

Differentiating organic matter and its interactions with metals in a semiarid equatorial estuary under severe drought.

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The Jaguaribe River is located predominantly in the rural semiarid northeastern Brazil (NE-BR) with two climatological seasons (dry and wet). The dryer periods can turn its estuary hypersaline and negative, promoting the retention of water and materials like organic matter [1]. During this time, the organic matter retained can contribute to the bioavailability of contaminants, such as mercury, even without direct anthropogenic sources [2]. This study aimed to evaluate the dissolved organic matter quality and its interaction with different metals under a severe drought period. Then, carbon analyses, fluorescence spectroscopy, ultrafiltration technique, and determinations of metals by ICP-MS were performed. The dissolved organic carbon (DOC) and the particulate organic carbon (POC) concentrations mean were 597.0 ± 149.1 and $180.4 \pm 88.5 \mu\text{mol L}^{-1}$, respectively. They presented non-conservative mixing, with intense removal of DOC and input of POC up to salinity 7, indicating the occurrence of repartitioning reactions of OM in the estuary (Figure 1). The low ratio between POC and chlorophyll-*a* indicated that POC was predominantly phytoplankton derived. While the DOM was preponderantly composed by terrestrial-derived humic compounds, as shown by its fluorescent excitation-emission matrices and optical characteristics. Three fluorescent components (C1, C2 and C3) were identified using the PARAFAC. C1 corresponded to a mixture of humic compounds of marine and terrestrial origin, while C2 and C3 to terrestrial humic compounds. The major fraction of DOC ($80 \pm 2\%$) was truly dissolved (<1 kDa) and the colloidal fraction (>1 kDa) comprised only $6 \pm 1\%$. The metals (Sr, Al, Rb, Fe, Li, Mo, U, V, Cu, Ni, Pb, Cr, Sn) were distributed mainly in the truly dissolved phase (more than 90% of the bulk sample to each metal). Some of them (Cu, Fe, Cr and, V) correlated positively with DOC. Besides, the non-conservative reduction of metals and DOC, with salinity increase, showed DOC as an important driver of metal availability at the semiarid Jaguaribe River estuary.

[1] Dias et al. (2016). *Estuar. Coast. Shelf Sci.* 258–274.

[2] Lacerda, Marins & Dias (2020). *Front. Earth Sci.* 1 - 12.

Figure 1 - Concentrations of (a) POC and (b) DOC plotted against salinity with conservative mixing line calculated from fluvial (FL) and marine (MA) endmembers. SF station corresponded to a tidal creek impacted by shrimp farm and the AC to a tidal creek surrounded by a well-preserved mangrove area. Numbers and letters refer to the samples from temporal and spatial sampling, respectively.

