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1 **Tracing dissolved organic matter in a contrasted alkaline tropical wetland using**
2 **fluorescence spectroscopy, Pantanal of Nhecolândia, Brazil**

3

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17

18 **Abstract**

19 The Nhecolândia is a sub-region of the Brazilian Pantanal wetland, where saline and
20 freshwater lakes coexist in close proximity. Measurements of dissolved organic carbon
21 (DOC) content and analysis of fluorescence excitation-emission matrices (EEM) were
22 conducted in an effort to characterize spatial variability in concentration and source of
23 dissolved organic matter (DOM). Increasing pH under the influence of evaporation resulted in
24 an increasing DOC solubility ranging from 50 to over 300 mgC L⁻¹ in surface water.
25 Spectrofluorescence characterisation indicates several families of dissolved organic matter,
26 relatively stable in a given environment, but with contrasted signatures, which are related to
27 the type of lake and its hydro-bio-geochemical functioning. Moreover, the fluorescence

28 signature from water and from the extracts of the surrounding soil samples shows strong
29 similarities although disappearance of some labile proteinaceous compounds during
30 humification. These results on the organic matter fluorescence EEM (stability, contrasted
31 signatures and similarities between soil and related water samples) suggest that
32 spectrofluorescence is a reliable technique for the tracing of water flows, but also for the
33 marking of the origin of organic horizons in this environment.

34

35

36 **1. Introduction**

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

45 Although the organic compounds are quickly degraded by biological activity, their wide range
46 and diversity offer the possibility to consider their use as tracers or markers in some particular
47 and favourable ecosystems. However, the difficulties in the characterisation of the organic
48 compounds constitute a major challenge for their use in hydrochemical studies.

49 Spectroscopic techniques are widely used to acquire a first qualitative description of complex
50 mixtures of organic compounds. Among these techniques, molecular fluorescence has gained
51 a strong interest in the last decades (Powe et al., 2004). When UV-Visible spectrometry
52 informs about the light absorption pattern of a sample, fluorescence introduces a second

53 descriptive pattern corresponding to the energy emitted in response to the excitation. This
54 two-dimensional information enables the separate description (two different emission
55 wavelengths) of compounds absorbing light similarly (identical excitation wavelengths).
56 Emission scans recorded for a whole range of incrementing excitation wavelengths are used
57 to create three-dimensional data sets called excitation-emission matrices (EEMs),
58 representative of the total luminescence spectra. They are presented as contour maps of the
59 fluorescence landscape with iso-intensity levels delineating various peaks. They can therefore
60 be of great help to differentiate complex mixtures of fluorophores, based on their specific
61 peaks. This technique has gained a lot of interest in the environmental field since Coble et al.
62 (1990) first introduced its use for the study of dissolved organic matter (DOM) from sea
63 waters. EEMs have since been recorded for numerous types of samples including humic acid
64 in coral reefs (Matthews et al., 1996), saline soils (Cilenti et al., 2005), coastal and deep-sea
65 sediments (Sierra et al., 2001), landfill leachates (Baker and Curry, 2004), farm wastes
66 (Baker, 2002), natural waters (Marhaba et al., 2000; Parlanti et al., 2002) soil extracts
67 (Cannavo et al., 2004) and tropical wetlands (Mladenov et al., 2005). As EEMs provide a
68 detailed overview of the environmental samples, it is also used to trace the origin of
69 individual DOM peaks (Katsuyama and Ohte, 2002; Stedmon et al., 2003; Alberts and
70 Takacs, 2004; Baker, 2005; Sierra et al., 2005), to monitor organic contamination (Jiji et al.,
71 1999) or the interaction between dissolved organic matter and metals (Dudal et al., 2006).
72 The objective of the present work is to assess if a comprehensive characterisation of dissolved
73 organic matter could be used as tracer or marker of water flows and origins at the landscape
74 scale. The Pantanal of Nhecolândia, Brazil, was selected for this study. This tropical wetland
75 consists of thousands of lakes with very contrasted range of salinity and pH but coexisting in
76 close proximity. The contrasted environmental conditions of the Nhecolândia, which has been
77 recently the support for various studies in hydro-bio-geochemical sciences, are particularly

78 favourable for the application of spectrofluorescence to the discrimination and
79 characterisation of dissolved organic matter.

80

81 **2. Study site**

82 The Pantanal wetland is a huge and still active alluvial plain situated between 16° and 20° S
83 and 58° and 55° W, with a total area of about 200,000 km² of which 140,000 km² is located in
84 Brazil. The vast tectonic depression of the Pantanal provides a gigantic natural flood control
85 device for the storm waters resulting from torrential rainfall occurring during the wet period at
86 the boundary between the Paraguay and Amazon basin. The plain, characterized by extremely
87 low slopes (0.03 to 0.50 m/km) and altitudes between 100 and 200 m (Scott, 1991; Silva,
88 1986) is partially reached by summer flood (November to March). During the dry season, the
89 floodwaters recede, resulting in a complex mosaic of grasslands and forests dotted with
90 countless lakes and marshes.

91 Quaternary sediments carried from surrounding highlands cover the plain along alluvial fans,
92 built by the Paraguay river and tributaries (Del'Arco et al., 1982; Por, 1995). The
93 Nhecolândia is one of the main sub-region (27 000 km²) of the Pantanal depression, located
94 on the southern half of the Taquarí alluvial fan. The sediments are mainly sandy (95%,
95 Cunha, 1980) and the dominant soil orders are Spodosols and Entisols, both with less than
96 15% of clay in superficial and sub-superficial horizons. These soils are locally associated with
97 alkali soils (solonetz) with Na equivalent fractions higher than 15%.

98 The Nhecolândia includes about 12 000 round shaped lakes, among which Morisson et al.
99 (2000) identified about 500 saline lakes, making up about 1 % of the total surface area of the
100 region (Fig. 1). The co-existence of freshwater and saline lakes occurs mainly in the south
101 western, lowland portion of Nhecolândia. The landscape is constituted by special features
102 which will be referred throughout the article: 1- The freshwater lakes are temporary lakes of

103 the most variable forms and dimensions. They can reach approximately 2-m depths; 2- The
104 temporary channels are formed by the coalescence of freshwater lakes during the flooding
105 periods. They can be several kilometres long and 10 to 30 m wide; 3- The saline lakes are
106 permanent rounded salt lakes that have generally 500 to 1000 m in diameter and are 2 to 3 m
107 deep. Most commonly, they are isolated depressions inside sand hills, and they occupy the
108 lowest topographical position of the landscape. 4- The sand hills are narrow (200-300 m
109 wide), elongated, 2 to 3 m higher than the surrounding and covered by dense Savannah
110 vegetation. These higher stripes of dry land are not submerged by superficial waters during
111 flooding.

112 The ground water flows connecting the different lakes have been described by Barbiero et al.
113 (2007). The saline lakes are encircled by a sandy clay horizon, with low permeability, high Na
114 equivalent fraction and frequently indurate by amorphous silica. This horizon is rising up into
115 the sand hill and behaves as a “threshold”, provoking a flow of water usually directed towards
116 the saline lake. During the wet season, the water table rises and moves from the freshwater
117 lakes and upland, into the sand and over the sandy clay horizon towards the depression of the
118 saline lakes. On the contrary, during the dry season, the water table is lower and the sandy
119 clay horizon acts as a barrier against the back flow of saline water towards the fresh sandy
120 aquifer. The water flows towards the saline lakes and evaporates, and the ion contents
121 increases in the saline lakes and the shore. The specific hydrological regime explains how
122 saline and freshwater lakes having such different dissolved ion concentration, and subjected
123 to the same amount of evaporation and rainfall, coexist in close proximity. The authors
124 concluded that saline water results from present day evaporation and it is not necessary to
125 resort to inheritance from arid period during the Pleistocene (Ab’Saber, 1988) to explain the
126 presence of saline waters in some lakes of the Nhecolândia.

127 Drastic changes in the chemical profile of the water are observed at short distance, resulting
128 from the above described local flows and evaporation. The less mineralised waters
129 (freshwater lakes and temporary channels) can reach pH near to 5.5, and electrical
130 conductivity about 0.02 mS.cm^{-1} . They have a carbonate-chloride and sodic-potassic chemical
131 profile. On the other hand the most mineralised waters (saline lakes and surrounding
132 watertable) have pH values ranging from 9 to 10.5, an electrical conductivity from 4 to 20
133 mS.cm^{-1} and a carbonate and sodic chemical profile. In addition, it was verified a significant
134 decreasing of Ca^{2+} and Mg^{2+} activities in the most mineralised waters (Barbiero et al., 2002,
135 2007). Two independent processes have been identified as responsible for the geochemical
136 control of Ca and Mg contents as the solution become more saline. One is the formation of
137 Mg-calcite, and the other one is the precipitation of Mg-silicates, namely stevensite and
138 saponite.

139 The tropical climate is of Aw type according to Koeppen's classification, with a mean annual
140 temperature about 22°C and mean annual precipitation about 1000 mm mostly concentrated in
141 summer (December to March). The mean annual evapotranspiration is around 1400 mm (Por,
142 1995; Alvarenga et al., 1984) resulting in an annual hydrological deficit of about 400 mm. At
143 the local scale, the strong spatial variability of temperature and humidity according to land
144 cover type (saline water, sand, savannah vegetation and grassland) induce a breeze system
145 with diurnal and nocturnal alternation between the saline lake and the sand hills, increasing
146 significantly the evapotranspiration (Quénol et al., 2005).

147

148 **3. Material and methods**

149 *3.1. Fieldwork and Sampling*

150 The study was carried out at the Nhumirim experimental farm, which is known to be
151 representative of the Nhecolândia's ecosystem. The wetlands selected for this study are

152 located between 18° 57' and 18° 59' S and 56° 37' and 56° 40' W. Samples have been
153 collected in 6 waterbodies: 3 saline lakes, called Salina do Meio (SM), Salina do Oito (SO)
154 and Salina da Ponta (SP), 1 lake with intermediate electrical conductivity called Salitrada
155 (SL) and 2 freshwater lakes called Baia da Sede (BS) and Banhado (B). These lakes were
156 selected so as to cover a large range of pH and conductivity. The distribution, shape and size
157 of the lakes is presented on Fig. 1. Each lake exhibits special feature which will be used in the
158 discussion. SM is a permanent saline lake with regular round shape and about 600 m in
159 diameter. The electrical conductivity is regularly recorded since 1998 and ranged from 2.5
160 $\text{mS}\cdot\text{cm}^{-1}$ during the rainy season to 15 $\text{mS}\cdot\text{cm}^{-1}$ at the end of the dry season. SP is a permanent
161 saline lake, which usually presents an electrical conductivity around 1/3 of that of SM. SO has
162 a shape of “8” delimiting two units. The eastern part is permanent with EC values showing a
163 large range from 2 $\text{mS}\cdot\text{cm}^{-1}$ during the rainy season and up to exceptional values of 75 $\text{mS}\cdot\text{cm}^{-1}$
164 during the driest period. The western part of the lake is occasionally drying during the dry
165 season. A detailed geophysical study have revealed a seasonal subsurface entrance of
166 freshwater into the western part of SO during the flooding period. The saline lakes are
167 delimited by a white sandy beach induced by the high conductivity and the alkaline pH
168 (above 9) of the water preventing from the development of vegetation. However, in the
169 western part of SO, a grass vegetation is temporary developing down to the lake, when the
170 freshwater is flowing in subsurface towards the saline lake. Microalgae are permanently (SM
171 and SP) or periodically (SO) developing in the saline lakes (Souza Santos et al., 2004;
172 Medina-Júnior and Rietzeler, 2005). Low redox conditions have been recorded ranging from
173 -180 mV to $+150\text{ mV}$ in the water, and from -370 mV to -200 mV in the sediment of these
174 saline lakes (Barbiero et al., 2007).

175 Among the non permanent freshwater lakes, B is located along a temporary channel whereas
176 BS is surrounded by “sand hills” with dense savannah. SL is supposed to be a former saline

177 lake, which has recently desalinated. Its electrical conductivity is monitored every year since
178 1998 and shows a decreasing trend from about 1.5 to 0.5 mS cm⁻¹. Redox conditions are
179 ranging from +150 mV to +380 mV in the water and about +200 mV in the sediments of the
180 freshwater lakes. The depressions of B, BS and SL are covered by a grass vegetation and the
181 lakes are temporarily occupied by floating and rooted emergent aquatic vegetation during
182 flooding (Costa and Telmer, 2006).

183 Samples were taken in June 2006, i.e. at the beginning of the dry season, in each lake in order
184 to estimate the internal variability of each system (saline: 23 samples; intermediate: 7
185 samples; freshwater lakes: 4 samples). Temperature (T), electrical conductivity (EC), redox
186 (Eh) and pH were determined in the field before samples were filtered, collected in pre-
187 washed polyethylene bottles and poisoned with HgCl.

188 Soil samples were taken in excavated pits around SM and SL in order to compare the soil
189 organic matter with the DOM, to check for similar origins, and to estimate to which extent the
190 organic matter is affected during the humification process. Both soil and water samples were
191 kept frozen and stored in the dark until analyses within 30 days.

192

193 *3.2. Laboratory work*

194 Soil-water extracts: For soil samples, a solution was extracted from a paste made of soil-water
195 in a 1:5 weight ratio, after agitation (1 hour). The extracted solution was filtered through pre-
196 combusted Whatman 2V glass fibre filters. The filtrate was subsequently passed through 0.45
197 µm nylon filters.

198 DOM analysis: Samples (5ml) were initially bubbled in acidic conditions in order to remove
199 inorganic carbon. Dissolved Organic Carbon was quantified by combustion at 550°C using a
200 Shimadzu TOC-meter (5050A fitted with laser CO₂ detector).

201 Fluorescence emission analysis: fluorescence data acquisition was performed using a Perkin-
202 Elmer LS-55 Luminescence Spectrometer equipped with the FL Winlab Software. Excitation-
203 Emission Matrices were collected every 10 nm over an excitation wavelength range of 200 -
204 600 nm, and a scan speed set at 1200 nm per min.

205

206 **4. Results**

207 *4.1. Dissolved organic matter contents*

208 The surface water DOC concentrations are high with a mean value reaching 192 mg.L⁻¹, and a
209 standard deviation of 118 mg.L⁻¹, i.e. a coefficient of variation of about 61%. Large variations
210 are observed depending upon the sampling location. Mean DOC values and standard
211 deviation for each lake are plotted on Fig. 2. Three groups are easily discriminated. The first
212 one consists of freshwater lakes (SL, B and BS) with low DOC contents. The pH values are
213 ranging from 6.6 to 7.6 and conductivity from 0.15 to 0.5 mS.cm⁻¹ (Fig. 3). The second group
214 consists of SO and SP, with higher electrical conductivity (1.5 to 2 mS.cm⁻¹) and pH (8.6 to
215 9). The third one is SM, which has the highest pH values (9.6 to 9.8) and conductivity (3.5 to
216 4 mS.cm⁻¹).

217 Examples of 3D-EEMs for the studied surface waters can be seen on Fig. 4 to 7. The results
218 presented in Table 1 show that the type of EEM is contrasted between the different
219 environments although the fluorescence peak positions were identical in one given waterbody,
220 indicating low variability in the type of dissolved organic matter. In lake B, although low
221 DOC have been recorded, high fluorescence intensity is observed (Fig. 5), suggesting the
222 presence of humified organic matter, i.e. humic acids with high molecular weight and hardly
223 degradable by biological activity. The peak positions (λ_{ex} / λ_{em}) were estimated as
224 220 / 430 nm and 335 / 430 nm.

225 The fluorescence emissivity ($F/[DOC]$) is much lower in SL (Fig. 4), where also low amounts
226 of dissolved organic matter were detected (Table 1). It suggests that the organic matter
227 consists likely of small stable fulvic acids.

228 The type of EEM observed in SM (Fig. 6) is clearly different from the previous ones, and in
229 particular with two peaks observed at 230 / 340 nm and 290 / 350 nm, i.e. with emission
230 domain typical of protein-like substances emphasising intense microbial activity. The same
231 type of EEM was observed at SO and SP lakes, which appears therefore representative of the
232 saline lakes.

233 Two different EEM signatures have been obtained in SO, opposing samples from the eastern
234 part of the lake with EEMs similar to that of other saline lakes, and samples from the western
235 part where the proteinaceous peaks are not detected, leading to an EEM similar to that
236 observed with SL samples (Fig. 7).

237

238

239 *4.2. Particulate organic matter contents.*

240 The results of soil-water extracts from samples taken around SM and SL are presented on Fig.
241 8. A significant difference in the DOC extracted from SM and SL is obtained and the
242 proportion of DOC found from the water of the corresponding lakes (SM and SL) are
243 respected (Fig. 2 and 8). EEMs show similarities between DOC from water and from SM soil
244 extracts (Fig. 6 and 9), with two peaks at about 270 / 460 nm and 380 / 450 nm, whereas the
245 peaks previously identified at 230 / 340 nm and 290 / 350 nm have disappeared. Both DOC
246 and fluorescence are high.

247 EEMs obtained after soil-water extraction from sediments around SL are very similar to
248 EEMs obtained directly from collected water samples (Fig. 4 and 10) showing excitation-
249 emission with the same wavelengths.

250

251 **5. Discussion**

252 The results obtained on the sampled lakes emphasized the interaction between inorganic and
253 organic chemistry. A previous study carried out at the regional scale have shown a unique
254 geochemical family of water evolving currently in an alkaline manner under the influence of
255 evaporation (Barbiero et al., 2002). The geochemical composition changes from the weakly
256 mineralised waters that flood the region during the rainy season, to the strongly mineralised
257 and alkaline one in the saline lakes. The increase in the pH value favours the dissolution of
258 organic matter and consequently high DOC contents are found there (average DOC values in
259 saline lakes of $262 \pm 118 \text{ mg.L}^{-1}$). Basic pH are known and used to dissolve natural organic
260 matter and such high concentrations are therefore not surprising. Because the increases in the
261 pH value is due to the evaporation process, these high DOC contents are also directly related
262 to high electrical conductivities (Fig. 3). Moreover, the dissolved organic matter mainly
263 consists in ionisable compounds due to the presence of a wide variety of oxygen containing
264 functional groups. Usual pKa values for natural organic matter are determined by the two
265 most abundant functional groups and are 4.7 (carboxyl group) and 10 (phenol group).
266 Consequently, at the observed pH values the dissolved organic compounds are mostly anionic
267 and are also partly contributing for the high electrical conductivity.

268 Along the concentration process of the water, three systems have been differentiated (fresh,
269 intermediate and saline) and each shows a specific and contrasted type of dissolved organic
270 matter, which is the result of physical-chemical and biological processes. In the saline-
271 alkaline systems, that have not recently been fed by freshwaters (sampling was performed
272 after a cumulative rainfall of 4 mm over three months and temperature averaging 30°C), the
273 biological activity is strongly dominated by micro-algal vegetation as emphasized by a green
274 colour clearly noticed during sampling in these stagnant waters. This is in line with the strong

275 presence of protein-like material observed from the fluorescence excitation-emission matrices
276 of the saline lake waters (see Figure 6 and Table 1). Peaks at $\lambda_{\text{ex}} 230 - \lambda_{\text{em}} 350$ and $\lambda_{\text{ex}} 280 -$
277 $\lambda_{\text{em}} 350$ nm have been related to the presence of the tryptophan and tyrosine (the two aromatic
278 amino-acids) in proteins (Baker, 2002). Two aspects of the saline ecosystem contribute to the
279 presence of labile proteinaceous material. On the one hand, the high algal activity
280 permanently supplies such proteinaceous material, which is maintained by the fast turn-over
281 in the biological cycle. On the other hand, the organic matter arising from micro-algae,
282 consisting mainly of Cyanophytes, Chlorophytes, Chrysophytes and Euglenophytes (Souza
283 Santos et al., 2004), has a low polymerisation rate with low molecular weight and therefore is
284 easily degradable by the biological activity. The high velocity of organic matter degradation
285 induces very reducing conditions, and the absence of oxygen could also explain the
286 persistence of labile proteinaceous material. The strong microbial activity seems to be a
287 peculiarity of the saline lakes.

288 The input of freshwater in this system has interesting implications regarding its
289 biogeochemical functioning. These implications are revealed in SO, where such an entrance
290 has been detected at the west end of the lake (Fig. 1). The freshwater has a pH value around
291 6.8 and an electrical conductivity of about 60 to 80 $\mu\text{S}\cdot\text{cm}^{-1}$. Samples from the lake taken in
292 this area allow us to observe the evolution: decrease in pH (7 instead of 8.8 in average for the
293 rest of the lake), decrease in DOC content (120 mg L^{-1} instead of about 250 mg L^{-1} in average
294 for the rest of the lake) and total disappearance of the proteinaceous fluorescence peaks (Fig.
295 7). Only the longer wavelengths peaks ($\lambda_{\text{ex}} 220 - \lambda_{\text{em}} 425$ and $\lambda_{\text{ex}} 330 - \lambda_{\text{em}} 440$ nm) are still
296 present, showing a more stable type of organic matter (Baker & Curry, 2004). This behaviour
297 is comparable to the one observed in SL (Fig. 4 and Table 1), which is intermediate to the
298 freshwater lake type. The similarity in the EEMs between SL and the west end of SO is in

299 agreement with the 8-year salinity monitoring carried out in SL that suggests a former saline
300 lake currently following a dynamic of de-salinisation.

301 The freshwater lake B is characterised by neutral pH freshwater, with high fluorescence in the
302 longer wavelengths (Fig. 5) corresponding to highly stable “humic-type” aromatic material
303 (Parlanti et al., 2002). In this system, no algal development is observed, and vegetation is
304 found all around, which contributes to the lignin-type compounds found in the fluorescence
305 excitation-emission matrices (Sierra et al., 2005). The higher redox values and the slow
306 humification of the polymerised organic matter favour a fluorescence with peaks on a wider
307 wavelengths range.

308 The stability of the DOM signature in each system is emphasized by the data from the 34
309 samples presented in table I. The stability suggests that the use of the spectrofluorescence
310 technique is relevant to trace the origin of the organic matter in this apparently complex
311 ecosystem.

312

313 *Particulate versus dissolved organic matter*

314 Several modes of organic matter accumulation are possible in the Pantanal environment,
315 namely simple sedimentation in lakes with various pH-EC conditions, burying of former
316 topsoil horizon with organic matter of various origin, migration of dissolved organic matter
317 under alkaline conditions and accumulation due to a pH-barrier or because of intense
318 evaporation. Although the spatial variations in the pH values seems to have a major influence
319 in the control of DOC content, the nature of the organic matter could be different according to
320 its origin.

321 From a quantitative point of view, the dissolved organic matter in the soil water extracts
322 confirms the results described in the water samples, i.e., higher values are observed in extracts
323 from alkaline systems than from freshwater systems. It suggests that part of the organic matter

324 from the sediments (organic acids with low molecular weight) can be easily remobilised by
325 the water during the flood period.

326 Moreover, and from a qualitative point of view, strong similarities are detected in the
327 fluorescence signature of the organic matter between samples from soil extracts and water. In
328 both water and soil-water extracts from SL, the organic matter consists of small stable acids,
329 probably fulvic acids or association of phenolic acids, in low quantity and with low
330 fluorescence emissivity. In SM, the similarity between water and soil water extracts is still
331 observed, except for the most labile proteinaceous material. It seems that when the lake is
332 drying, the oxygenation of the sediment affects only a part of the fluorescence signature
333 consisting of the labile compounds but preserve the non proteinaceous material. The organic
334 matter collected around the lakes maintained the signature of its origin. As a consequence, a
335 certain persistence of the organic matter signature is occurring and it emphasises the relevance
336 of the spectrofluorescence technique to trace the origin of the organic matter.

337

338 **6. Conclusion**

339 The shallow groundwaters of the Nhecolândia are relatively depleted in calcium with respect
340 to alkalinity and evolve into high alkalinity and high pH as solutions become more saline
341 under the influence of evaporation. The increasing pH results in an increasing solubility of the
342 organic matter, and consequently to a strongly structured distribution of the organic matter in
343 the landscape. The freshwater lakes surrounding by herbaceous vegetation have low dissolved
344 organic matter contents, whereas the alkaline lakes surrounded by a sandy beach sterilised by
345 high pH and conductivity have much higher dissolved organic matter contents. The
346 spectrofluorimetric characterisation shows several families of organic matter, which are
347 relatively stable in space. The freshwater environments exhibit humic acids with strong

348 fluorescence, whereas the saline alkaline environments have very different functional groups
349 and proteinaceous material.

350 The organic matter contents and its characteristics are closely related to the biological
351 functioning of the waterbodies. It is also noticeable that the organic matter sampled around
352 and in the lakes showed similar fluorescence characteristics, highlighting a certain stability of
353 the criteria for organic matter characterisation. Only some labile functional groups, such as
354 proteins, disappear during the maturation in the soil.

355 Because of the stability of the parameters used for the discrimination, spectrofluorescence is a
356 reliable technique for the tracing of water flows, but also for the marking of the origin of
357 organic horizons.

358 The study reveals the influence of the herbaceous vegetation around and in freshwater lakes
359 and algal vegetation in saline lakes, but the influence of the forest in the sand hill has not been
360 detected. Further study should focus on this point in order to better understand the migration
361 of carbon in this environment.

362 Previous study in this area have shown a strong spatial heterogeneity in the inorganic
363 chemistry attributed to physico-chemical processes. The results of the present study also show
364 the heterogeneity in the distribution of the organic matter, but attributed to the interactions
365 between physico-chemical conditions and the biogeochemical functioning of the landscape
366 units.

367

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374

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498 Fig. 1 : Aerial view of the study site (dry season) : sampled waterbodies are SM (Salina do
499 Meio), SP (Salina da Ponta), SO (Salina do Oito), SL (Salitrada), B (Banhado) and BS (Baia
500 da Sede). The arrow denotes the seasonal entrance of freshwater into SO.

501

502 Fig. 2. Dissolved Organic Carbon from the studied lakes: SM = Salina do Meio, SO = Salina
503 do Oito, SP = Salina da Ponta, SL = Salitrada, BS = Baia da Sede, B = Banhado).

504

505 Fig. 3 : Relationship between Dissolved Organic Carbon and Electrical Conductivity of the
506 studied lakes.

507

508 Fig. 4 : Excitation-Emission Matrice of the lake Salitrada (SL) - Note the low reactivity of
509 the organic matter.

510

511 Fig. 5 : Excitation-Emission Matrice of the lake Banhado (B) - Although the DOC content is
512 low, note the high reactivity of the organic matter.

513

514 Fig. 6 : Excitation-Emission Matrice of the lake Salina do Meio (SM) – Note the
515 fluorescence at about $\lambda_{ex}=230\text{nm}$ and $\lambda_{ex}=290\text{nm}$ corresponding to proteinaceous material.

516

517 Fig. 7 : Excitation-Emission Matrices of the lake Salina do Oito (SO) showing the differences
518 between the eastern saline part of the lake (b) and the western part (a) where an entrance of
519 freshwater have been detected.

520

521 Fig. 8 : Organic Carbon contents from soil-water extracts in the Salina do Meio (SM) and
522 Salitrada (SL) lakes.

523

524 Fig. 9 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salina do
525 Meio (SM) – Note the similarity with Fig. 6 and disappearance of peaks of proteinaceous
526 material.

527

528 Fig. 10 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salitrada
529 (SL) – Note the similarity with Fig. 4.

530

531 Table 1. Dissolved organic matter's characteristics

532

533

Figure

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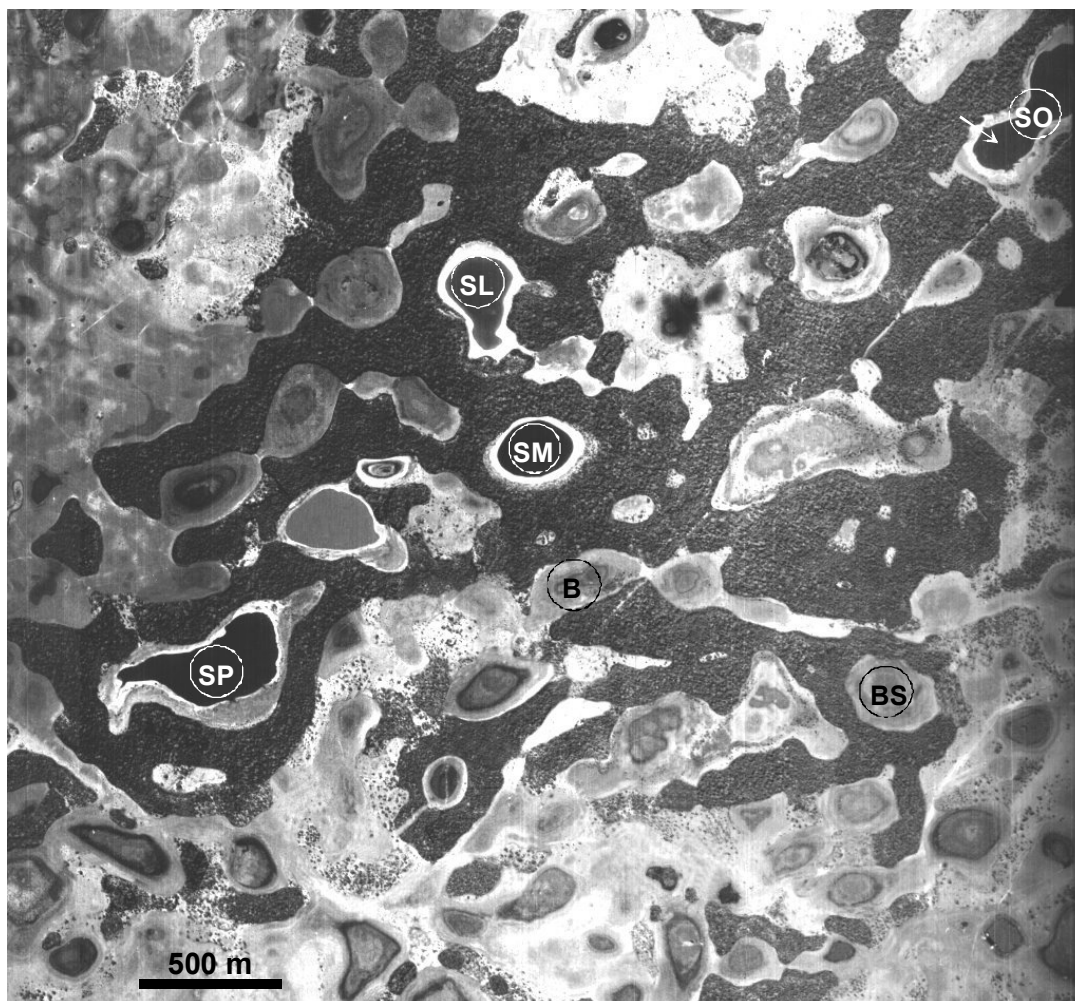


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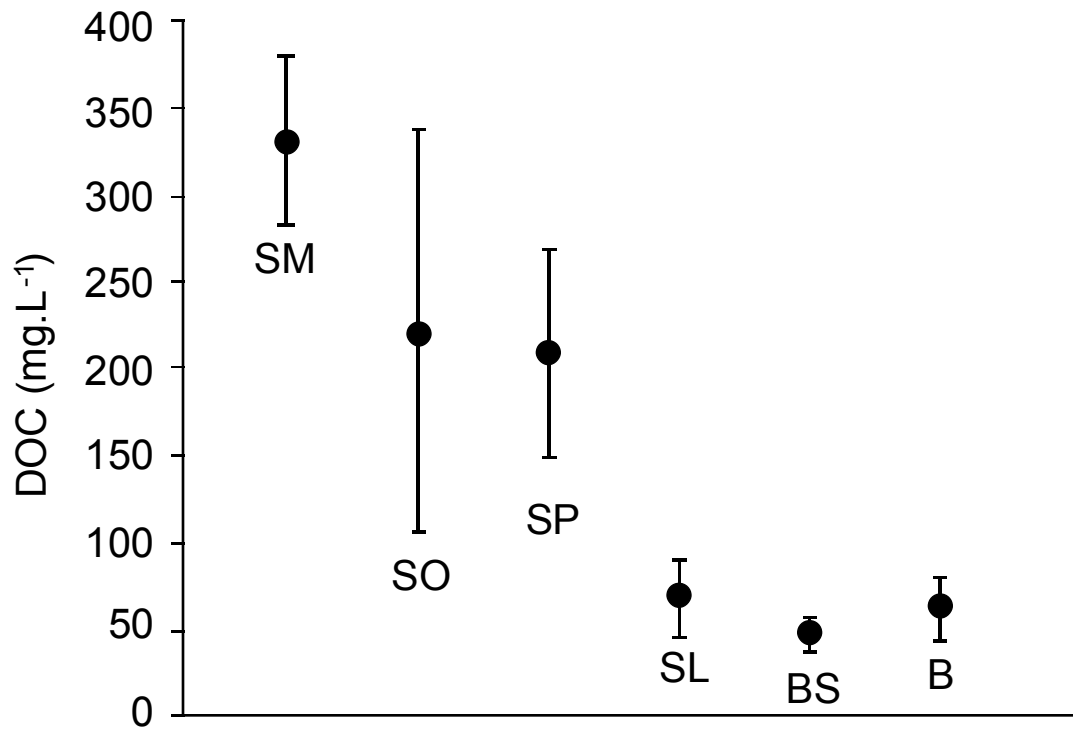


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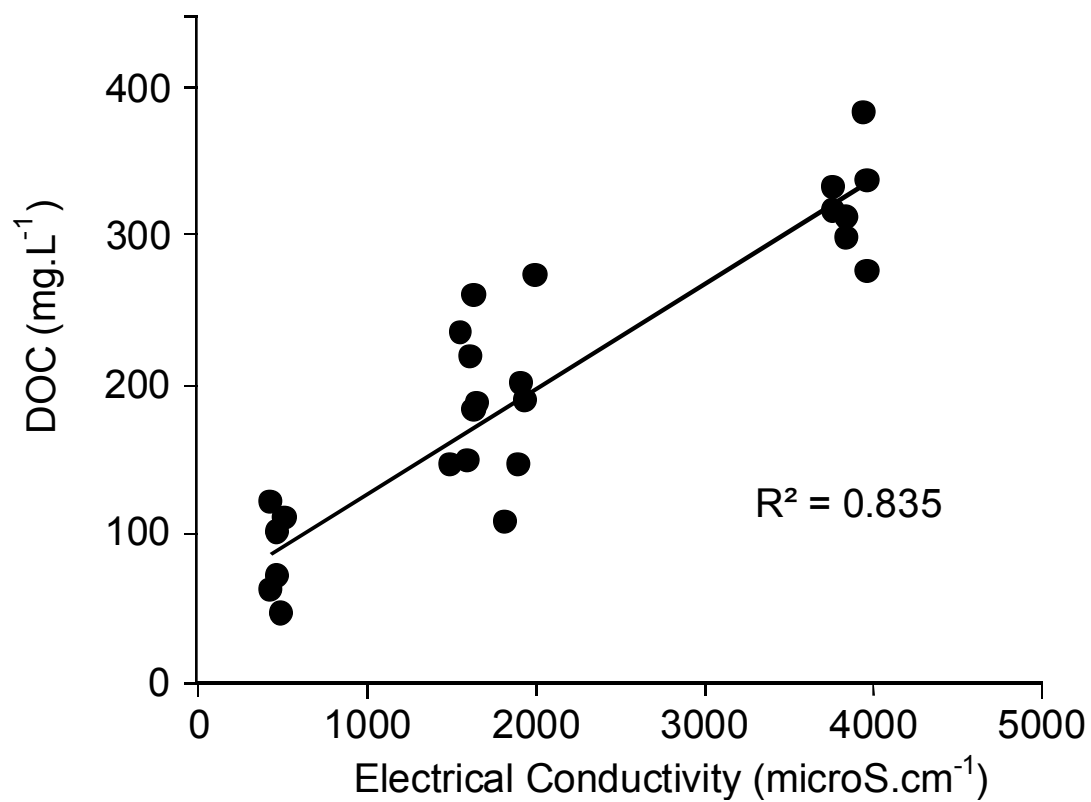


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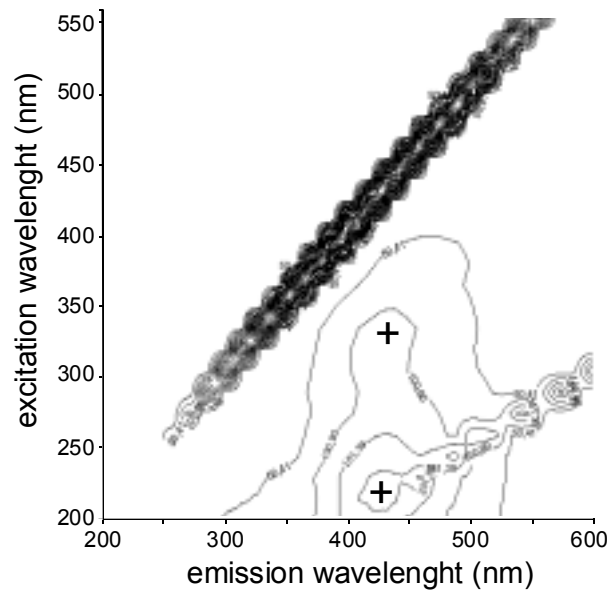


Fig. 4 : Excitation-Emission Matrice of the lake Salitrada (SL) - Note the low reactivity of the organic matter.

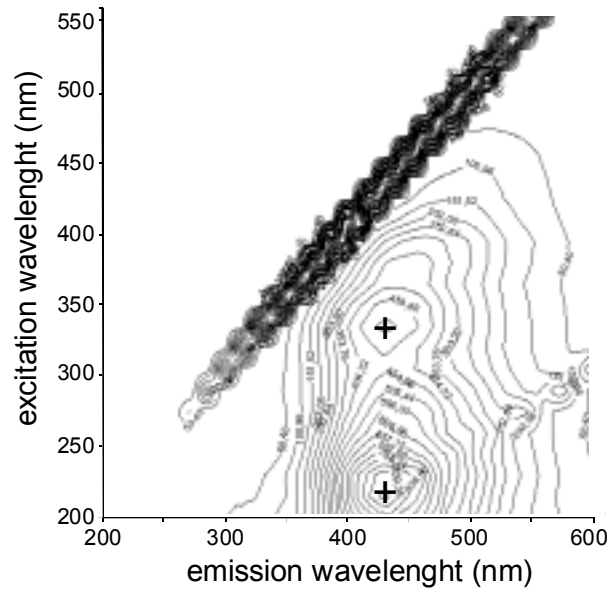


Fig. 5 : Excitation-Emission Matrice of the lake Banhado (B) - Although the DOC content is low, note the high reactivity of the organic matter.

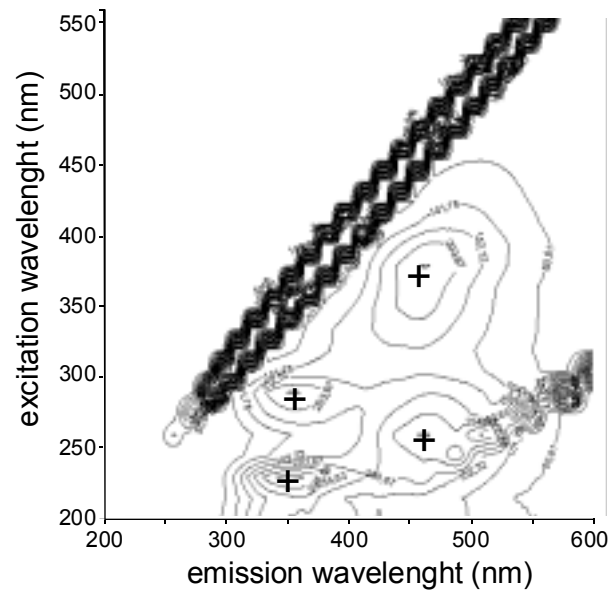


Fig. 6 : Excitation-Emission Matrix of the lake Salina do Meio (SM) – Note the fluorescence at about $\lambda_{ex}=230\text{nm}$ and $\lambda_{ex}=290\text{nm}$ corresponding to proteinaceous material.

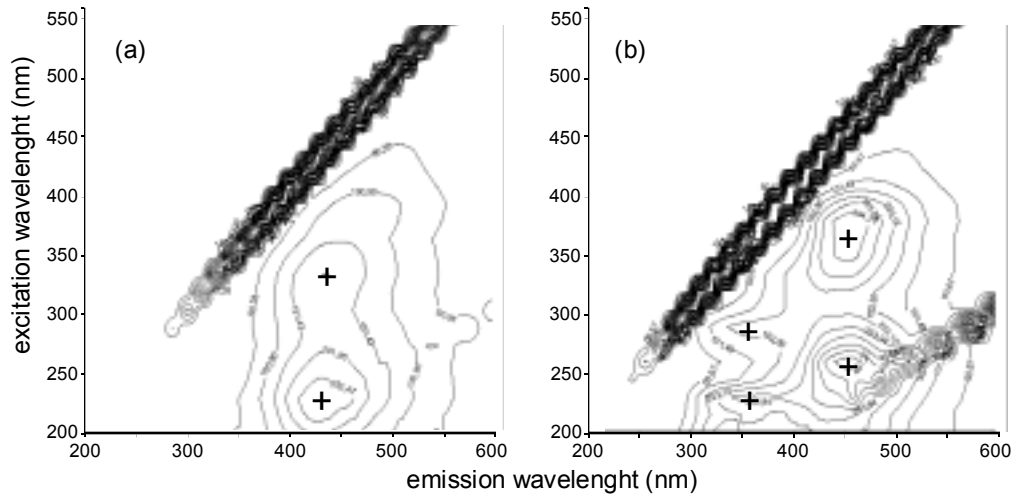


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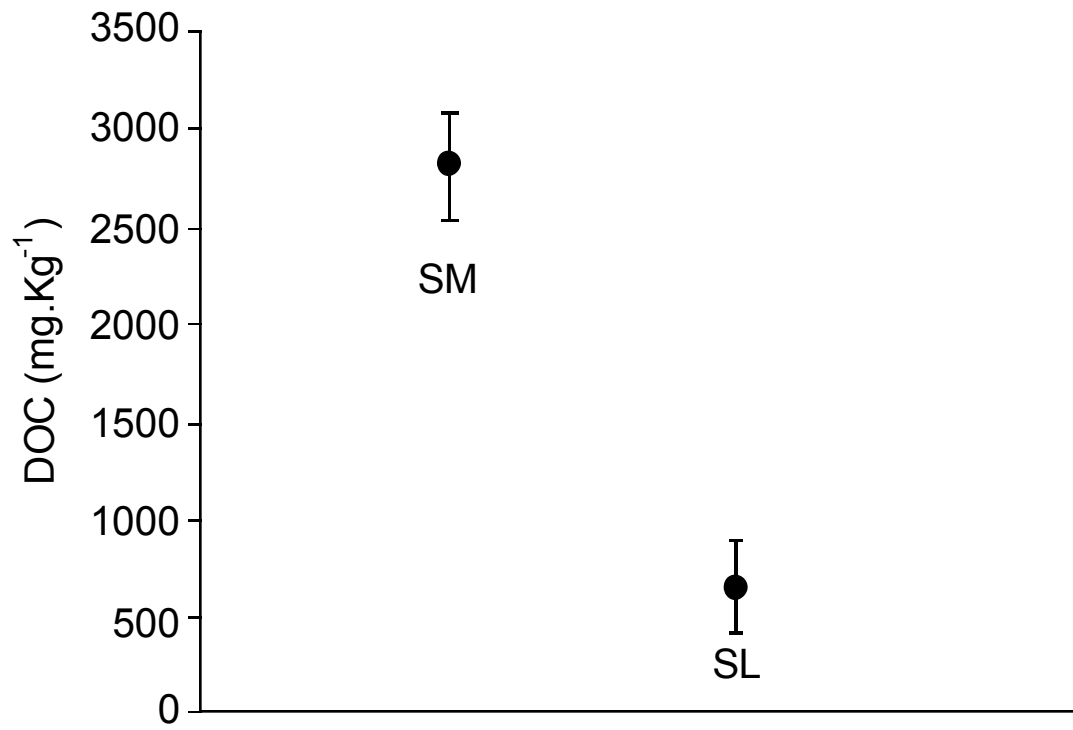


Fig. 8 : Organic Carbon contents from soil-water extracts in the Salina do Meio (SM) and Salitrada (SL) lakes.

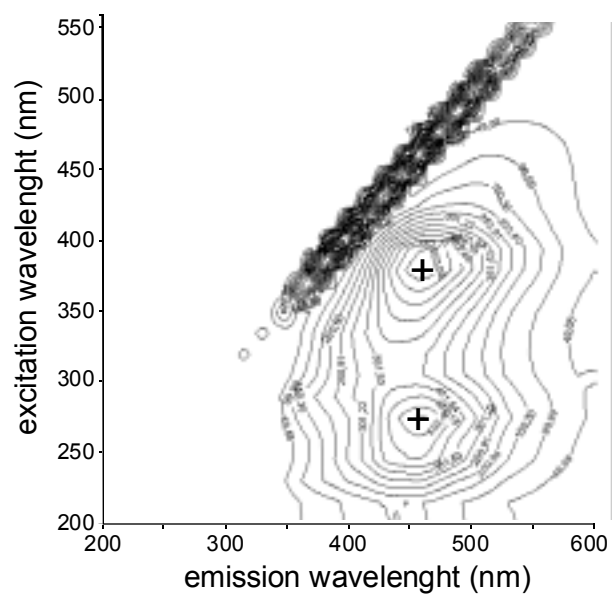


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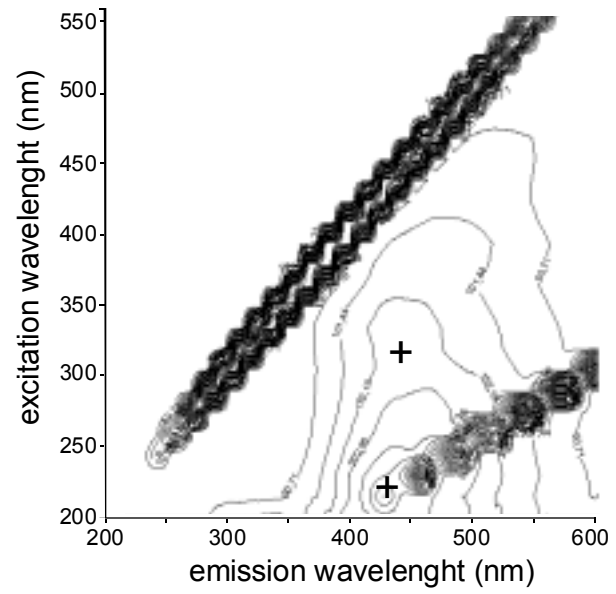


Fig. 10 : Excitation-Emission Matrice of soil-water extracts from sediments of lake Salitrada (SL) – Note the similarity with Fig. 4.

Table 1. Dissolved organic matter's characteristics

Water body	Number of samples	λ_{ex} (nm)	λ_{em} (nm)	F (a.u.)	[DOC] (mg L ⁻¹)
Banhado (B)	4	220	425.5→431.5	705→915	}47.2→52.6
		335	425.5→431.5	374→622	
Salitrada (SL)	7	220	422→424.5	232→332	}44.8→117.7
		320	422→424.5	112→141	
		230	333→355	207→711	
Salinas (SM, SO, SP)	21	290	342→362	133→438	}144.7→381.6
		260	433→458	125.8→585	
		380	450→484	161.1→463	
		230	431→438	300	
		350	431→438	181.4→241.5	

λ_{ex} : excitation wavelength; λ_{em} : emission wavelength; F (arbitrary units): fluorescence intensity