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Copper(II) and Nickel (II) Complexation Capacity of Dissolved Organic Matter from Rivers of Agricultural and Urban Areas in the State of São Paulo

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Este estudo teve como principal objetivo determinar a capacidade de complexação da Matéria Orgânica (MO) de regiões tipicamente agrícolas e urbanas, com os íons de cobre e níquel. As amostras foram coletadas durante as estações de seca e chuva e submetidas ao estudo da capacidade de complexação e da constante de estabilidade condicional da MO com os íons Cu(II) e Ni(II) usando um Espectrofluorímetro de Luminescência e o Sistema de Ultrafiltração de Fluxo Tangencial. Os valores da constante de estabilidade condicional (log K_c) da MO com o íon cobre variaram de 0,04 a 1,35 sendo o maior valor obtido para o local com maior carbono orgânico dissolvido (COD 2,73-2,43 mg L^{-1}) e o menor para local de menor COD, corroborando com o grau de aromaticidade. Conclui que a Matéria Orgânica Dissolvida (MOD) de rios de áreas agrícolas e urbanas continha um número menor de sítios de ligação, quando comparado com outros locais.

This study had as main objective to determine the complexing ability of the Organic Matter (OM) from typical agricultural areas and from urban areas with copper and nickel ions. The samples were collected during the dry and rainy seasons and were subjected to study the complexing capacity and OM conditional stability constant with Cu(II) and Ni(II) ions using a luminescence spectrofluorometer and tangential flow ultrafiltration system. The conditional stability constant values (log K_c) of OM with the copper ion varied from 0.04 to 1.35 with the highest value obtained for the place with the largest dissolved organic carbon (DOC 2.73-2.43 mg L^{-1}) and the lowest for the smallest site DOC, corroborating the degree of aromaticity. We can conclude that the Dissolved Organic Matter (DOM) of the bodies of water in agricultural and urban areas contained a lower number of binding sites when compared with other locations.

Keywords: dissolved organic matter, metals, stability constant

Introduction

The natural organic matter (NOM) present in environmental areas is the result of several stages of chemical and microbiological degradation involving plant and animal residues and can vary from one body of water to another, depending on the type of use and the occupation of the land.[1-7] The NOM participates in many chemical and biological processes in natural waters, playing an important role in the speciation of metals, having a greater affinity for divalent cations, such as copper and nickel, in aquatic environments.[8,9] Changes in the soil composition and water cycle caused by anthropic or natural sources can interfere with the quantity and chemical nature of the natural organic matter present in such ecosystems.[1-3,10-14]

Another property of NOM is its ability to complex pollutants, especially metals, which may result in complexation and/or reduction reactions, absorption and desorption and other one whose are known to affect the availability of metals for the biota, may affect the transport, accumulation and concentration of these metal species in the planktonic food chain through changes in turbidity and interaction with nutrients, altering the photic zone.[3,4] This process can influence the toxicity of the metal in the environment, once the form of the complex, the metal, is generally less available to interact with the biota.[13,15] In the characterization of the formation of the NOM-metal complex, it is important to consider factors such as the

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level of functional groups, the complexing capacity, the molecular size of the NOM and the thermodynamic and kinetic stability of the NOM-metal complex.

The evaluation of the complexing capacity of the metal with NOM can be performed using molecular fluorescence, which is a nondestructive versatile technique that enables investigation of the chemical properties of NOM and classification of the NOM origin.[11,16-19] The use of molecular fluorescence to determine the conditional stability constant of the NOM has been the subject of several studies.[19-23] In these studies, metal titrations were performed with the organic matter (OM) while suppressing the intensity of the fluorescence signal when the metal was added (NOM-metal). The conditional stability constant was obtained using the mathematical model from Stern-Volmer.[24] Another manner in which to conduct this study is using a tangential flow ultrafiltration system,[25-31] which makes it possible to determine the concentration of the metal not complexed to NOM.

The prominent position occupied by Brazil in the production of ethanol and sugar from sugarcane is already well known and is still expanding in several regions, especially in the state of São Paulo, which is responsible for 52% of the Brazilian production, with a cultivated area of 4.4 million hectares of sugarcane. It is noteworthy that the orange production in the state of São Paulo is also prominent, with 0.6 million hectares of planted area.[32] The northwestern region of the state of São Paulo (study region) has an average production of 2 million tons of oranges per year and a planted area of sugarcane of 0.9 million hectares, corresponding to a production of 59 million tons of sugarcane.[33] Studies of the complexing capacity of the NOM of typical agricultural areas in a tropical country where the predominant crop is sugarcane are virtually nonexistent.

The northwestern region of São Paulo was selected for this study because the production of sugarcane in this region is expanding. This region occupied a prominent position in 2012 because it was the leading sugarcane producer in the state. Monitoring of the metal concentration along the rivers included in this study in 2008 and 2009 indicated that the highest concentrations of total metal were observed for some elements, notably nickel and copper. In this context, the selection of these two metals is justified for environmental studies in this region.[34] In view of these findings, the present study aimed to determine the conditional stability constant of dissolved organic matter (DOM) with the Cu(II) and Ni(II) ions from rivers of typical agricultural regions where there is a predominance of sugarcane and orange production, as well as from urban areas.

Experimental

Area of study

The northwestern region of the state of São Paulo, the target of this study, has distinct characteristics because it is an agricultural region with expanding sugarcane production and orange production to a lesser degree. This region is called the Turvo/Grande River Basin and is composed of 64 municipalities. The region has a drainage area of 16,037 km², and the main bodies of water that compose this drainage area are the Turvo, Grande and Preto rivers.

The region is situated at an altitude of approximately 500 m, and 78% of its territory contains an undulating topography, while 19% is flat and 3% is mountainous. Yellow-red argisol, yellow latosol and red latosol are the predominant soil types in the region.[35] According to a survey from the Turvo/Grande River Watershed Committee, much of the territory has a high risk of erosion. Regarding the industrial activity in the region, the presence of food industries, metallurgy and jewelry, sugar and alcohol plants, slaughterhouses, plastic industries and paper/cardboard mills are noted. It is also worth noting that of the municipalities belonging to the basin, São José do Rio Preto is the most populous, with approximately 415 thousand inhabitants and high urbanization rates. This municipality plays an important role as a center of trade, industry and services in the region.

The region has a very significant number of inhabitants, with approximately 1.2 million people, 91% of whom are located in urban areas, with the remainder being located in rural areas. Sampling locations were selected to attempt to distinguish the different types of activities performed in the river basin, as illustrated in Figure 1. The collection points were as follows: point 1 (Preto River headwaters), which corresponded to the reference area; point 2 (Preto River), which corresponded to an urban area; point 3 (Turvo River), which was representative of typical agricultural regions with an emphasis on sugarcane and orange production; and point 4 (Grande River), which was representative of an area that receives all the pollution load from the basin.

Sample collection

The procedures for sample collection and cleaning of the containers employed for metal and dissolved organic carbon quantification, such as for the studies of NOM, followed the recommendations described in method 1669 of United States Environmental Protection Agency (USEPA),[36] and Fu and co-authors.[19] The surface water samples were obtained from point 1 - Preto River headwaters (20°55'11.3"S,
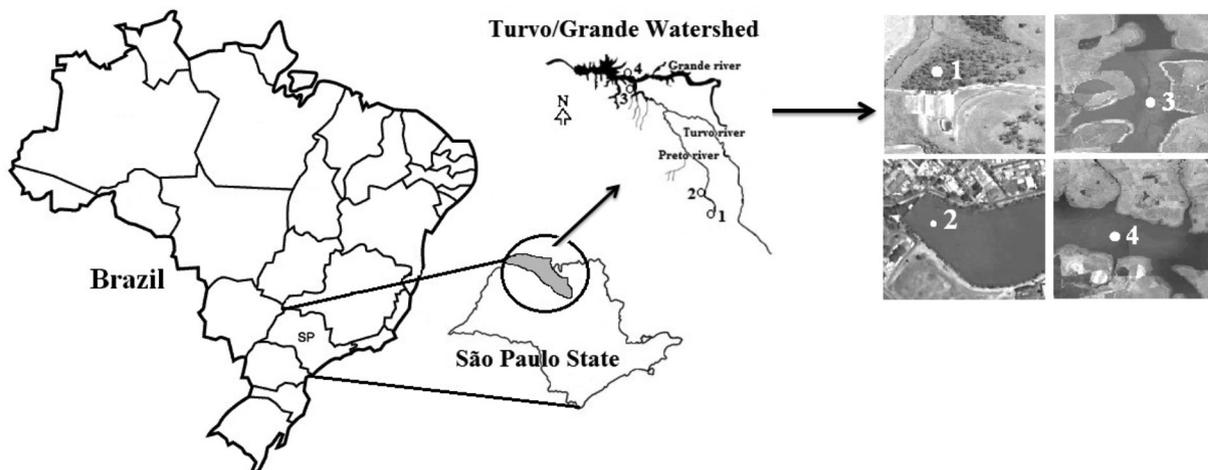
Figure 1. The sampling sites at points 1 (Preto River headwaters), 2 (Preto River), 3 (Turvo River) and 4 (Grande River) belonging to the Turvo/Grande Watershed (adapted from Google Maps).

049°17'59.9" W), point 2 - Preto River (20°48'40.94"S, 49°21'13.62"W), point 3 - Turvo River (19°58'09.8" S, 049°53'37.1"W) and point 4 - Grande River (19°56'28.7"S, 049°55'23.1"W) and were sampled in 2009 and 2010 during two distinct periods: the dry season and the rainy season. The samples were then transported to the laboratory, filtered through a 0.45 µm membrane (Millipore) and stored for later analysis, following the recommendations described by Sodré and Grassi.[37]

Chemical analyses

The reagents and solutions used in this work were all of high purity (Sigma-Aldrich - St. Louis - USA, Fluka-Buchs SG-Switzerland and Synth – Diadema – São Paulo - Brasil)), and the solutions were prepared using deionized water (ultrapure). The parameters of temperature (24.6-30.4 °C), pH (6.10-7.20), electrical conductivity (31-115 µS), turbidity (8.2-64.7 FTU) and dissolved oxygen (0.5-7.3 mg L^{-1}) were quantified in the field with the aid of previously calibrated portable meters. The dissolved organic carbon content was determined using catalytic combustion in an oxygen atmosphere and a non-Dispersive infrared detector (Shimadzu, TOC – VCSN analyzer, Tokyo, Japan). Potassium hydrogen phthalate was used to prepare the total organic carbon analytical curve. A mixture of carbonate and sodium bicarbonate was used to prepare the analytical curve for the quantification of the total inorganic carbon content. Measurements of the total organic carbon content were performed in triplicate, and the standard deviation was less than 1%. The total amounts of copper and nickel in the surface water samples were quantified in accordance with method 200.9,[38] using a graphite furnace atomic absorption spectrophotometer (GFAAS) with Zeeman background correction.

Molecular fluorescence analyses

Fluorescence spectra were obtained using a luminescence spectrofluorometer (Varian brand, Cary Eclipse model) in emission mode using a quartz cuvette with a 1-cm optical path and an excitation-emission slit of 10 nm. To obtain the fluorescence emission spectrum, an excitation wavelength of 332 nm was used, and sample scanning from 350-650 nm was performed.[20] The spectra for the blanks were obtained under the same conditions.

Study of the DOM complexing capacity with Cu(II) and Ni(II) ions by molecular fluorescence

Studies of the DOM complexing capacity with Cu(II) and Ni(II) ions were performed by titrating known concentrations of metal and determining the suppression of the molecular fluorescence signal intensity according to the procedure proposed by Ryan and Weber.[39] The use of this technique behind some limitations, such as maintaining control of pH and ionic strength, and possible experimental errors, however it is a technique that allows fast and easy results experimentation.[39] To accomplish this process, 45 mL of the filtered sample with a preset ionic strength (0.01 mol L^{-1} with KNO_3) was transferred to a beaker and subjected to agitation with the aid of a magnetic stirrer. A volume of 4.0 mL of this sample was transferred to a 1-cm quartz cuvette, and then, a reading was taken in the spectrofluorometer in emission mode. The sample in the cuvette was returned to the beaker containing the solution under stirring, and then, increasing volumes of standard $CuCl_2$ solution (1,000 mg L^{-1}) were added; readings were then performed again. The same procedure was repeated with a standard $NiCl_2.6H_2O$ solution (1,000 mg L^{-1}). The errors observed in the triplicates were less than 5%.

Data treatment

To evaluate the conditional stability constants, whose binding sites caused the suppression of the fluorescence signal, it was assumed that in the reaction between the DOM and the Cu(II) and Ni(II) ions, 1:1 complexes (DOM/Cu(II) and DOM/Ni(II), respectively) were formed.[39] Thus, to calculate the conditional stability constant, the model proposed by Stern-Volmer,[40] was used as follows:

$$\frac{I_0}{\Delta I} = \frac{1}{f} + \frac{1}{\left(f \cdot k_c \cdot [Cu(II)] \right)} \qquad (1)$$

where I_o: sample fluorescence *in nature* (without the addition of the standard copper solution), I: ligand fluorescence, $\Delta I = I_o - I$, f: fluorescent structures accessible for complexation, [Cu(II)]: concentration of free copper and k_c: conditional stability constant. The conditional stability constant was calculated using the linear coefficient of the graph $I_o/\Delta I$ *vs.* 1/[Cu(II)].

Study of the complexing capacity using a tangential flow ultrafiltration system

The study of the complexing capacity of the DOM with Cu(II) was conducted using a tangential flow ultrafiltration system (TF-UF) and more details are presented in Burba et al.[26,27] Samples of surface water from point 1 and point 2, corresponding to urban areas and the reference area, respectively, were subjected to complexing capacity studies. With the aid of a peristaltic pump (Ismatec brand, ISM1931C model), the solution of 1.0 mg L⁻¹ of DOC (point 1 or point 2) contained in the beaker was pumped through a Tygon tube to the TF-UF, which was equipped with a 1-kDa (Millipore) membrane.[26,27,41] At experimentally determined time intervals, the TF-UF flow was interrupted, and 2.0 mL of the sample was collected to quantify the amount of Cu(II). The complexation capacity was determined according to Scatchard model, which is determined by the intersection of two linear sections of the titration curve as a function of the quantity of carbon present in the initial solution.[42,43]

Cu(II) was quantified in samples collected during the experiments to assess the complexing capacity of the DOM with Cu(II) using graphite furnace atomic absorption spectrometry (GFAAS) (Varian brand, model AA280Z) and the Zeeman correction. The instrumental conditions used for quantification were adapted from Pereira et al.,[44] and the wavelength used to determine the total amount of copper was 327.4 nm. The pyrolysis and atomization temperatures were 800°C and 2,300°C, respectively. The

volume of the injected sample was 5 μL, and the chemical modifier consisted of a solution containing 1,500.0 mg L⁻¹ Pd and 1,000.0 mg L⁻¹ Mg(NO₃)₂.[45] The detection limit obtained for copper was 1.53 μg L⁻¹. A certified sample and a standard solution were quantified every ten sample readings. The solutions used in the quantification of total copper were prepared from the dilution of certified standard solutions (Sigma Aldrich). The laboratory where the experiments from this study were performed constantly participates in proficiency testing for the determination of metals in water samples (INMETRO – Institute of Metrology, Standardization and Industrial Quality) and plant tissue (EMBRAPA – Brazilian Agricultural Research Corporation), and the results obtained during this period were determined to be satisfactory ($z \leq 2$).

Characterization of DOM

UV/Vis spectrophotometry

The absorption spectra in the UV/Vis region of the filtered samples were obtained in the range of 200-800 nm using a Thermo Scientific Evolution 300 spectrophotometer and a quartz cuvette with a 1-cm optical path and ultrapure water as a reference. The absorbance at 254 nm changed according to the amount of dissolved organic carbon present in the sample, which enabled inference of the degree of aromaticity of the DOM present in the samples.[46-48] The specific ultraviolet absorbance ($SUVA_{254}$) is defined as the water sample absorbance at a given wavelength (254 nm) normalized to the corresponding concentration of dissolved organic carbon.

Fluorescence spectrometry

The characterization of the DOM was obtained using a luminescence spectrofluorometer (Varian brand, Cary Eclipse model) in synchronized mode using a quartz cuvette with a 1-cm optical path. To obtain the fluorescence synchronized spectrum, scanning of the sample was performed from 350 to 650 nm, with an excitation-emission slit of 10 nm and a wavelength variation ($\Delta\lambda$) of 20 nm adapted from Sodré and Grassi.[37] The spectra for the blanks were obtained under the same conditions.

Results and discussion

Figure 2a-d presents the synchronized spectra from the DOM of surface water samples from point 1 (Preto River headwaters), point 2 (Preto River), point 3 (Turvo River) and point 4 (Grande River). We observe peaks near 405 nm, which can be associated with aromatic groups containing five and seven rings; these peaks are more intense for
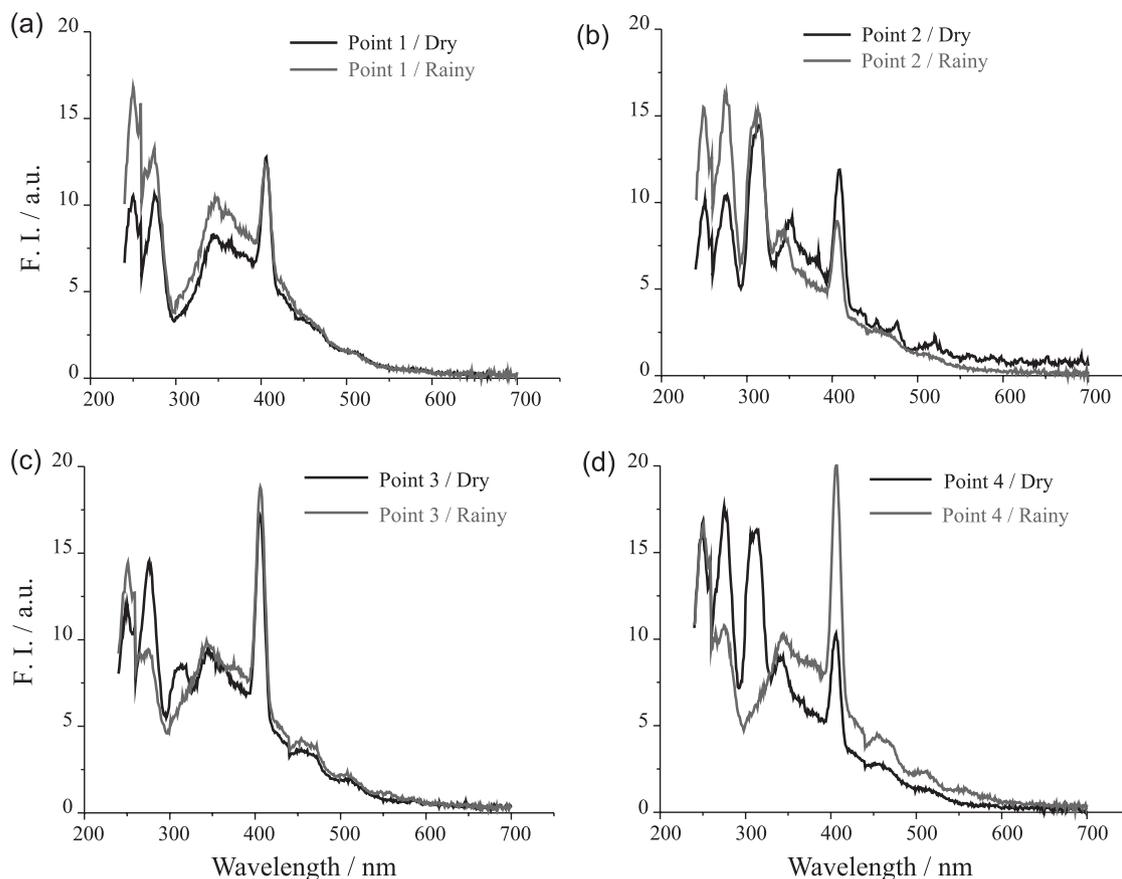
Figure 2. Synchronized spectra obtained for surface water samples (*in nature*) collected along the Turvo/Grande Watershed normalized for DOC during dry and rainy period from (a) Preto River headwaters, (b) Preto River, (c) Turvo River and (d) Grande River.

the regions of study with agriculture influence such as points 3 and 4.[13,37,49,50] Peravouri and co-authors,[49] conducted tests on samples of surface water from lakes in Southern Finland in synchronized mode, and the results showed peaks $\lambda_{ex}/\lambda_{em}$ to 400/418 nm can be attributed to polycyclic aromatic compounds with five rings fused benzene. The highlighted peaks between 278 and 280 nm for all the sampling locations suggest the presence of proteic and monoaromatic materials, which can be associated with primary microbian production, indicating a fraction more labile of DOM,[17,50] and can be assigned mainly to aromatic amino acids and other volatile acids containing highly conjugated aliphatic structures.[37] A more intense peak was observed at 312 nm for point 2 (urban area) and point 4 (an area that receives all the pollution load from the basin) during the rainy period and was attributed to compounds containing two condensed rings.[19]

The DOM for rivers sampled ranged according to the season, with higher values obtained for the dry period (point 1, point 2 and point 3; Table 1), suggesting that the burning of sugarcane may be one of the factors responsible for the increase of organic matter during the harvest period. Highlighted in Table 1, point 2 (urban area) represents the

highest value of nickel for both periods. The values of total copper were higher for all points during rainy period, with the exception of point 1. Point 3 (a typical agricultural area with an emphasis on sugarcane and orange production) exhibited a higher total copper concentration, which can be associated with the impurities contained in fertilizers. Campanha and co-authors,[51] calculated the metals fluxes (Pb, Ni, Cu and Cr) from a sediment/water interface for the same sampling points studied in this work. These authors concluded that sediments from the Turvo/Grande watershed act as a source of metals for the water column, especially nickel and copper, according to the season. Table 1, it can be seen that the highest aromaticity were obtained for the point 2 (urban area), which had the highest stability constant for Cu (II) and Ni (II), what corroborate with the aromatic groups present in its structure as can be seen in the emission spectra for both metals (Figures 3 and 4), however the lowest values were obtained for the point 1 and 4, corresponding to Preto River headwaters (reference area) and Grande River (area that receives all the pollution load from the basin) respectively.

Figure 3a-d presents the emission spectra for the DOM interaction with Cu(II) for the water samples from

Table 1. Properties of surface water samples

Sample	DOC / (mg L⁻¹)[a]		Degree of aromaticity / %		$[Cu]_{total}$ / (µg L⁻¹)[a]		log K_c - Cu(II)		$[Ni]_{total}$ / (µg L⁻¹)[a]		log K_c - Ni(II)	
	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy	Dry	Rainy
Point 1	1.31	1.56	7.22	11.25	1.70	1.07	0.41	0.04	<0.20[b]	<0.20[b]	2.84	0.04
Point 2	2.73	2.43	28.29	37.77	1.54	1.69	1.35	0.36	0.80	0.79	0.73	0.19
Point 3	2.33	2.10	24.78	27.49	1.73	2.26	0.72	0.29	<0.20[b]	<0.20[b]	0.88	0.30
Point 4	1.60	1.81	6.59	5.82	1.34	1.87	0.41	0.27	<0.20[b]	0.24	0.47	0.21

[a]Standard deviations of values were below 5%; [b]Values below the quantification limit of the method.

point 1 (the Preto River headwaters), point 2 (Preto), point 3 (Turvo) and point 4 (Grande), providing evidence of significant variation due to seasonality. It is possible to verify the suppression of the fluorescence signal after the addition of the standard Cu(II) solution and a signal with a maximum intensity at 420-440 nm. These results (Figure 3) can be associated with low aromatic content and molecular weight components, such as presence of electron-donating groups, e.g. hydroxyls, methoxyls, which are commonly observed structures in humic and fulvic acids.[17,52]

Figure 4a-d presents the emission spectra of the DOM interaction with the Ni(II) ions for the water samples from rivers along the Turvo River/Grande River watershed. A decrease in the fluorescence signal intensity is observed with an increase in Ni(II) metal concentration, corroborating other studies in the literature with Ni and other elements.[40,53,54]

The results of the conditional stability constant calculated as described in the *Data treatment* for the Cu(II) and Ni(II) ions are provided in Table 1. The log K_c results for Cu(II) were lower than those observed by other
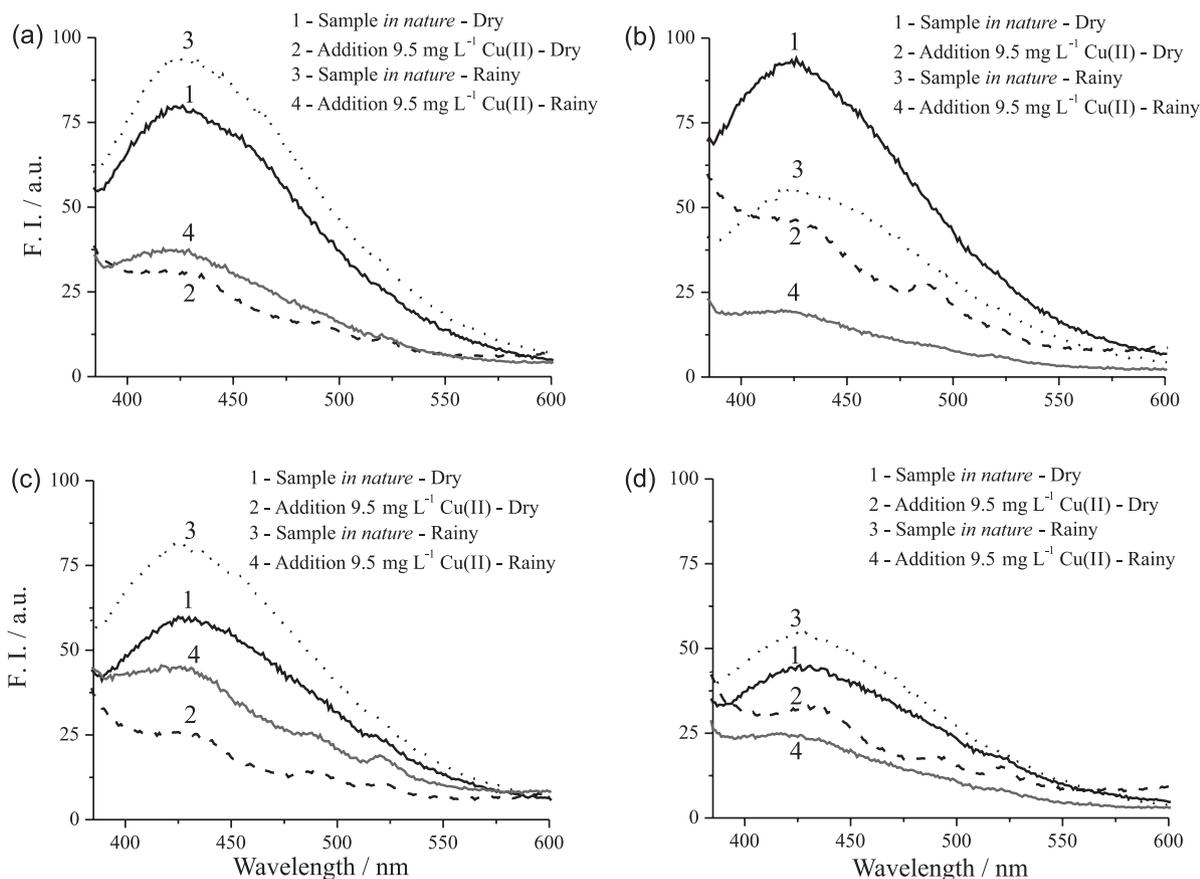

Figure 3. Emission spectra obtained for samples collected along the Turvo/Grande Watershed with (1) the sample control for the dry period; (2) the addition of Cu(II) for the dry period; (3) the sample control for the rainy period; and (4) the addition of Cu(II) for the rainy period, and it refers to (a) 1- Preto River headwaters, (b) 2- Preto River, (c) 3- Turvo River and (d) 4- Grande River.
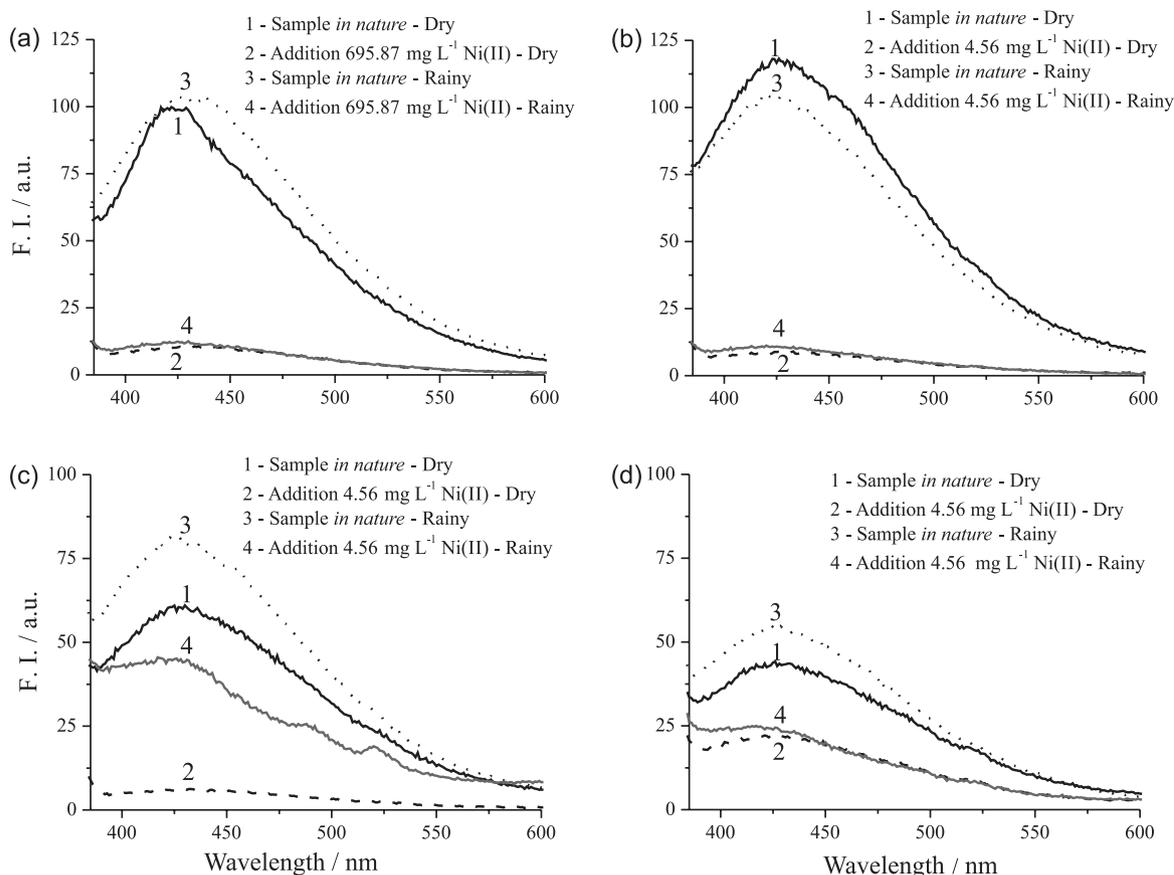
Figure 4. Emission spectra obtained for samples collected along the Turvo/Grande Watershed with (1) the sample control for the dry period; (2) the addition of Ni(II) for the dry period; (3) the sample control for the rainy period; and (4) the addition of Ni(II) for the rainy period, and it refers to (a) 1- Preto River headwaters, (b) 2- Preto River, (c) 3- Turvo River and (d) 4- Grande River.

researchers.[20,55-58] It can be inferred that point 2 (urban area) exhibited the greatest stability constant for the Cu(II) ion when compared with the other rivers analyzed in the present study, and point 1 (reference area) had the lowest value. The highest stability constant for the Ni(II) ion was observed for the reference area.

Sodré and Grassi[37] determined the stability constant of Cu(II) with DOM from the Iraí (sparsely populated area) and Iguaçu (urban area) rivers, located in the state of Paraná. The authors observed log (K_c) values between 4.28 to 5.90 and 4.83 to 6.38 for the Iraí and Iguaçu rivers, respectively, and concluded that the OM of the sparsely populated area exhibited a higher aromaticity than that of the urban area. A similar log (K_c) result using the Stern-Volmer model was obtained by Esteves da Silva et al.,[40] with Cu(II) and fulvic acid (FA) extracted from soils in the Netherlands; this log (K_c) value was 4.6. The authors observed that the greater the FA concentration of the samples, the greater the values obtained for the conditional stability constants.

The stability of the DOM-Cu(II) complexes is directly related to the number of binding sites present in the structure of the DOM; therefore, the values of log Kc imply

that the DOM present in the Preto, Turvo and Grande rivers contains smaller quantities of binding groups.[59] Figure 5 presents the UV/Vis spectra of the DOM samples of points 1, 2, 3 and 4, with the following decreasing order of aromaticity: point 2 > point 3 > point 1 > point 4. These results agree with the values obtained from the conditional stability constants (K_c) presented in Table 1.[46-48]
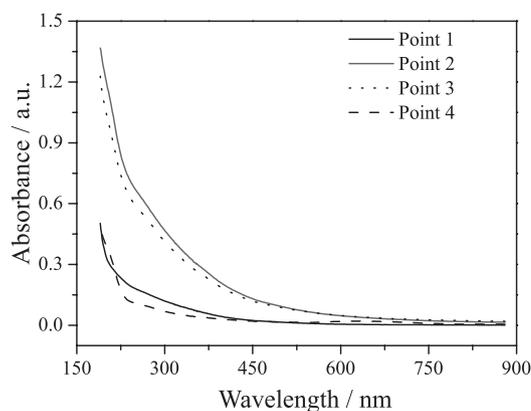

Figure 5. Spectra of UV/Vis samples of Dissolved Organic Matter from points 1 (Preto River headwaters), 2 (Preto River), 3 (Turvo River) and 4 (Grande River) for the rainy period.

The DOM complexing capacity of points 1 and 2 (reference area and urban area, respectively) with the copper ion was determined in this study. In point 1, the complexing capacity was 0.7 mmol Cu(II) g^{-1} DOC, approximately 42 times lower than the value obtained for point 2 (29.5 mmol Cu(II) g^{-1} DOC). These results suggest that the DOM from the urban area of this region contains a larger number of binding sites in its structure and, consequently, higher values of complexing capacity. The values obtained in the present study for point 2 (urban area) were higher than those observed in other studies described in the literature.[60,61]

Conclusions

The present study concludes that the conditional stability constants of DOM with Cu(II) and Ni(II) ions determined in the present study were lower than those obtained by other authors in other regions, and the DOM complexing capacity with the Cu(II) ion values observed in the urban area were as much as 42 times higher than those observed in the agricultural areas where sugarcane and oranges were produced. The NOM present in the agricultural regions contains a low number of carboxylic, carbonyl and phenolic groups, thus yielding a smaller number of binding sites in its structure, as calculated using $SUVA_{254}$, corroborating the low values of the conditional stability constant.

Acknowledgements

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