). The water depth gradient covered a range from a minimum of 5 meters to a maximum of 30 meters.

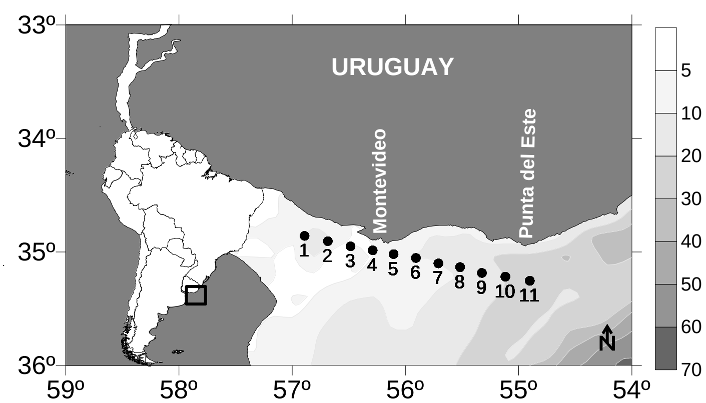

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Figure 1: Locations of the study area and sampling sites.

Water column depth, temperature and conductivity from the water column from the surface to the bottom were measured. Surface water samples were taken to assess total chlorophyll and suspended particulate matter. Sediment samples were collected using a Smith-McIntyre bottom grab sampler for the analysis of the following variables: grain size composition, grain size parameters (mean diameter and sorting), C_{org}, N_t, bulk organic $\delta^{13}C$ and $\delta\ ^{15}N$, $CaCO_3$ content, major and trace elements (Ti, Al, Fe, Cu, Cr, Ni, Zn, Ca, P and Ba).

To differentiate between biogenic and terrigenous barium from the bulk sediment composition a normative calculation was applied (Dehairs *et al*., 1980; Klump *et al*., 2000). Separate samples were taken to study the benthic foraminifera fauna. The uppermost 3 cm layer of the sediment was taken forming a volume of about 50 cm^3 per sample. Immediately after sampling, the material was stained with buffered rose Bengal dye (1 g of rose Bengal in 1000 ml of alcohol) for 48 h to differentiate between living and dead foraminifera (Walton, 1952). Foraminiferal assemblage parameters were calculated. The diversity (H, $\log_e$) was estimated by the Shannon-Wiener index, and evenness (*J'*). The species richness (*S*) was determined as the total number of species. The mean diversity ($\overline{H'}$) was obtained according to Burone and Pires-Vanin (2006).

A principal component analysis (PCA) was carried out for the ordination of sample locations in relation to environmental parameters.

To ordinate groups of stations with similar foraminiferal fauna composition, a non-metric multi-dimensional ordination (nMDS, Kruskal and Wish, 1978) was performed using the density similarity matrix, in which the Bray-Curtis similarity index was employed. In each sample the total density was considered.

In order to relate environmental to biological data (species density foraminifera matrix) and explain the biological pattern observed, the BIO-ENV procedure was applied (Clarke and Ainsworth, 1993).

A positive steep seaward salinity gradient was detected with the lowest values associated to the riverine stations S1, S2 and S3 with values of 1.7, 3.4 and 8.2 PSU, respectively, for the superficial water and 12.1, 15.9 and 27 PSU, respectively, at the bottom water. The frontal zone is represented by stations S3, S4 and S5 where the steeper salinity gradient was registered. From station S6 to S11, a practically homogenous marine water column was found. The vertical distribution of temperature showed a seaward decrease with values between 19.4 and 24 °C for the superficial water and 16.6 and 26.5 °C at the bottom. From S9 to S11 high stratification was found. The surface suspended particular matter (SPM) concentration showed a clear declining trend with the marine influence with S3-S5 showing the highest concentration values. Organic matter, chlorophyll a, and phaeopigments from the water column increased sharply from S3 to S5 reaching their maximum in this late station, and then decreased with the oceanic influence.

Grain size distribution shows a gradual increasing distribution with high percentages of silt + clay from station S1 to S8 (between 48 and 61 %) and a increase of sand contents in the more outer stations (between 99.5 and 100%). This change is accompanied by an increase in

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depth (about 7 metres). The values of the mean diameter are between 2.75 and 4.52 ϕ. The sediment is very poorly and poorly sorted between stations S1 and S8 and medium and well sorted from station S9 on.

The C_{org} values range between 0.05 and 1.25 % with the highest values in stations S5, S6 and S7. It is relevant to point out that other proxies of productivity such as N_t, P and $CaCO_3$ also show an increased sharply from station S3 to S7 associated with the frontal zone.

C/N ratios range between 2.79 and 8.60, indicating mixed origin (from station S1 to S7) and more marine origin (from station S8 to S11) of the organic matter. A similar behaviour is presented by $\delta\ ^{13}C$ isotopes showing a clear gradient with an increase in the values from the inner stations (more continental organic matter, values around -23 ‰) to the outermost (more marine organic matter, around -21‰). The correlation between Al and Ti was considered as statistically significant ($R^2 = 0.74$) allow to consider the Al as terrigenous and non-reactive. In a general way, the Ti, Al and Fe present a decreasing seaward gradient indicating more terrestrial influence in the inner stations. The same trend is observed in the other elements such as Zn, Cr and Ni as well as with de Fe/Ca, Fe/Al and Ti/Ca ratios. Consequently, the inverse behaviour is observed for the Al/Ti and Ba/Al rates, Ba and Ca values that show an increased seaward gradient. The Ba_{bio} contents and the Ba_{bio}/Ti, Ba_{bio}/Al and Ba_{bio}/Ca ratios in the surface sediments show an outward increase. By plotting Ba_{bio} against Ca it can be seen that Ba_{bio} increases linearly with the Ca.

In the whole area a total of 55 species of living benthic foraminifera belonging to the suborders (Rotaliina 39 species), (Textulariina 11 species) and (Miliolina 5 species) were registered. Also, two species of the order Thecolobosa were recorded.

The result of the nMDS ordination analysis allowed the recognition of three groups of stations highlighting an environmental gradient. Group I, bunched the more riverine stations and it is characterized by thecamoebians and *Miliammina fusca* and *Psammosphaera* sp. (agglutinated foraminifera). From station 2 on, the presence of *Ammonia tepida* (a mixholaine euribiontic species) can be observed. This sub-environment appears to be under strong influence of the Rio de la Plata waters. Group II clustered stations S6-S8 and it is represented by the *Ammonia tepida* assemblage that included other 13 hyalines species (*Boilivina* spp., *Buliminella elegantissima*, *Hopckinsina pacifica*, *Pseudononion atlanticum*, etc), one porcelanoid species (*Quinqueloculina milletti*), 4 agglutinant species and one thecamoebians species. All these species are characteristic of more estuarine-marine conditions and are typical in organically enriched environments. Group III linked the outermost stations and it is characterized by the *Buliminella elegantissima* assemblage and show the highest number of calcareous species (35). In this group it is possible to observe more marine species with the presence of some species that typically inhabit shelf environments (*Labrospira* sp., *Poroeponides lateralis*, *Nonion* sp., *Pyrgo* sp.).

Results show that at least 3 different sub-environments could be determined through the river/sea gradient in relation to geological, physicochemical and biological parameters.

The frontal zone and the turbidity front associated were characterized by peaks in organic matter, chlorophyll a, and general availability of nutrients which are responsible for the

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highest organic matter concentration and silt percentages registered in sediment especially in station S5. These characteristics create oxygen stress.

The chemical elements analysed in this work (Ti, Al, Fe, Zn, Cr, Cu and Ni) are related with terrigenous inputs except Ca and Ba which indicate marine influence from station S7 on. This probably shows the limit of the estuarine zone.

Regional Ba terrigenous value was determined (0.0031) and significant correlation between Ba_{bio} versus Ca was obtained

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