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Origin, transport and fate of the dissolved organic matter produced in the watershed of the Paraíba do Sul River, Brazil.

Jomar Marques da Silva Junior (1), Tassiana Soares Gonçalves Serafim (1), Marcelo Gomes de Almeida (1), Thorsten Dittmar (2), and Carlos Eduardo de Rezende (1)

(1) Universidade Estadual do Norte Fluminense, Campos dos Goytacazes, Brazil (jomar.uenf@gmail.com), (2) ICBM Group Marine Geochemistry, Carl von Ossietzky University, PO Box 2503 26111 Oldenburg, Germany

The Paraíba do Sul River (PSR) is an important river from Southeastern Brazil that flows through the states of São Paulo, Minas Gerais and Rio de Janeiro. The PSR is responsible for the water supply of over 14 million of the habitants. Due the human occupation and anthropic pressure, only 8% of it is original forest cover remains in the form of small fragmented patches. The remaining of the basin is mostly covered by grasses, such as pasture and sugar cane. Isotopic studies allows the monitoring of ecosystem changes and promotes specific links between ecology, land use and biogeochemical processes. We investigated the isotopic composition of the dissolved organic matter (DOM) in PSR. Our objective was to identify how extensive land use changes, from forest (C3 Plants) to pasture and sugar cane (C4 Plants), have affected river biogeochemistry of organic matter transported by PSR. Water samples were collected at 24 sites along the main channel of the PSR, 14 sites samples at the tributaries and 21 sites samples in the estuarine and marine environmental until 35km of the coast. Sampling was performed in the wet season of the 2013 and the dry season of the 2013. The fluvial and estuarine samples were processed with conventional filtration and the marine samples were processed with the cross-flow filtration. The dissolved organic matter (DOM) was isolated by solid-phase extraction (SPE) with the PPL cartridges (Styrene divinyl benzene polymer). Isotope measurements, organic carbon and nitrogen concentration were performed with a isotope-ratio mass spectrometry (Thermo Finningan). The [U+F064]13C and the [U+F064]15N values ranged from -20.0‰ and -29.0‰ and from -0.80 to 4.59 respectively, while the (C/N)a ratio varied between 8 and 41. The [U+F064]13C were depleted in 13C at the river samples from the wet season, and in the estuary and marine areas as well. The [U+F064]13C average values observed during the wet season in the PSR and in the estuarine samples are close to those recorded for the soil of the Rain Forest and mangrove species, respectively. These results suggest an input contribution of the allochthonous organic matter due to washing of the soil during the rainy season. The [U+F064]13C values found in the samples more distant from the coast showed a terrigenous organic matter input in marine environmental due the high flow. In the dry season the [U+F064]13C values showed indicated predominance of the autochthonous production. Downstream of the PSR, the [U+F064]13C and [U+F064]15N values were enriched in both seasons, showing the influence of the cover substitution from Rain Forest to pasture and sugar cane, that has more enriched values of the 13C and 15N. In conclusion, DOM transported by PSR is formed by multiple sources (a mixture of C3 and C4 plants and autochthonous production), showing that the land use in the watershed and the discharge of domestic and industrial effluents promote a qualitative change in the MOD of the water column of the river.