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Seasonal variation of dissolved organic carbon (DOC) and optical properties of organic matter in different pasture and soybean systems in the State of Mato Grosso

Variação sazonal do carbono orgânico dissolvido (COD) e propriedades ópticas da matéria orgânica em diferentes sistemas de pastagem e de soja no estado de Mato Grosso

Douglas Dias de Morais[1], Higo José Dalmagro[1], Osvaldo Borges Pinto Junior[1,2], Carlo Ralph de Musis[1] e Eduardo Guimarães Couto[2] and Mark Stephen Johnson[3]

[1]Universidade de Cuiaba, MT, Brasil
Douglasdias_1991@hotmail.com; higojdalmagro@gmail.com; osvaldo.borges@kroton.com.br;carlo.demusis@gmail.com

[2]Universidade Federal de Mato Grosso MT, Brasil
couto@ufmt.br

[3]University of British Columbia, Vancouver, British Columbia, Canada
Mark.johnson@ubc.ca

Abstract

The objective of this study is to characterize the quantity and quality of dissolved organic carbon (DOC) in different water conditions in pasture and soybean production systems in the state of Mato Grosso. Sampling was carried out in the wet seasons (February-March) and the dry season (September-October). The DOC concentration and its optical fluorescence properties were measured from samples collected in different ecosystems in the State of Mato Grosso (Savanna, Wetland, Amazonian and Savanna / Amazonian Ecotone). DOC concentration varied significantly between different systems and hydrological periods. The FI (fluorescence index) varied significantly only between hydrological seasons. FI values characterize mainly allochthonous sources of organic matter. SR analysis also indicated significant differences between sites, ecosystems, and hydrological seasons. The analysis of optical properties suggested a large amount of humic components in the grazing systems, which is suggestive of the presence of leachates, and the rapid and inefficient decomposition of aquatic plants. In the soybean areas, high intensity peaks were identified for the tyrosine component in the Savanna biome. With this, the concentration of DOC, and the summary referring to its quality, differed between study ecosystems and hydrological periods.

Keywords: Fluorescence of organic matter, Biomes of Mato Grosso, Ecology of Ecosystems.

Resumo

O objetivo deste estudo é caracterizar a quantidade e a qualidade do carbono orgânico dissolvido (COD) em diferentes condições hídricas nos sistemas de produção de pastagem e soja no estado de Mato Grosso. As amostragens foram realizadas nas estações úmidas(Fevereiro-março) e nas estações secas (setembro-outubro). A concentração de COD e suas propriedades de fluorescência óptica foram medidos a partir de amostras coletadas em diferentes ecossistemas no Estado de Mato Grosso (Cerrado, Pantanal, Amazônia e ecótono Cerrado/Amazônia). A concentração de COD variou significativamente entre diferentes sistemas e períodos hidrológicos. O IF (Índice de fluorescência) variaram significativamente apenas entre as estações hidrológicas. Os valores de IF caracterizam principalmente fontes alóctones de matéria orgânica. A análise de SR também indicou diferenças significativas entre locais, ecossistemas e estações hidrológicas. A análise das propriedades ópticas sugeriu uma grande quantidade de componentes húmicos nos sistemas de pastagem, o que sugere a presença de lixiviados e a rápida e ineficiente decomposição das plantas aquáticas. Nasáreasdesoja, picosdealtaintensidadeforamidentificadosparaocomponentedetirosinanobiomaCerrado. Com isso, a concentração de COD, e os índices referentes a sua qualidade, diferiu entre ecossistemas de estudo e períodos hidrológicos.

Palavras-chave: Fluorescência de matéria orgânica, Biomas de Mato Grosso, Ecologia de Ecossistemas.

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1 Introduction

The state of Mato Grosso is characterized by three large biomes: Wetland, Savanna and Amazonian. The expansion and intensification of soybean and livestock production have caused the conversion of native forests into productive agricultural areas, and this has contributed to Brazil being one of the largest exporters of soybeans and meat in the world. Fluvial biogeochemical processes are extremely important because they affect the balance of carbon and nutrients (Aufdenkampe et al., 2011). The organic matter dissolved in aqueous systems is a mixture of aromatic and aliphatic organic compounds (usually less than 0.7 μm) that perform ecologically important functions in various biogeochemical and physical processes, participating in the carbon, nitrogen, phosphorus and sulfur cycles (Singh et al., 2013).

Knowledge of the temporal and spatial variability of the small-scale carbon cycle allows understanding of how changes in land use and occupation affect the functioning of ecosystems as carbon sources (Wohl et al., 2012). Many studies have quantified DOC concentration in soils and aquatic ecosystems, but few have identified its origin or its responses to conduction factors, climatic conditions, or changes in vegetation and soil. This research aims to contribute to the clarification of the global carbon cycle in these environments, considering how the type of soil cover and hydrological conditions influence the temporal variations in quantity and quality of DOC. Considering the differences in the environmental characteristics of the biomes and ecosystems, this work makes it possible to determine whether the carbon present in the streams of different agricultural systems (pasture and soybean) is of allochthonous or autochthonous origin.

Recently techniques of optical absorption and fluorescence spectroscopy have been widely used (Singh et al., 2013); (Dalmagro et al., 2017) to evaluate water quality in agricultural river basins (Fellman et al., 2010). The biogeochemical characterization of the dissolved organic matter (DOM) based on fluorescence allows the detection of differences between natural and anthropogenic DOM sources in rivers impacted by agricultural residues (Baker et al., 2003);(Wilson e Xenopoulos, 2008). A combination of optical properties (fluorescence and absorption), coupled with conventional DOC measurements, can be used to understand how changes and intensification in agricultural land use can modify the quantity and composition of DOM (Graeber et al., 2015).

Agricultural practices can alter the amount and composition of DOM since the DOM exported from agricultural basins are often altered so that it can be potentially more reactive in aquatic ecosystems and thus can increase the productivity of the system (Williams et al., 2010). A further intensification of agriculture in tropical developing countries is expected since, in addition to population growth, food demand per capita will increase with the increase in gross domestic product in the future (Graeber et al., 2015). Thus, intensification of agriculture may result in the release of large quantities of biogeochemically reactive DOM to river networks, altering the DOM-related biogeochemical cycles, and increasing the productivity, respiration, and depletion of CO_2 from river networks (Graeber et al., 2015).

The objective of this work is to characterize DOC quantity and quality in different water conditions, and under two different uses of the soil (pasture and soybean) in the state of Mato Grosso.

2 Material and methods

2.1 Study Sites

The study was carried out in four locations in the state of Mato Grosso (Figure 1) during two distinct hydrological seasons (dry and wet). These encompass the different biomes of the state (Amazonian, Savanna, Wetland, and Amazonian/Savanna ecotone), and include pasture systems (in the Amazonian Forest and Pantanal), and soybean production areas (in the Amazonian/Savanna ecotone).

In the Pantanal, the study area is located approximately 160 km from Cuiabá and 60 km southeast of Poconé, at the coordinates 16°39’50 "S, 56°47’50”W and an altitude of 116 m, in the Private Reserve of Natural Patrimony (RPPN) of SESC Pantanal (Dalmagro et al., 2014). In the Amazonian region sampling was carried out at Fazenda Pedra Alta in the municipality of Alta Floresta (09°59’03 ”S and 56°07’47”W).

In the Cerrado, samples were collected at Pirassununga Farm in the municipality of Campo Verde. Located in the southwest of Mato Grosso, 130 km from Cuiabá, the climate here is tropical sub-humid and hot.

In the Amazonian / Cerrado forest ecotone region, samples of the soybean areas were obtained at Fazenda Maracaí, located 50 km from the municipality of Sinop, at the coordinates 11°24’43.4"S, 55° 19’25.7" W, at an altitude of 435 m (Souza et al., 2014).

2.2 Sampling and Analysis

Water samples for analysis of DOC (dissolved organic carbon) in the Wetland and other biomes were collected during the flooding cycles of 2015. The samplings were performed in triplicate. A silicone hose was inserted 30 cm deep in the aquatic system, and the water was pumped with a 20 mL syringe using a pre-calcined glass fiber filter (nominal porosity 0.7 μm) and stored in an amber glass bottle (60 mL) with a Teflon-coated cap. The samples obtained were stored in a thermal box and taken to the FAMEV

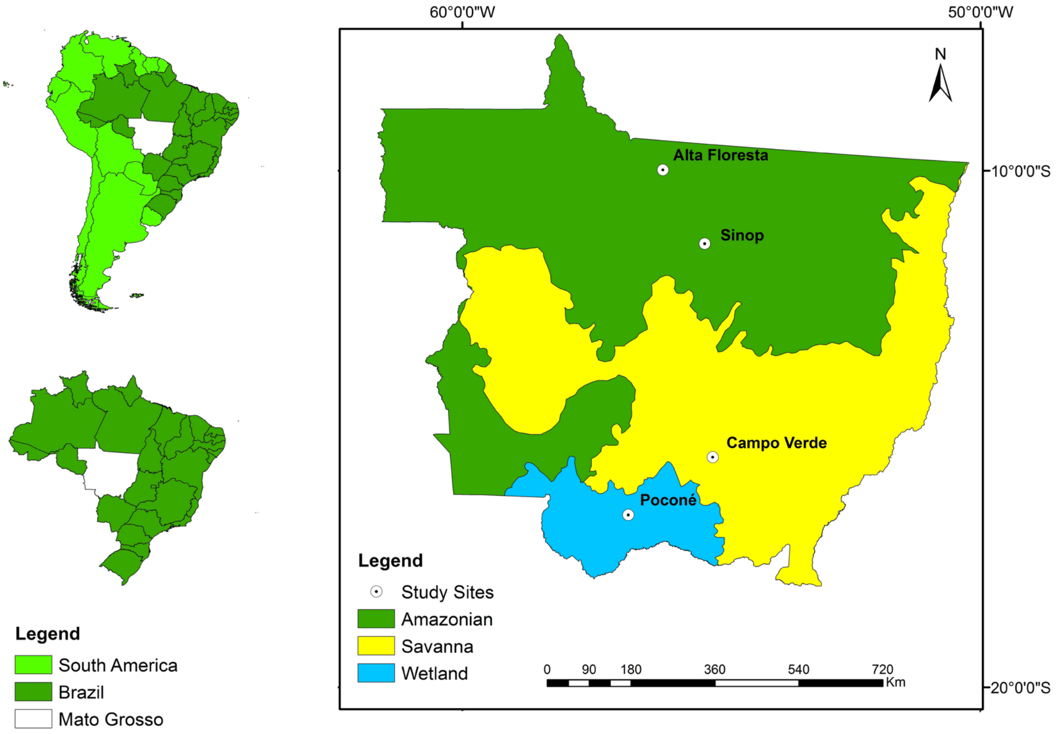

Figure 1: Location of Study Sites

(Faculty of Agronomy and Veterinary Medicine) laboratory for analysis of the DOC concentration and determination of EMMs (Excitation-Emission Matrices).

The DOC concentrations and fluorescence characteristics were analyzed in the Faculty of Agronomy and Veterinary Medicine (FAMEV) laboratory of the Federal University of Mato Grosso (UFMT). The samples from the field were divided into two aliquots, one for the absorption spectroscopy analysis and the other for analysis by fluorescence spectrometry for the preparation of the EMMs.

The HI (Humification Index) was calculated by dividing the emission wavelength of 435 and 480 nm by the measured fluorescence intensity, between 300 and 345 nm with excitation at 254 nm. The FI (Fluorescence Index) was derived from SEM using the ratio of fluorescence emission intensities at 470 and 520 nm resulting from an excitation at 370 nm McKnight et al. (2001).

2.3 Statistical Analysis

Multivariate analysis of variance (MANOVA) was used to determine the statistical differences of the dependent variables: DOC, FI (Fluorescence index), S_R (Spectral Slope), E_2: E_3 and E_4: E_5 ratios as a function of agriculture type (pasture and soya), ecosystem (Wetland, Savanna, Amazonian and Amazonian/Savanna ecotone) and the hydrological period (dry and wet).

3 Results and discussion

3.1 DOC Quality Indexes

The DOC concentration showed a significant difference between the sites ($F_{2,\ 73}$ = 2993, p <0.0001), between ecosystems ($F_{2,\ 73}$ = 960, p <0.0001), and between different hydrological periods ($F_{2,\ 73}$ = 2105; p <0.0001). The Wetland region presented the highest DOC concentration (2.40 mg.L^{-1}) among the ecosystems; the soybean agricultural region it was 0.62 mg.L^{-1}, followed by the area of Ecotone (1.79 mg.L^{-1}), Amazonian (1.68 mg.L^{-1}) and Savanna (0.80 mg.L^{-1}) (Figure 2). The DOC concentration in the pasture presented higher mean values for the Amazonian ecosystem (1.67 mg.L^{-1}) and Savanna (1.20 mg.L^{-1}) in the dry season (Figure 2), while in the Wetland there were higher concentrations during the wet season (1.34 mg.L^{-1}).

In the Wetland, biomass burning often occurs in the dry season, in which carbon is accumulated on the landscape before being transferred to the bodies of water through surface runoff, explaining a higher average in this biome during the rainy season (Ding et al., 2014). For the soybean area, higher mean DOC values were observed during the dry season. The lowest mean among the ecosystems was for the ecotone during the dry season (0.78 $mg.L^{-1}$) and for the Savanna during the wet season (0.41 $mg.L^{-1}$).

The fluorescence index varied significantly between hydrological periods ($F_{2, 73} = 7.21$, $p < 0.010$), but not between sites ($F_{2, 73} = 2.81$, $p < 0.070$) and the ecosystem ($F_{2, 73} = 0.34$, $p < 0.797$). The mean value for the sites was 1.56, and for the ecosystems 1.54. During the wet period, the mean value of the FI was 1.58, while in the dry period it was 1.52. The FI does not provide information on the source of DOC water flow, though it may be useful to assume a substantial change in the organic matter equilibrium (Hood et al., 2006). Low values (1.2-1.5) are characteristic mainly of allochthonous sources of organic matter (plants, soil organic matter), while high values (1.6-2.0) are indicators of microbial activities characterizing production (McKnight et al., 2001).

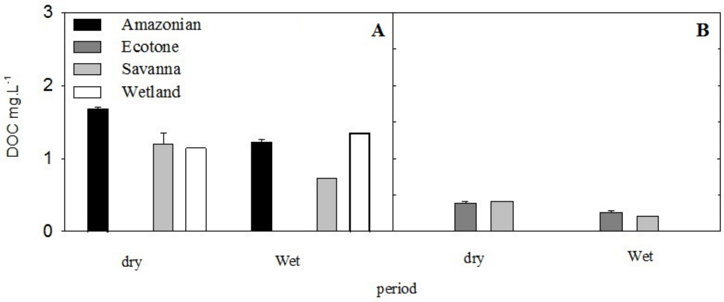

Figure 2: Mean (±standard error) of DOC in the different Biomes/Ecosystems. (A) Pasture (A) (B) Soybean

For pasture areas in the Amazon forest only there was increase of FI (1.70) in the wet period (Figure 3), suggesting that the environment is strongly influenced by the microbial synthesis process; for example, leachate from plants and periphyton (a complex community of algae, bacteria, fungi and animals). This indicates that pasture areas were strongly enriched by labile organic matter Wynn e Bird (2007) during this period.

The low values observed of FI in the soybean area during the dry season, 1.55 (Ecotone) and 1.40 (Savanna), suggest a predominance of mainly allochthones sources (Figure 3). Möller et al. (2005) and Sanderman et al. (2008), point out that agricultural soils are largely derived from solid phase organic matter originating in native soil, and only a small part comes from microbial activity, which explains the higher allochthonous production in these systems. Williams et al. (2010), also point out that the conversion of forests into agricultural areas can lead to an abundance of refractory components during transportation.

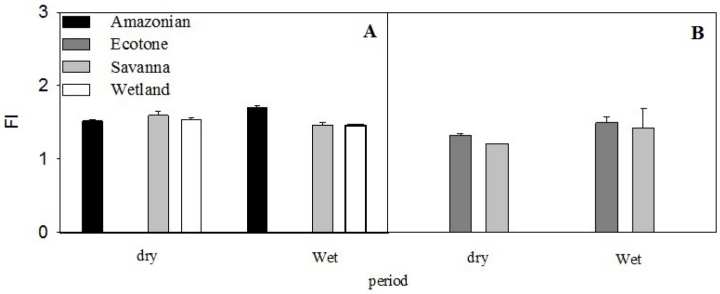

Figure 3: Mean (±standard error) of the FI in the different Biomes / Ecosystems. (A) Pasture (A) (B) Soybean

The spectral ratio (S_R) is proposed with an indicator of the molecular weight of organic matter. Maximum S_R values are characteristic of low molecular weight organic matter, and vice versa (Helms et al., 2008). The application of spectral ratios in the study of ecosystems is important as it has been used to evaluate seasonal changes of organic matter in tropical rivers (Yamashita et al., 2010). Significant differences were observed both in the site ($F_{2, 73} = 58.58$, $p < 0.0001$), in the ecosystem ($F_{2, 73} = 6.52$, $p < 0.0001$), in the hydrological periods ($F_{2, 73} = 58.58$, $p < 0.0001$) 45.67, $p < 0.0001$). Differences were observed between the Wetland ecosystem with the Amazonian and between the Ecotone and the Savanna, however, significant differences were observed between the Wetland and Amazonian ecosystems and the Ecotone and Savanna ecosystems. In the pasture ecosystems, the highest mean values of S_R were during the wet period, being the highest average obtained in the Wetland (Figure 4). These values indicate the strong presence of high molecular weight compounds of humic origin.

The highest S_R values were observed in the soybean crop system (Figure 4), which had the highest average during the rainy season in both ecosystems. This is due to the reduced tree cover and ciliary forest over water bodies in this environment, which increases the penetration of solar radiation, decreasing the DOC molecular weight through photo degradation (Williams et al., 2010). The authors further claim that agricultural land use changes the processing of dissolved organic matter by reducing its form.

The E_2:E_3 is the absorbance ratio between 250 and 365 nm, which is proposed as an inversely correlated indicator of the relative size of the organic matter molecules Helms et al. (2008);Spencer et al. (2009). This inverse relationship is due to the strong absorption of light by heavy molecules (Helms et al., 2008). The E_2: E_3 ratio varied significantly between the sites ($F_{2;73} = 38.70$; $p < 0.0001$) and the mean was higher in areas with soybean presence (2.33), being significantly different from pasture areas (2.72). In addition, it differed among all ecosystems (Savanna = 2.30, Ecotone = 2.51, Wetland = 2.76 and Amazonian = 3.10) (Figure 5). There was significant interaction between the ecosystem, the site and the station for E_2: E_3 ($F_{2;73} = 22.63$; $p < 0.0001$). In the pasture systems, higher mean values were observed for the Amazonian ecosystem during the dry season (3.17), characterized DOM OF low molecular size, whereas higher values were recorded at the other sites during the wet season.

For soybean area the highest mean E_2: E_3 ratio was obtained during the dry season in the studied biomes, the transition region with highest average, indicating the presence of molecules of low Molecular size, being confirmed when compared to the IF result, which was higher for this biome in that period indicating that the MOD is labile.

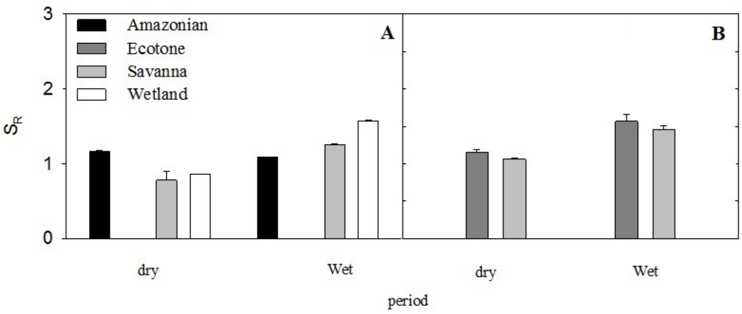

Figure 4: Mean (±standard error) of the FI in the different Biomes / Ecosystems. (A) Pasture (A) (B) Soybean

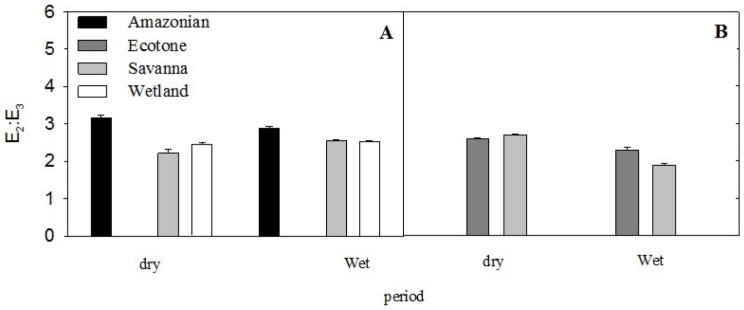

Figure 5: Mean (±standard error) of E_2:E_3 in the different Biomes / Ecosystems. (A) Pasture (B) Soybean

The ratio E_4: E_6 corresponds to the absorbance ratio between 465 and 665 nm, which is directly related to the structural condensation and aromaticity of the humic substances. Lower values of E_4: E_6 indicate a high degree of condensation, while high values characterize low structural condensation (SANCHES et al, 2007). For pasture areas, the highest averages of the E_4: E_6 index were during the dry period (Figure 6), which suggests a lower degree of structural condensation. Landgraff et al. (1999) also point out that high values characterize a greater amount of aliphatic structure in the chain of humic substance molecules, and therefore less aromatic structure, attributing this to the fact that organic matter is more labile.

In the soybean area, the lowest averages were obtained in the wet season in both biomes (1.77 and 1.65, respectively). (Sanches et al., 2007) point out that the E_4:E_6 ratio is influenced by several variables including molecular size, as well as the higher condensation observed in this period. It is observed that the molecules in this period were of a larger size, as indicated by the values of E_2: E_3.

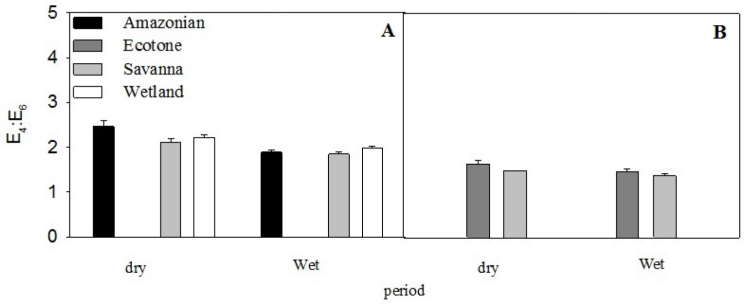

Figure 6: Mean (±standard error) of E_4:E_6 in the different Biomes / Ecosystems. (A) Pasture (B) Soybean

3.2 Properties of Organic Matter

The Figure 7 shows representations of EEMS derived from pasture ecosystems, and a representation of the intensity (RU) peaks of the components identified in this ecosystem.

For the Amazon rainforest, three peaks were identified in the dry season, the highest representing humic acid (A) at an average intensity of 0.090. Its abundance is attributed to low and inefficient decomposition of terrestrial organic matter originating mainly from vascular plants. During the dry season the maximum peak reached by this component was 0.102, and the minimum was 0.088.

In the Amazonian forest and in the other biomes, the highest peak was observed for the tryptophan component (wet period), with a mean of 0.285 and maximum of 0.731. This compound is associated with semi-labile dissolved organic matter, which is common in systems under anthropogenic impacts, and is associated with the leaching process within the basin (Stedmon e Markager, 2005). This explains the greater bioavailability in the Wetland during the dry season (Lambert et al., 2016);(Dalmagro et al., 2017).

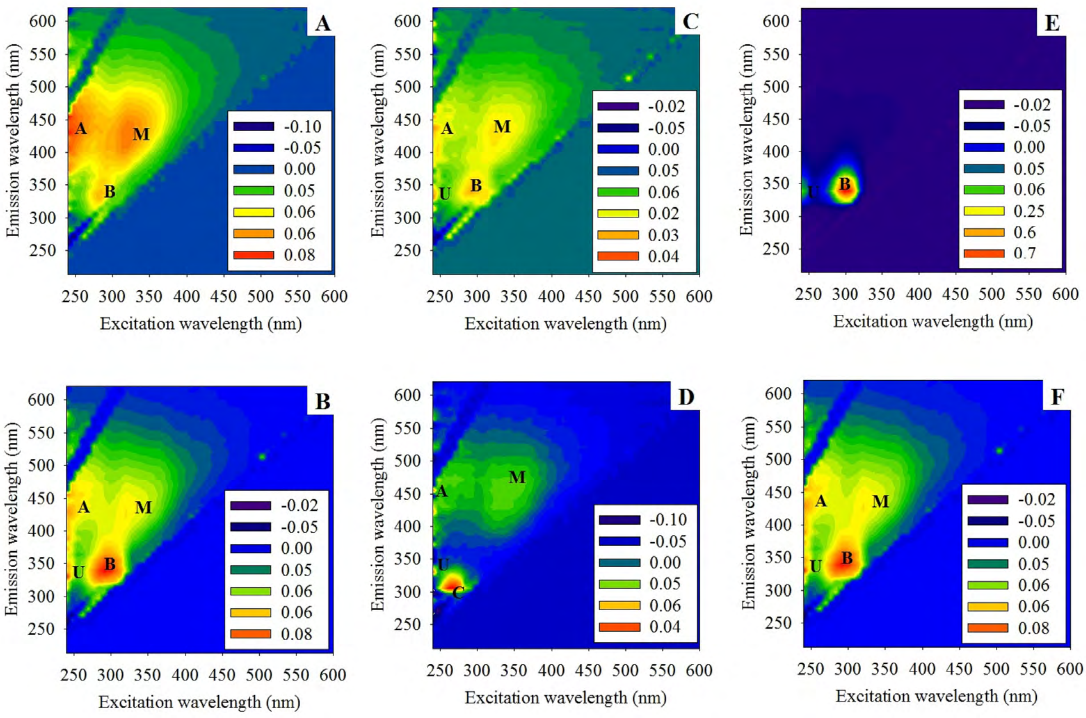

Figure 7: Representative emission and excitation matrices (EEMS) for pasture in the different regions and hydrological seasons of Mato Grosso. (A) Amazonian in the dry season, (B) Amazonian i n the wet season, (C) Savanna in the dry season, (D) Savanna in the wet season, (E) Wetland in the dry season, and (F) Wetland in the wet season

Four peaks were identified in the Savanna during the dry season, of which the highest represented tryptophan, with a maximum intensity of 0.230. Humic acid, fulvic acid, an unknown peak component and the tyrosine peak were identified during the wet period, with the latter having a higher intensity with mean and maximum peaks of 0.050.

In the Wetland , a smaller number of components was identified, with tryptophan being the most intense in both hydrological periods. In the dry period the maximum peak was 0.860, and in the wet period it was 0.117. According to Inandar et al. (2012) tryptophan is a less degraded and high molecular weight peptide material. The results of E_4:E_6 ratio suggest the presence of this component in this biome and period. In addition, in the humid season, peaks were identified referring to humic acid and fulvic acid.

In the soybean ecosystems, a smaller number of components were identified (Figure 8), with the highest intensity being the unknown peak compounds (U) in both hydrological periods in the Amazonian/Savanna forest ecotone region. In the dry season the average intensity was 0.050 and the maximum was 0.054, and in the wet season the average was 0.040 and the maximum was 0.062. This may be associated with dissolved organic matter (DOM) produced in agricultural areas being less present, and distinct from that produced in natural ecosystems, suggesting that agricultural areas promote the formation of reduced organic matter due to land use processing, with the conversion of forests and other natural environments decreasing transport and increasing the abundance of refractory components (Williams et al., 2010);(Lambert et al., 2016). In addition, we identified three more peaks in this region, representing humic acid, tryptophan, and fulvic acid.

In the Savanna, the tyrosine component had the highest peak for both hydrological periods. This is because it is an agricultural region where there is a greater enrichment of nutrients and biological activity caused by the longer residence time of the water (Balcarczyk et al., 2009);(Cory et al., 2007);(Williams et al., 2010);(Wilson e Xenopoulos, 2009) highlight that water bodies that flow through agricultural environments tend to present an increase in the incidence of solar radiation due to the reduction of the vegetation cover, which is responsible for stimulating the production of this protein. In addition to the tyrosine component, peaks indicating humic acid and fulvic acid were identified in the dry season, with maximum intensities of 0.05 and 0.03 respectively; while in the wet season, peaks were also identified, suggesting unidentified components with a maximum intensity of 0.05.

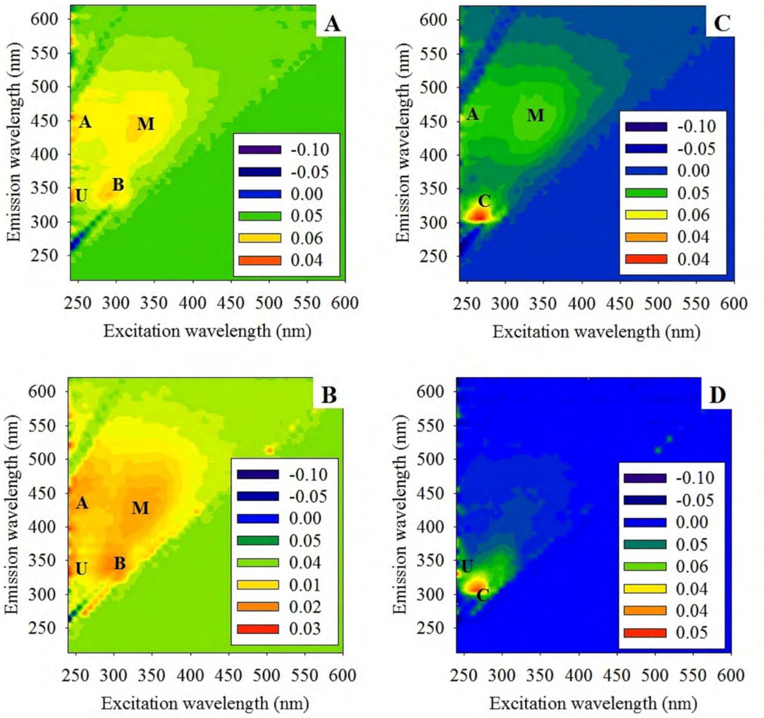

Figure 8: Representative emission and excitation matrices (EEMS) for soybean in different hydrological seasons. (A) amazonian/Savanna forest ecotone in dry season, (B) amazonian/Savanna forest ecotone in wet season, (C) Savanna in dry season, and (D) Savanna in wet season.

4 Conclusion

The DOC concentration differed between sites, ecosystems and hydrological seasons, with the highest average being in the Pantanal biome.

The results concerning the FI differed significantly between the seasons, but there was no difference between the sites and ecosystems, as is shown by the DOC from the Amazonian region pasture during the rainy season being mainly autochthonous, while it is mainly allochthonous in the dry season in this area and in the soybean areas.

The S_R differed significantly among sites, ecosystems and hydrological seasons, as well as in the interaction between them. The ratios of E_2:E_3 and E_4:E_6 did not change significantly between hydrological seasons, but did between ecosystems and land use types, with the E_2:E_3 ratio being the highest in the soybean agricultural areas, with a higher than average value in the ecotone region, indicating the presence of labile organic matter.

The analysis of the optical properties of the dissolved organic matter indicated a large amount of humic components in the pasture ecosystems, which was attributed to the presence of soil-derived dissolved organic matter leachates, and the rapid decomposition of aquatic plants. In the soybean ecosystems, high intensity peaks were identified for the tyrosine component in the Savanna biome, originated from mainly native sources.

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References

Aufdenkampe, A. K., Mayorga, E., Raymond, P. A., Melack, J. M., Doney, S. C., Alin, S. R., Aalto, R. E., Yoo, K. (2011). Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. *Frontiers in Ecology and the Environment*, *9*(1), 53–60.

Baker, A., Inverarity, R., Charlton, M., Richmond, S. (2003). Detecting river pollution using fluorescence spectrophotometry: case studies from the ouseburn, ne england. *Environmental Pollution*, *124*(1), 57–70.

Balcarczyk, K. L., Jones, J. B., Jaffé, R., Maie, N. (2009). Stream dissolved organic matter bioavailability and composition in watersheds underlain with discontinuous permafrost. *Biogeochemistry*, *94*(3), 255–270.

Cory, R. M., McKnight, D. M., Chin, Y. P., Miller, P., Jaros, C. L. (2007). Chemical characteristics of fulvic acids from arctic surface waters: Microbial contributions and photochemical transformations. *Journal of Geophysical Research: Biogeosciences*, *112*(G4).

Dalmagro, H., Lobo, F. d. A., Vourlitis, G., Dalmolin, Â., Antunes Jr, M., Ortíz, C., Nogueira, J. d. S. (2014). The physiological light response of two tree species across a hydrologic gradient in brazilian savanna (cerrado). *Photosynthetica*, *52*(1), 22–35.

Dalmagro, H. J., Johnson, M. S., Musis, C. R., Lathuillière, M. J., Graesser, J., Junior, O. B., Couto, E. G. (2017). Spatial patterns of doc concentration and dom optical properties in a brazilian tropical river-wetland system. *Journal of Geophysical Research: Biogeosciences*.

Ding, Y., Cawley, K. M., Da Cunha, C. N., Jaffé, R. (2014). Environmental dynamics of dissolved black carbon in wetlands. *Biogeochemistry*, *119*(1-3), 259–273.

Fellman, J. B., Hood, E., Spencer, R. G. (2010). Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review. *Limnology and Oceanography*, *55*(6), 2452–2462.

Graeber, D., Boëchat, I. G., Encina-Montoya, F., Esse, C., Gelbrecht, J., Goyenola, G., Gücker, B., Heinz, M., Kronvang, B., Meerhoff, M., et al. (2015). Global effects of agriculture on fluvial dissolved organic matter. *Scientific reports*, *5*.

Helms, J. R., Stubbins, A., Ritchie, J. D., Minor, E. C., Kieber, D. J., Mopper, K. (2008). Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. *Limnology and Oceanography*, *53*(3), 955–969.

Hood, E., Gooseff, M. N., Johnson, S. L. (2006). Changes in the character of stream water dissolved organic carbon during flushing in three small watersheds, oregon. *Journal of Geophysical Research: Biogeosciences*, *111*(G1).

Lambert, T., Teodoru, C. R., Nyoni, F. C., Bouillon, S., Darchambeau, F., Massicotte, P., Borges, A. V. (2016). Along-stream transport and transformation of dissolved organic matter in a large tropical river. *Biogeosciences*, *13*, 2727–2741.

McKnight, D. M., Boyer, E. W., Westerhoff, P. K., Doran, P. T., Kulbe, T., Andersen, D. T. (2001). Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, *46*(1), 38–48.

Möller, A., Kaiser, K., Guggenberger, G. (2005). Dissolved organic carbon and nitrogen in precipitation, throughfall, soil solution, and stream water of the tropical highlands in northern thailand. *Journal of Plant Nutrition and Soil Science*, *168*(5), 649–659.

Sanches, S., Campos, S., Vieira, E. (2007). Caracterização das frações das substâncias húmicas de diferentes tamanhos moleculares. *Eclética Química*, *32*(1), 49–56.

Sanderman, J., Baldock, J. A., Amundson, R. (2008). Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils. *Biogeochemistry*, *89*(2), 181–198.

Singh, S., Inamdar, S., Scott, D. (2013). Comparison of two parafac models of dissolved organic matter fluorescence for a mid-atlantic forested watershed in the usa. *Journal of Ecosystems*, *2013*.

Souza, M. C., Biudes, M. S., Danelichen, V. H. d. M., Machado, N. G., Musis, C. R. d., Vourlitis, G. L., Nogueira, J. d. S. (2014). Estimation of gross primary production of the amazon-cerrado transitional forest by remote sensing techniques. *Revista Brasileira de Meteorologia*, *29*(1), 01–12.

Spencer, R. G., Aiken, G. R., Butler, K. D., Dornblaser, M. M., Striegl, R. G., Hernes, P. J. (2009). Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the arctic ocean: A case study of the yukon river, alaska. *Geophysical Research Letters*, *36*(6).

Stedmon, C. A., Markager, S. (2005). Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis. *Limnology and Oceanography*, *50*(5), 1415–1426.

Williams, C. J., Yamashita, Y., Wilson, H. F., Jaffé, R., Xenopoulos, M. A., et al. (2010). Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnology and Oceanography*, *55*(3), 1159.

Wilson, H. F., Xenopoulos, M. A. (2008). Ecosystem and seasonal control of stream dissolved organic carbon along a gradient of land use. *Ecosystems*, *11*(4), 555–568.

Wilson, H. F., Xenopoulos, M. A. (2009). Effects of agricultural land use on the composition of fluvial dissolved organic matter. *Nature Geoscience*, *2*(1), 37.

Wohl, E., Barros, A., Brunsell, N., Chappell, N. A., Coe, M., Giambelluca, T., Goldsmith, S., Harmon, R., Hendrickx, J. M., Juvik, J., et al. (2012). The hydrology of the humid tropics. *Nature Climate Change*, *2*(9), 655–662.

Wynn, J. G., Bird, M. I. (2007). C4-derived soil organic carbon decomposes faster than its c3 counterpart in mixed c3/c4 soils. *Global Change Biology*, *13*(10), 2206–2217.

Yamashita, Y., Scinto, L. J., Maie, N., Jaffé, R. (2010). Dissolved organic matter characteristics across a subtropical wetland's landscape: application of optical properties in the assessment of environmental dynamics. *Ecosystems*, *13*(7), 1006–1019.