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# Dissolved organic matter fluorescence as a water-flow tracer in the tropical wetland of Pantanal of Nhecolândia, Brazil

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**Abstract**

The Nhecolândia is a sub-region of the Brazilian Pantanal wetland, where saline and freshwater lakes coexist in close proximity. Measurements of dissolved organic carbon (DOC) content and analysis of fluorescence excitation–emission matrices (EEM) were conducted in an effort to characterize spatial variability in concentration and source of dissolved organic matter (DOM) and to further understand the hydrochemical functioning of this complex environment. Increasing pH under the influence of evaporation resulted in an increasing DOC solubility ranging from 50 to over 300 mgC $L^{-1}$ in surface water. Spectrofluorescence characterisation indicates the presence of several families of dissolved organic matter (fulvic and humic-type and proteinaceous materials), which are related to the type of lake and its hydro–bio–geochemical functioning. Moreover, the fluorescence signatures from lake water DOM and from surrounding soil–water-extracted organic matter (WEOM) show strong similarities although some labile proteinaceous compounds disappeared during humification. Results from the characterisation of DOM and WEOM not only suggest that spectrofluorescence is a reliable technique for the tracing of water flows, but also for the marking of the origin of organic horizons in this environment.


*Keywords:* Spectrofluorecence; Organic matter; Tracing; Alkaline wetland; Pantanal; Brazil

## 1. Introduction

In most hydrochemical functioning studies, inorganic chemical tracers are used to decipher the water pathways at the landscape scale. The recent technical development for chemical and isotopic tracing have ensured significant advances in surface hydrology and hydrogeology. However, although the number of chemical elements available for the tracing is large, the number of available tracers is limited, in practice, by their interaction with the solid phases and the biological activity, which can significantly affect the information carried by the chemical elements. Moreover, many of these elements behave similarly in a given environment and their use leads to redundant information.

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Although organic matter can be quickly degraded through biological activity, its chemical diversity offers the possibility to consider its use as a tracer or a marker of water flows in some particular and favourable ecosystems. However, the difficulties in the characterisation of this organic matter constitute a major challenge for its use in hydrochemical studies.

Spectroscopic techniques are widely used to acquire a first qualitative description of complex mixtures of organic compounds. Among these techniques, molecular fluorescence has gained a strong interest in the last decades (Powe et al., 2004). When UV–Visible spectrometry informs about the light absorption pattern of a sample, fluorescence introduces a second descriptive pattern corresponding to the energy emitted in response to the excitation. This two-dimensional information enables the separate description (two different emission wavelengths) of compounds absorbing light similarly (identical excitation wavelengths). Emission scans recorded for a whole range of incrementing excitation wavelengths are used to create three-dimensional data sets called excitation–emission matrices (EEMs), representative of the total luminescence spectra. They are presented as contour maps of the fluorescence landscape with iso-intensity levels delineating various peaks. They can therefore be of great help to differentiate complex mixtures of fluorophores, based on their specific peaks. This technique has gained a lot of interest in the environmental field since Coble et al. (1990) first introduced its use for the study of dissolved organic matter (DOM) from sea waters. EEMs have since been recorded for numerous types of samples including humic acid in coral reefs (Matthews et al., 1996), coastal and deep-sea sediments (Sierra et al., 2001), landfill leachates (Baker and Curry, 2004), farm wastes (Baker, 2002), natural waters (Marhaba et al., 2000; Parlanti et al., 2002) soil extracts (Cannavo et al., 2004) and tropical wetlands (Mladenov et al., 2005). As EEMs provide a detailed overview of the environmental samples, it is also used to trace the origin of individual DOM peaks (Katsuyama and Ohte, 2002; Stedmon et al., 2003; Alberts and Takacs, 2004; Baker, 2005; Sierra et al., 2005), to monitor organic contamination (Jiji et al., 1999) or the interaction between dissolved organic matter and metals (Dudal et al., 2006).

The objective of the present work is to use the fluorescence of natural dissolved organic matter as a tracer or a marker of water flows and origins at the landscape scale. The Pantanal of Nhecolândia, Brazil, was selected for this study. This tropical wetland consts of thousands of lakes with a very contrasted range of salinity and pH but coexisting in close proximity. The contrasting environmental conditions of the Nhecolândia (wide range of salinity, of pH, of vegetation), which has been recently the support for various studies in hydro–bio–geochemical sciences, are particularly favourable for the application of DOM's fluorescence to further understand the complex hydrochemical functioning of this site.

## 2. Study site

The Pantanal wetland is a huge and still active alluvial plain located between 16° and 20° S and 58° and 55° W, with a total area of about 200 000 $km^2$ of which 140 000 $km^2$ is located in Brazil (Por, 1995). The vast tectonic depression of the Pantanal provides a gigantic natural flood control device for the storm waters resulting from torrential rainfall occurring during the wet period at the boundary between the Paraguay and Amazon basin. The plain, characterized by extremely low slopes (0.03–0.50 m/km) and altitudes between 100 and 200 m (Scott, 1991; Silva, 1984) is partially reached by summer flood (November–March). During the dry season, the floodwaters recede, resulting in a complex mosaic of grasslands and forests dotted with countless lakes and marshes.

The Nhecolândia includes about 12 000 round shaped lakes, among which Morrison et al. (2000) identified about 500 saline lakes, making up about 1% of the total surface area of the region (Fig. 1). The co-existence of freshwater and saline lakes occurs mainly in the south western, lowland portion of Nhecolândia. The landscape is constituted by special features which will be referred throughout the article: 1—The freshwater lakes are temporary lakes of the most variable forms and dimensions. They can reach approximately the 2-m depth; 2—The temporary channels are formed by the coalescence of freshwater lakes during the flooding periods. They can be several kilometres long and 10–30 m wide; 3—The saline lakes are permanent rounded salt lakes that have generally 500–1000 m in diameter and are 2–3 m deep. Most commonly, they are isolated depressions inside sand hills, and they occupy the lowest topographical position of the landscape. 4—The sand hills are narrow (200–300 m wide), elongated, 2–3 m higher than the surrounding and covered by dense savannah vegetation. These higher stripes of dry land are not submerged by superficial waters during flooding.

The ground water flows connecting the different lakes have been described by Barbiero et al. (2007). The saline lakes are surrounded by a low permeability sandy clay horizon, which rises up into the sand hill and behaves as a "threshold", provoking a flow of water usually directed towards the saline lake. During the wet season, the water table rises and moves from the freshwater lakes and