



Dissolved black carbon along the land to ocean continuum of Paraíba do Sul River, Brazil

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Rivers annually carry 25-28 Tg of pyrogenic dissolved organic matter (or dissolved black carbon, DBC) into the ocean, which is equivalent to about 10% of the entire land-ocean flux of dissolved organic carbon (Jaffé et al., *Science* 340, 345-347). Objective of this study was to identify the main processes behind the release and turnover of DBC on a riverine catchment scale. As model system we chose the land to ocean continuum of Paraíba do Sul River (Brazil), the only river system for which long-term DBC flux data exist (Dittmar, Rezende et al., *Nature Geoscience* 5, 618-622). The catchment was originally covered by Atlantic rain forest (mainly C3 plants) which was almost completely destroyed over the past centuries by slash-and-burn. As a result, large amounts of wood-derived charcoal reside in the soils. Today, fire-managed pasture and sugar cane (both dominated by C4 plants) cover most of the catchment. Water samples were collected at 24 sites along the main channel of the river, at 14 sites of the main tributaries and at 21 sites along the salinity gradient in the estuary and up to 35 km offshore. Sampling was performed in the wet seasons of 2013 and 2014, and the dry season of 2013. DBC was determined on a molecular level as benzenepolycarboxylic acids after nitric acid oxidation (Dittmar, *Limnology and Oceanography: Methods* 6, 230-235). Stable carbon isotopes ($\delta^{13}\text{C}$) were determined in solid phase extractable dissolved organic carbon (SPE-DOC) to distinguish C4 and C3 sources. Our results clearly show a relationship between hydrology and DBC concentrations in the river, with highest DBC concentrations in the wet season and lowest in the dry season. This relationship indicates that DBC is mainly mobilized from the upper soil horizons during heavy rainfalls. A significant correlation between DBC concentrations and $\delta^{13}\text{C}$ -SPE-DOC indicated that most of DBC in the river system originates from C3 plants, i.e. from the historic burning event of the Atlantic rain forest. A simple mixing model could largely reproduce the observed concentrations within the catchment and the land to ocean continuum. Thus, within the river system and estuary, DBC concentrations behaved mainly conservatively.