Organic matter partitioning and geochemical characteristics related to sources and processes in two Brazilian Southeast estuaries

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Constant inflow between continents and oceans directly affect coastal environments. Mixture zones amplify the material variability and intensify microorganism activities, directly increasing the organic matter recycling. The generation of microorganism biomass, forming particulate organic carbon is a fundamental contribution to carbon and energy flow for higher trophic levels. The measurement of biopolymers and specific lipid markers, as sterols, can provide a better understanding of those interactions between land and ocean, including elucidating human impacts. However, there are few works that related to lipid composition through analysis of sterols in different fraction of organic matter. This study aims to identify the origin of organic matter, through the identification and quantification of sterol markers for the particulate and dissolved material in estuaries under different hydrodynamic conditions and human impacts: Sepetiba Bay (SB) and Paraíba do Sul River (PSR) estuary, both in Southeast Brazil. The samples were collected during rainy and dry seasons in 2010 and 2011, considering tide variations and salt gradient (0 to 35 PSU). A variety of sterols found in the

dissolved material and particulate fractions points to multiple sources, indicating that the system is highly complex because of the input routes and diagenetic transformations of organic matter. Overall, the particulate fraction (average of 1330.8 and 5944.6 ng.L⁻¹ in PSR and SB, respectively), were above the concentration of sterols found in others impacted estuaries. Regarding particulate organic matter, the dissolved fraction showed a concentration of two orders of magnitude lower (average of 20.8 and 17.0 ng.L⁻¹ in PSR and SB, respectively), presenting the range of concentrations found in others works for surface waters. The β-sitosterol was predominant in both fractions, followed by stigmasterol and cholesterol being the proximate indicator of land plants and the ultimate present in heterotrophic organisms. The other sterols were found in lower concentration. Coprostanol was identified in dissolved fraction in 3 samples of RPS and 5 samples in BS, tracing faecal influence. In all samples of the particulate fraction of the two estuaries, coprostanol were present predominantly in the inner regions of estuaries, noting the presence of domestic sewage. The results indicate a high vegetation debris contribution from the drainage basins of both estuaries. Plant sterols predominate in the particulate matter and decrease with increasing salt concentration. In brackish waters, primary producer sterols are enriched in the dissolved fraction. Sterols in particulate fraction were higher at BS than RPS and almost two orders of magnitude higher than those found in the dissolved fraction. The hydrological conditions of SB define it as a retainer estuary with a higher primary production compared to PSR estuary, which can be defined as a continental material exporter estuary.

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