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Dissolved organic matter photodegradation in a water supply reservoir on temperate oceanic climate (Cfb): a case study of Passaúna reservoir, Brazil

Fotodegradação da matéria orgânica dissolvida em um reservatório de abastecimento de água em clima oceânico temperado (Cfb): um estudo de caso do reservatório de Passaúna, Brasil

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Abstract

Photodegradation is an important process for aquatic metabolism, related to the dissolved organic matter (DOM) transformation in water. For example, in a water supply reservoir, DOM is an important parameter since it can react and form disinfection by-products during water treatment. Thus, the understanding and determination of photodegradation rates are especially relevant for water resources management since they can influence DOM transformation in the water column. However, besides its relevance, few studies were conducted in the southern hemisphere for photodegradation rates determination. Therefore, we carried out field experiments to characterize and evaluate DOM photodegradation rate – at different depths and in two solar irradiation periods – through the application of absorption spectroscopy techniques in the UV-Vis region and fluorescence excitation-emission matrices (EEM) combined with the dissolved organic carbon (DOC) measurement. Low concentrations of natural DOM and nutrients in the aquatic environment were measured during the field monitoring. Our results indicate that photodegradation rates for a temperate oceanic climate reservoir were proportional to the availability of solar radiation, being more representative considering the time scale.

Keywords: DOM photodegradation; Aquatic organic matter; Water quality; Reservoirs.

Resumo

A fotodegradação é um processo importante para o metabolismo aquático, estando relacionado à transformação da matéria orgânica dissolvida (MOD). Em um reservatório de abastecimento de água, por exemplo, a MOD é um importante parâmetro, pois durante o tratamento de água pode ocorrer a formação de subprodutos de desinfecção. Assim, a compreensão e determinação das taxas de fotodegradação são especialmente relevantes em termos de gestão de recursos hídricos, uma vez que este processo influencia na transformação da MOD na coluna de água. No entanto, apesar de ser um processo relevante, poucos estudos foram realizados no hemisfério sul para a determinação das taxas de fotodegradação em reservatórios com tal característica climática. Sendo assim, realizamos experimentos de campo para caracterizar a MOD e avaliar as taxas de fotodegradação da MOD – em diferentes profundidades e em dois períodos distintos de insolação – por meio da aplicação de técnicas de espectroscopia de absorção na região UV-Vis e matrizes de excitação-emissão de fluorescência (MEE) combinadas com o teor de carbono orgânico dissolvido (COD). Foram encontradas baixas concentrações de MOD natural e de nutrientes no ambiente aquático. Nossos resultados indicam que as taxas de fotodegradação para um reservatório localizado em clima temperado oceânico foram proporcionais à disponibilidade de radiação solar, sendo mais representativas considerando a escala de tempo.

Palavras-chave: Fotodegradação da matéria orgânica; Matéria orgânica aquática; Qualidade da água; Reservatórios.

INTRODUCTION

The demand for drinking water has been growing as supply is on the way to collapse in various regions of the planet, conforming UN-Water estimates, which suggest that until 2025 almost two billion people will be in places with severe water scarcity and about 66.7% of the world's population may be living in conditions of water stress (Lartigue et al., 2016; World Water Council, 2021). Many studies discuss the quality of water bodies used for public supply worldwide (Lamparelli, 2004; Busch, 2009; Morling et al., 2017; Paraná, 2017; Santos, 2017; Godoy, 2017). Umpteen water sources have already become unfit for consumption due to the water quality deterioration (Santos, 2017), demonstrated by the different physical, chemical, and biological parameters monitoring, as well as calculations of water quality and trophic status indices (Lamparelli, 2004; Cunha et al., 2013). There is a complex interaction between biotic and abiotic agents, in which the quali-quantitative characterization of organic matter plays an important role for a better understanding of the water quality dynamics in a reservoir.

Dissolved organic matter (DOM) can be through autochthonous, allochthonous, or anthropogenic sources. Depending on its concentration, DOM can be a problem in water supply reservoirs. In underdeveloped countries, organic loads are a serious problem, because chlorination is usual water treatment method (Instituto Brasileiro de Geografia e Estatística, 2010), due to its low cost and antimicrobial efficiency without adding color to the water. However, DOM can react with chlorine, resulting in unwanted disinfection by-products, such as trihalomethanes, with carcinogenic effects (Meyer, 1994; Alegria et al., 1988; Brasil, 2006; Furtado, 2011).

Different factors contribute to the mineralization of aquatic organic matter, and it is already known that refractory DOM can be converted into substrates more susceptible to microbial degradation (Moran & Covert, 2002; Azevedo, 2005). However, studies on DOM photodegradation in water supply reservoirs are scarce, especially in temperate oceanic climate (Cfb) in the southern hemisphere, including Brazil (Table 1).

Previous DOM photodegradation research on aquatic environments, generally, was conducted in water bodies with high DOM concentrations. Therefore, it is relevant to assess if and how photodegradation is a crucial process for low DOM concentration environments, such as Passaúna Reservoir.

In addition, our algae and solids (dissolved and suspended) transportation, degradation, and assimilation are different from the studies majority, which may result in different organic matter sources and light attenuation in the water column. Therefore, to know and understand DOM concentration, composition, distribution, and transformation is fundamental to complement water quality monitoring, as well solar radiation effects on DOM transformation in the water column – mainly in the case of river basins located in large urban and their surroundings.

Thus, in this study, we investigated the solar effects on DOM photodegradation and its impacts on the aquatic organic matter dynamics at Passaúna reservoir. For this purpose, we performed a field experiment with water incubation in different water depths (to simulate the light attenuation). Also, we analyzed the dissolved organic carbon (DOC) variation combined with the organic matter signature, obtained through spectroscopy techniques (fluorescence and UV-Vis), to produce fluorescence excitation-emission matrices (EEM) and identify some of the most common components of DOM. The motivation for this approach was to understand the process of solar transformation and degradation of DOM in a temperate oceanic climate region, focusing on a more detailed investigation of the water quality dynamics in a water supply reservoir.

MATERIAL AND METHODS

Study area

The experiment was carried out at Passaúna reservoir located at Curitiba Metropolitan Region (CMR), South part of Brazil, between the cities of Curitiba, Campo Largo, and Araucária (Figure 1). Both the Passaúna reservoir and the river stretch upstream are under pressure from urban and rural uses (Rauen et al., 2017).

The reservoir is at the Iguaçu River catchment and Passaúna River sub-basin. Its watershed has a drainage area of 153 km^2. It is mainly characterized by silt-clay sediments, carried by erosion or fluvial transport (Carneiro et al., 2016; Rauen et al., 2017; Oliveira et al., 2019). The reservoir and upstream fluvial section are classified as class-II freshwater (Rauen et al., 2017) according to Brazilian legislation.

The Passaúna reservoir has an average depth of approximately 9 m, a surface area of 11 km^2, a water volume of 71.6 hm^3 (Rauen et al., 2017), and average transparency of 2 m (Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019). It produces between 1800 ls^{-1} and 2000 ls^{-1} of water that supplies about 20% of the Curitiba population, in addition to Araucária and Fazenda Rio Grande population's part (Paraná, 2013).

The local climate can be classified, according to Köppen (1936), as temperate oceanic, maritime temperate, or humid mesothermal (Cfb). It is characterized by humid summer with mild temperatures (average minimum and maximum temperatures are, respectively, 14.5 and 20.5 °C and the annual average is 17.3 °C). It does not have a well-defined rainy season that is rainfall is well distributed throughout the year, with an average rainfall of 150 mm in the wettest month and 100 mm in the driest month (Dias, 1997; Busch, 2009; Paraná, 2017; Rauen et al., 2017; Instituto Agronômico do Paraná, 2020).

We chose the local for sampling and experimenting (-25.5115711, -49.3716873) based on the following criteria: purpose and use of the resource (intake of the water treatment plant), ecological representativeness, the lentic regime of flow, restricted access, greater and more stable depth in relation to other sites of the reservoir, as well high transparency of the water column. Figure 1 indicates the experiment site (the water treatment plant intake).

Table 1. Comparison between studies about DOM photodegradation on diverse places and aquatic environments.

Study	Water body	Place (Climate)	Radiation	Depth (m)	Duration	Vessel	Sample	Vol. (ml)	Analysis
1st. field experiment	Passaúna reservoir (lacustrine zone)	Brazil (Cfb)	Natural	0.05; 0.5; 1.0; 1.5; 2.0	27.95 and 94.70 h	borosilicate tubes	Natural DOM	20	DOC; fluorescence and UV-Vis spectroscopy; phosphorus and total nitrogen; dissolved oxygen; temperature; transparency; turbidity; pH.
2nd. field experiment					24.62 and 93.27 h		Natural DOM Natural DOM+HA Natural DOM+ Tyr+Trp		
Geller (1986)	Lacustrine	Germany (Cfb)		–	06 weeks	borosilicate flasks with screw caps with Teflon gaskets and laboratory window lab glass	Sterile solution of DOM macromolecule concentrated 5 times	N/I	interference of photodegradation in biodegradation; DOC; Sephadex G-15 gel permeation chromatography
Reitner et al. (1997)		Austria (Cfb)		0.03	4 to 8 h	quartz bottles	DOC total, humic-DOC and non-humic DOC	120	Absorbance (365 and 250 nm); DOC; epifluorescence microscopy; pH.
Azevedo (2005)		Brazil (Cfa)	Natural (direct sunlight) and artificial	–	28 h (natural) 96 h (artificial)	borosilicate tubes	SH extracted from water, sediment, and soil adjacent to the lagoon	15	DOC; fluorescence and UV-Vis spectroscopy.
			Artificial And natural (direct sunlight and through the water column)	0; 0.2; 0.6; 1.7; 2.0	29 h (direct sunlight); 33 to 78 hours (sunlight through the water column) 96 hours (artificial)	borosilicate tubes	Natural DOM	15 (sunlight direct) and Complete tube (sunlight through the water column)	DOC; fluorescence and UV-Vis spectroscopy.
Obernosterer & Herndl (2000)	Marine	Croatia (Cfa) and Netherlands (Cfb)	Natural	Surface	5 to 8 hours	quartz bottles	DOC total, humic-DOC and non-humic DOC	1000	DOC, fluorescence and UV-Vis spectroscopy; BOD; fluorescence and UV-Vis; epifluorescence microscopy.
Miller & Moran (1997)	Salt wetland	USA (Cfb and Cfa)	Artificial	–	4 hours	Glass chamber with thermostat (20 ° C) with an optical quartz window and airtight quartz tubes	Natural salt DOM + humic substances or + deionized water; Artificial salt water + humic substances or + deionized water	1200 and 25	Bacterial protein production

Note: BOD = biochemical oxygen demand; DIC = dissolved inorganic carbono; QSU = quinine sulfate units.

Table 1. Continued...

Study	Water body	Place (Climate)	Radiation	Depth (m)	Duration	Vessel	Sample	Vol. (ml)	Analysis
Mopper & Stahovec (1986)	Coastal marine	USA	Natural and artificial	–	4 or 8 hours	quartz flasks	Natural DOM	–	DOC and DIC; fluorescence and UV-Vis spectroscopy; HPLC
Moran, et al., 2000 (2000)	Fluvial/ estuarine	(Cfb and Cfa)	Artificial		6 and 7 days			2000	DOC and DIC and UV-Vis spectroscopy; measurement of optical properties; bacterial breathing
Ziegler & Benner (2000)	Estuarine		Natural	0.01	24 hours	quartz bottles		90	Photochemical DOM effect on bacterial production; DAPI-stained epifluorescence microscopy; DOC and DIC; absorbance spectrophotometry; bacterial protein production.
Findlay et al. (2001)	Groundwater or underground aquifer	New Zeeland (Cfb)		–	2 hours	Shallow tanks		1000	labile DOM; fluorescence and UV-vis spectroscopy; phosphorus and nitrogen; bacterial metabolism
Jørgensen et al. (1998)	Lacustrine	Sweden (Cfb)		Surface	7 hours (irradiation period centered on solar noon)	Quartz tubes		190	HPLC and pulsed amperometric detection; epifluorescence microscopy; total dissolved nitrogen; bacterial protein production
Lindell et al. (1995)			Artificial	–	0; 0,5; 1 ;2; 4; 8; 16; 32; and 64 or 100 hours			40	Bacterial biomass; DOC; color and nitrogen and phosphorus;
Lindell et al. (1996)			Natural	Surface to depth measured with Secchi's disk	From sunrise to sunset	Quartz tubes (transparent) and borosilicate tubes (dark control)		190	Bacterial biomass; DOC; color; pH; bacterial protein production.
Tranvik & Bertilsson (2001)			Artificial	–	12 hours	Polypropylene bags transparent to UV radiation		400	COD; UV-Vis spectroscopy; photochemical production of carboxylic acid (difference between irradiated samples and dark controls at the end of radiation exposure; fluorimetric analysis of chlorophyll-α.
Bertilsson & Tranvik (2000)						Quartz tubes		70	DIC and DOC; fluorescence spectroscopy (in QSU) and UV-Vis; carboxylic acids: oxalic, malonic, formic and acetic (electrophoresis separation).

Note: BOD = biochemical oxygen demand; DIC = dissolved inorganic carbono; QSU = quinine sulfate units.

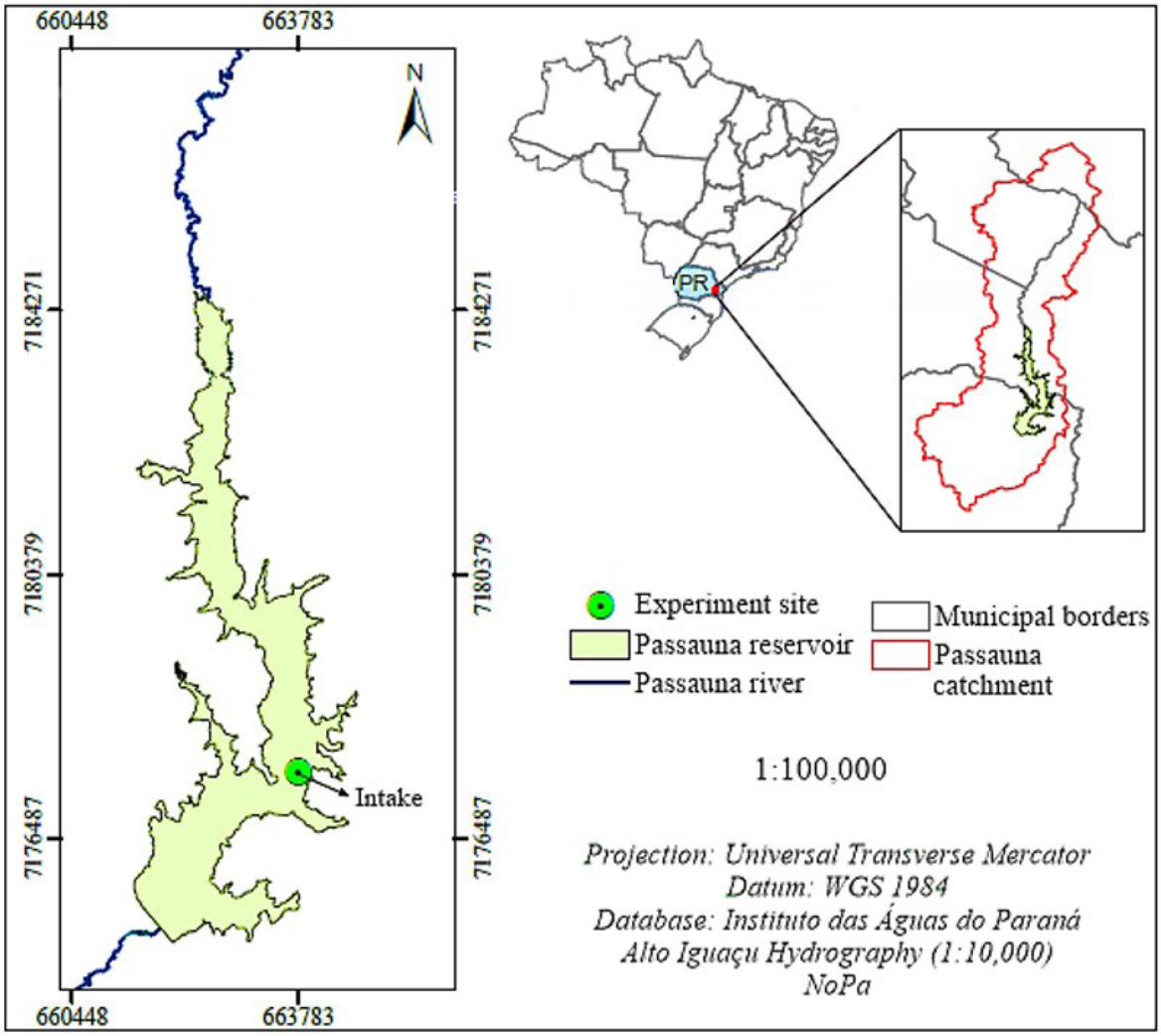

Figure 1. Passaúna Reservoir: emphasis on the experiment site (left) and its location in the state of Paraná and Brazil (in the middle, top) and drainage basin delimitation (right) (Adapted from Barreto et al., 2019).

Photodegradation experiment and water sampling

Two field experiments sets were conducted: the first one in April 2019, described by Souza et al. (2019), and the second in October of the same year. To investigate the photodegradation of natural DOM, in both the field experiments, borosilicate tubes with approximately 20 mL of sample were incubated (i.e., kept submerged in the Passaúna reservoir) with water previously collected from the reservoir.

We collect water samples at the surface of the WTP intake area using organic matter-free amber glass bottles (acid washing with HCl 1M, at 200 °C, and calcination at 400 °C for 4 h). After sampling, water samples were prepared as follows: 10% were filtered through a 0.45 µm membrane, for removing predators of bacteria and coarse particles, and 90% filtered in 0.22 µm, for removing bacteria (Azevedo, 2005).

The tubes were incubated for approximately seven days, with a partial sampling approximately two days after the beginning of the incubation period to investigate the DOM changes in the initial step. We had constant incubation depths during all two experiments (April and October 2019): surface (0.05 m); 0.50; 1.00; 1.50 e 2.00 m and the dark control (tubes wrapped in aluminum foil) incubated in 2.10 m (Figure 2).

For the second field experiment (October 2019), aliquots of water sample (prepared with the same filtered proportions adopted on the first field experiment) were supplemented with DOM standard solutions: part with 40 mgl^{-1} humic acid (HA) and part with tyrosine (Tyr) and tryptophan (Trp) – 20 mgl^{-1} of each of the amino acids).

Solar radiation and water quality data

Water transparency was measured before starting the experiment, during the experiment, and at the end of the field experiment (1st, 2nd, and 8th April 2019 and 8th, 10th and 15th October 2019). We also used water transparency measurements (approximate value) observed in measurements performed by the Mudak-WRM project over a year (prior to the start of the experiment).

At the field, we also analyzed turbidity, pH, and dissolved oxygen (DO) data from Sanepar's automatic monitoring station (Paraná, 2019a, 2019b) and the Mudak-WRM (Multidisciplinary

Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019) project. In addition, water samples were collected and transported to the laboratory, to quantify total nitrogen and phosphorus using the colorimetric method (American Public Health Association, 1999) and dissolved organic carbon (DOC) using carbon analyzer TOC-VCPH Shimadzu®. We analyzed DOM through UV-Vis spectroscopy (Varian Cary 50Conc®) and fluorescence spectroscopy (Cary Eclipse®).

We obtained solar radiation data from the Curitiba A807 automatic meteorological station (Instituto Nacional de Meteorologia, 2019), and calculated the solar radiation at each water depth (disregarding the flasks glass wall), during the incubation period (Figure 3**)** from the equation $I = Io - e^{Zk}$, where: I=radiation at a given depth, Io=surface radiation, Z=depth in meters, and k=vertical attenuation coefficient (Howard-Williams & Vincent, 1984). The vertical attenuation coefficient (k) was calculated from the equation $k = 1,7\left(Z_{SD}{}^{-1}\right)$, where: Z_{SD}=transparency measured with Secchi disk (in meters) (Poole & Atkins, 1929).

Characterization of organic matter based on peaks of fluorescence intensity (FI)

While DOC quantifies the DOM, fluorescence spectroscopy allows characterizing it. We treated the raw data from fluorimetry readings, combining them with the UV-Vis spectroscopy readings

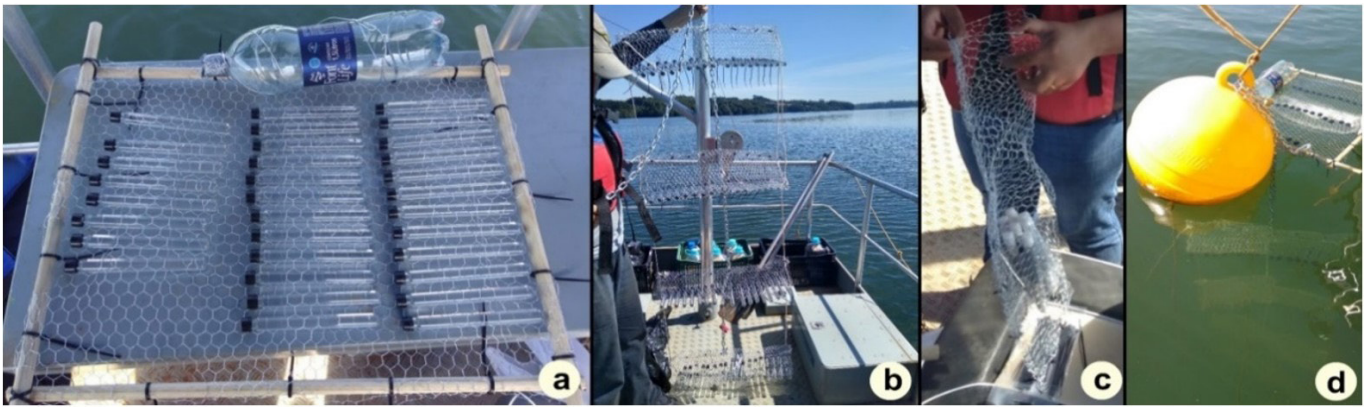

Figure 2. Sample fixing structure for photodegradation in different depths: photodegradation sets (a) on the surface; (b) every 0.5 m; (c) dark control (d) start of incubation in the reservoir (Souza et al., 2019).

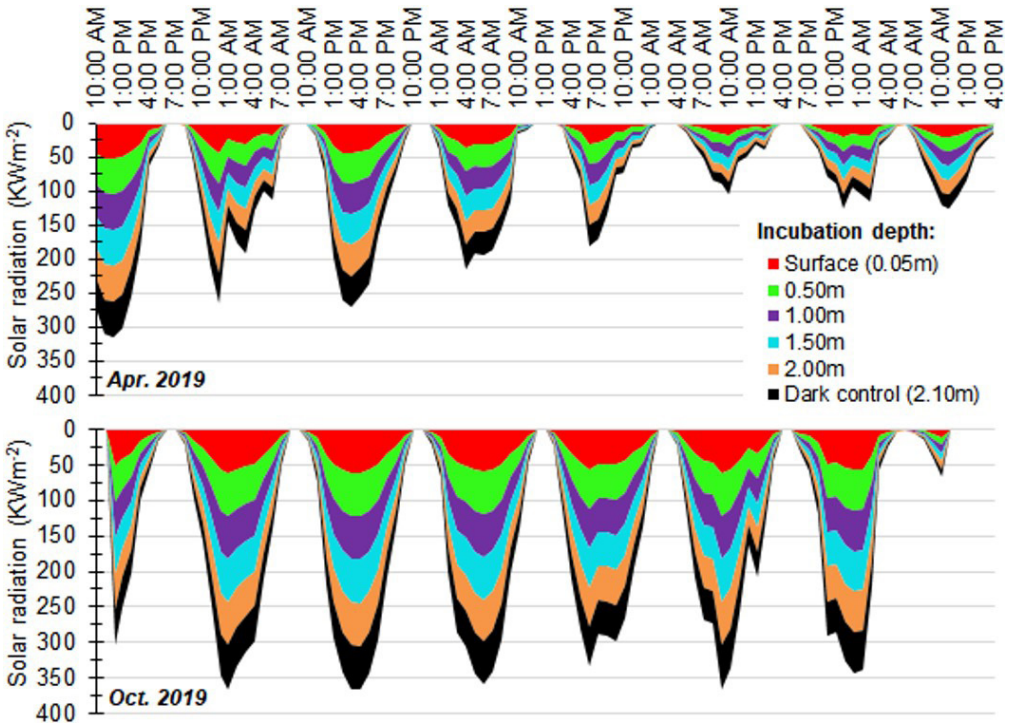

Figure 3. Variation of solar radiation corrected by the coefficient of vertical water attenuation in 1st. (upper) and 2nd. field experiment (bottom): each color band represents the radiation of each incubation condition (different water column depths). Note: The colored bands its been stacks to allow comparison between similar quantities that overlap, if shown otherwise.

and the DOC concentration, using the FEEMC 2.0 code (Kozak et al., 2019).

Each FI peak, usually represent as A, C, B, T1, and T2 labels, is produced from a specific wavelength and results from different compounds, or to a substance analogous to it: peaks A and C indicates refractory DOM (humic substances), as well peaks B, T1, and T2 indicate labile DOM presence (tyrosine and tryptophan respectively) (Knapik et al., 2014). In other words, FI peaks can be interpreted as a DOM fingerprint of the environment analyzed. The ranges of the excitation-emission matrices (EEM) that the different FI peaks are identified are summarized in Knapik et al. (2014).

RESULTS AND DISCUSSIONS

Water quality parameters for environmental characterization

On the 1st field experiment (April 2019), we verify the 2.1 m (±0.1 m) of average transparency, approximately 17.4% of water intake average depth (Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019), and this amount was in accordance with the time series recorded in the previous studies carried out the same reservoir area (Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019; Dias, 1997). However, we found during the 2nd field experiment (October 2019) higher transparencies than suggests by the measurements of Dias (1997) and Mudak-WRM (Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019): 5.0 m on the first day of DOM incubation in the reservoir and 7.0 m after in the next two days (Figure 4).

It is possible that the higher transparency observed in the 2nd field experiment (October 2019) was due to a dry period before the experiment, with less contribution of dissolved and suspended sediments carried throughout the watershed, as suggested by Oliveira et al. (2019) in a study conducted at Passaúna reservoir. Thus, with low turbidity, light penetration is facilitated in the water column (Mostofa et al., 2013; Suhett et al., 2006). Also, greater exposure to sunlight amplifies the bleaching of the colored DOC (Kieber & Mopper, 1987; Moran et al., 2000; Suhett et al., 2006).

The turbidity (Figure 5) measures during the entire experiment (April and October 2019) were very low compared to the maximum limit of 100 NTU established for freshwater class-II of the water bodies classification (Brasil, 2005). We show in Figure 5 the turbidity values (NTU) during the photoperiods in which the samples incubated in the reservoir were irradiated by sunlight.

The lower turbidities (Figure 5) and higher water transparency (Figure 4) observed during the second field experiment, compared to the first one, facilitated the light penetration into the water column, improving the potential for DOM photodegradation (Mostofa et al., 2013). Oliveira et al. (2019), found a satisfactory correlation between turbidity and solids in the Passaúna reservoir: Pearson's correlation coefficients (r) of 0.6844 (Spearman's $\varrho = 0.7283$) for total solids and 0.9653 (Spearman's $\varrho = 0.8264$) for total suspended solids.

The dissolved oxygen (DO) and the pH measured were within the water quality standard established by CONAMA – National Environment Council (Brasil, 2005): respectively,

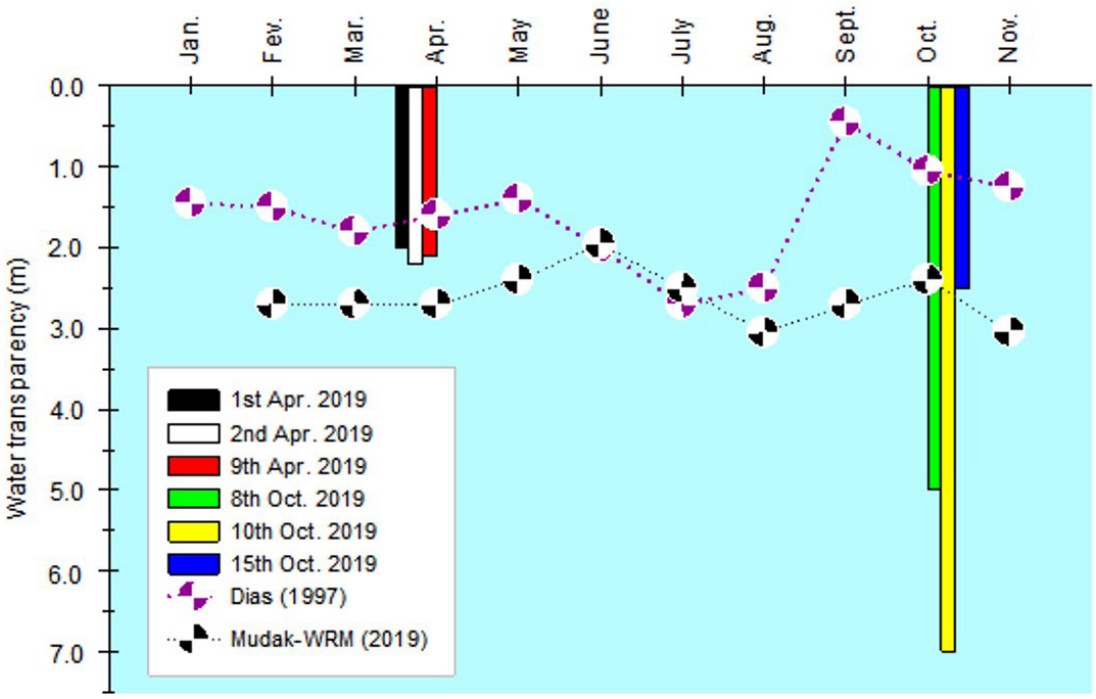

Figure 4. Water transparency in the region water intake at Passaúna reservoir, measured during 1st and 2nd field experiments, compared to the time series verified in previous research (Dias, 1997; Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019) for the same area. The vertical bars indicate the measurements we made during the experiment.

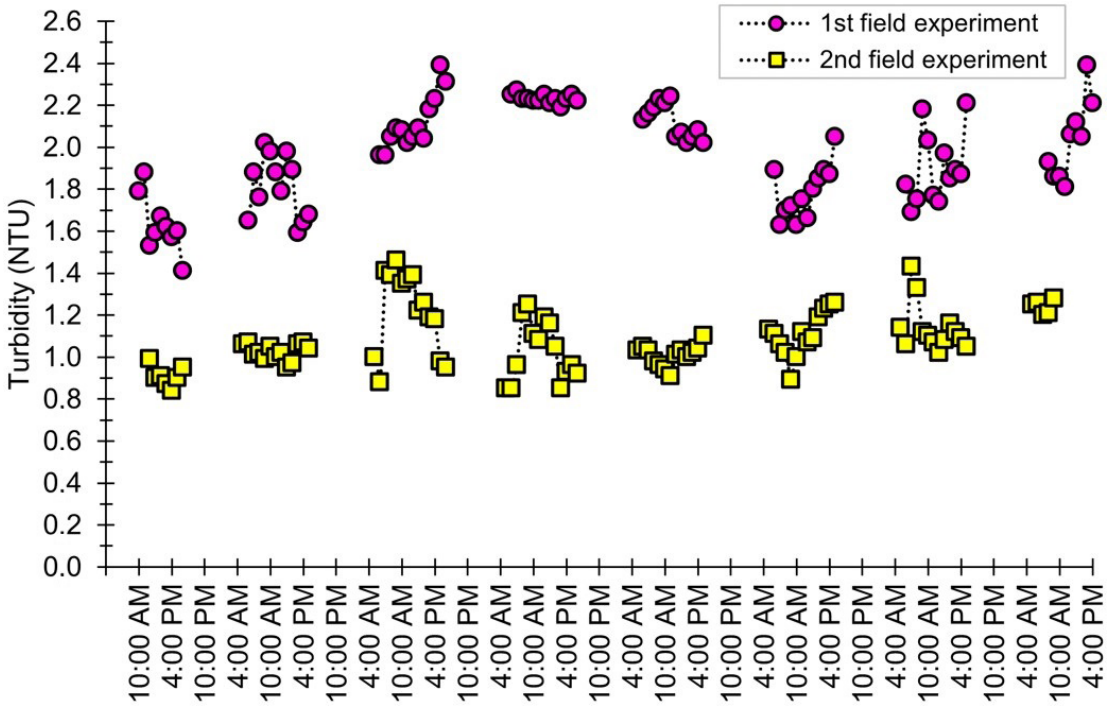

Figure 5. Variation of water turbidity at water intake area at Passaúna reservoir during the field experiments photoperiods, measured by the monitoring sensor fixed at the area where the DOM photodegradation experiment was carried out (Database: Multidisciplinary Data Acquisition as Key for a Globally Applicable Water Resource Management, 2019).

6.0 mgl^{-1} and between 6 and 9 units. In aquatic environments, most photochemical reactions involve DO, as it acts as an electron acceptor and participates in secondary reactions, i.e., under higher concentrations of DO, there are higher rates of photodegradation of the DOM. As well the water acidification (measured by the pH decrease) also can accelerate the DOM photodegradation (Mostofa et al., 2013).

Complementarily, total nitrogen (TN), which does not figure as a direct water quality parameter (Brasil, 2005), but the nitrogenous fractions – nitrate, nitrite, and ammoniacal nitrogen – have maximum tolerable values. However, the quantified TN concentrations were 0.61 mgl^{-1} (April 2019) and 0.07 mgl^{-1} (October 2019) – much lower than the maximum recommended sum of the nitrogenous fractions mentioned by the environmental regulation.

Total phosphorus (TP) was below the limit of quantification (i.e., <0.01mgl^{-1}) (American Public Health Association, 1999), in the experiment carried out in April 2019. In October 2019, TP concentration was 10.0% below the 0.03mgl^{-1} recommended by CONAMA for freshwater lentic environments (Brasil, 2005). It is essential that the demand for nutrients, inherent in each phytoplankton species, is properly supplied because these organisms are responsible for a significant part of the autochthonous DOC production. Also, DOC concentration is inversely related to the water body trophic state, i.e.: in environments with low nutrient concentrations, DOC excretion by phytoplankton, as well as by macrophytes, is usually high (Esteves, 1998).

Quantification and characterization of dissolved organic matter

In April (1st field experiment), only the natural DOM variation (over time) significantly impacted the DOC concentration, both among sample sets exposed to sunlight (variable along the water column due to vertical attenuation) and dark controls ($p>0.05$). In October (2nd field experiment), there was no statistical difference in temporal and spatial variations (Table 2).

In addition to DOC, peaks A, B, C, T1, and T2 of fluorescence intensity (FI), exhibit the transformations and decay suffered by the natural DOM throughout the incubation time (Figure 6).

In April, after 2-days, low increases of FI were observed at 1.5m depth in bands A, C, T1, and T2; and only tyrosine-associated FI decreased. At the end of the 7-days, all FI peaks decreased, compared to the sample before incubation and irradiation, except for the peaks associated with tryptophan in samplings incubated at 0.5m depth.

In October, after 2 and 7-days, there was a significant FI difference between water column depths ($p\approx0.03$ and $p\approx4.10\text{-}7$, respectively): on the first moment, a FI growth at 1.0m; and later, at the experiment end, greater degradability in the upper layers and minor in dark control.

In general, the spectra showed low FI, indicating probably a minor presence of anthropogenic allochthonous source, possibly carried via catchment runoff and/or the upstream fluvial section stream. We discard leading DOM point sources because compounds such as domestic effluents, leachate from sanitary landfills, etc.,

Table 2. Dissolved organic carbon concentration (DOC) in the Passaúna reservoir water intake area, at different times of the 1st and 2nd field experiment: t0=start of the experiment (incubation of the samples in the reservoir), t2=partial sampling carried out after approximately 2-days and t7= the field experiment end, after circa 7-days.

Experiment	Depth	DOC (mgl^{-1})			ΔDOC (%)		
		t0	t2	t7	t_0 regarding t_2	t_0 regarding t_7	t_2 regarding t_7
1st. field experiment (Apr. 2019)	0.05 m (surface)	2.616 Aa	3.059 Bb	3.866 Cc	16.9	47.9	26.4
	0.10 m (dark control)		3.183 BCb	3.386 Cc	21.7	29.4	6.4
	0.50 m		3.099 BCb	3.537 Cc	18.5	35.2	14.2
	1.00 m		3.049 Bb	3.701 Cc	16.6	41.5	21.4
	1.50 m		3.006 ACb	3.279 Cc	15.0	25.3	9.1
	2.00 m		3.105 BCb	3.557 Cc	18.7	36.0	14.6
	2.10 m (dark control)		3.443 Bb		31.6		
2nd. field experiment (Oct. 2019)	0.05 m (surface)	2.153 Dd	3.731 Dd	1.699 Dd	73.3	31.8	12.8
	0.50 m		2.516 Dd	2.837 Dd	16.9	30.5	15.9
	1.00 m		2.424 Dd	2.810 Dd	12.6	20.8	9.8
	1.50 m		2.369 Dd	2.601 Dd	10.0	30.9	-1.4
	2.00 m		2.858 Dd	2.818 Dd	32.8	14.3	
	2.10 m (dark control)			2.460 Dd			

Note: Concentrations identified with equal letters (uppercase in the columns and lowercase in the rows) do not differ statistically from each other by the Tukey test (α = 0.05). Negative percentages indicate a decrease, and positive percentages indicate an increase in the DOC concentration in relation to the reference period value.

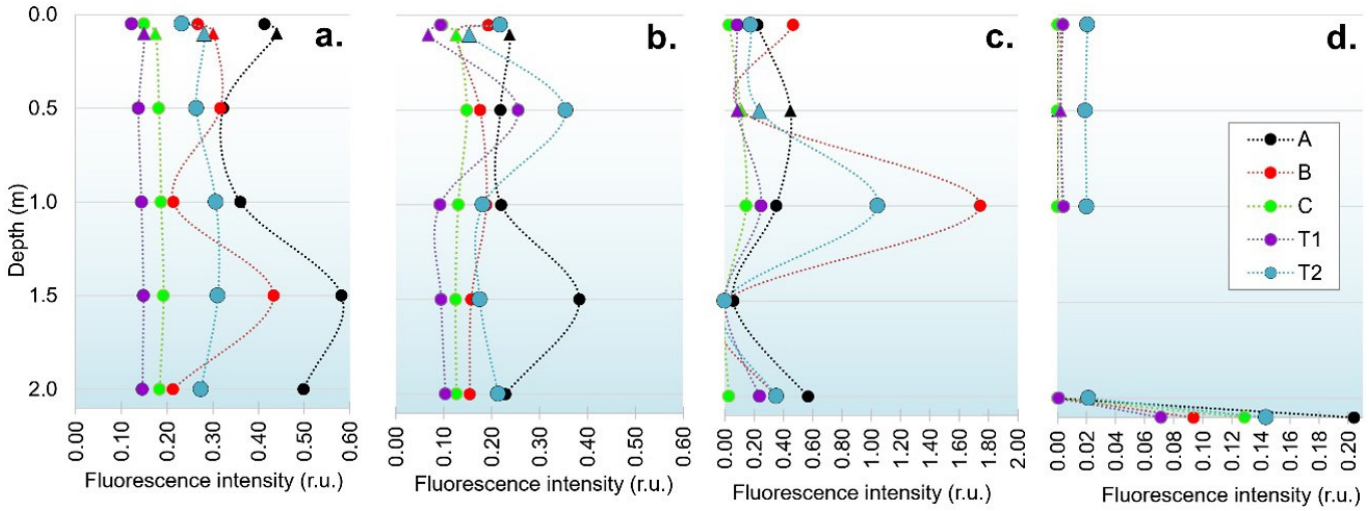

Figure 6. FI peaks (A, B, C, T1, and T2) of natural DOM at different depths in the Passaúna reservoir water intake area: (a) and (b), respectively, 2 and 7 days after starting the 1st field experiment (Apr. 2019); (c) and (d), respectively 2-days and 7-days after starting the 2nd field experiment (Oct. 2019). Points plotted on triangle form represent dark control, and circles the samples incubated exposed to solar radiation.

present higher FI, requiring sample dilution, which was not the case of our analysis.

The higher degradation rates in the surface can be attributed in part to photodegradation due to the lower solar radiation vertical attenuation. However, in the case of the samples affected by solar radiation, the FI variations can be related to the nanophytoplankton activity due to the radiation saturation region that is the area with the best lighting conditions for the primary production performance (Esteves, 1998) – where the limiting factors are commonly the presence of predators and shortages of nutrients.

Godoy (2017) also recorded significant seasonal variation in the FIs peaks ($p=0.03$) for sampling performed in the water intake in February 2016 (summer) and May 2017 (autumn). In a similar experiment, realized in Lagoa dos Patos-MS, Azevedo (2005) found higher photodegradation rates for natural DOM than those observed for Passaúna reservoir and higher concentrations of nutrients and organic matter than those we verified in this study.

Only the temporal variation of the DOC was significant for the experiment where we observed the photodegradation of DOM present on samples enriched with DOM standards solutions. We do not observe statistically significant variation between incubation depths (Table 3).

For both reservoir water solutions enriched with DOM standards, there was a significant difference ($p<0.05$) between the FIs, both as a function of the incubation conditions (position in the water column and photoprotection), and between the peaks A, B, C, T1, and T2 indicating DOM diversity and greater expressiveness of one compound at the expense of another (Figure 7).

Table 3. Variation of dissolved organic carbon dissolved (DOC) in reservoir water samples (from the intake) enriched with different standard solutions of DOM, at different times: t0=start sample's incubation in the reservoir, t2=partial sampling realized after circa 2-days, and t7=end of the experiment after circa 7-days

	DOC (mgl^{-1})			Δ DOC (%)		
	t_0	t_2	t_7	t_2 regarding t_0	t_7 regarding t_0	t_7 regarding t_2
Water sample from the Passaúna intake area enriched with a humic acid solution (W+HA)						
0.05m (surface)	4.8 a	5.1 a	2.8 b	7.2%	-41.4%	-45.3%
0.50m		5.6 a	5.1 a	17.6%	6.8%	-9.2%
1.00m		5.8 a	3.9 b	20.5%	-19.8%	-33.4%
1.50m		5.7 a	5.2 a	19.6%	8.5%	-9.2%
2.00m		5.5 a	4.8 a	15.1%	-1.1%	-14.1%
2.10m (dark control)		5.7 a	4.3 a	18.5%	-10.6%	-24.6%
Water sample from the Passaúna intake area enriched with a tyrosine and tryptophan solution (W+Tyr+Trp)						
0.05m (surface)	20.2 c	20.4 c	15.3 d	1.0%	-24.2%	-25.0%
0.50m		21.2 c	17.4 d	5.1%	-13.6%	-17.7%
1.00m		20.4 c	15.3 d	1.0%	-24.2%	-25.0%
1.50m		21.4 c	17.1 c	6.3%	-15.1%	-20.1%
2.00m		21.3 c	15.6 d	5.7%	-22.6%	-26.8%
2.10m (dark control)		20.0 c	15.9 d	-0.6%	-21.1%	-20.6%

Note: Concentrations identified with equal letters do not differ statistically from each other by the Tukey test (α = 0.05). Negative percentages indicate a decrease and, positive percentages indicate an increase in the DOC concentration concerning the reference period value.

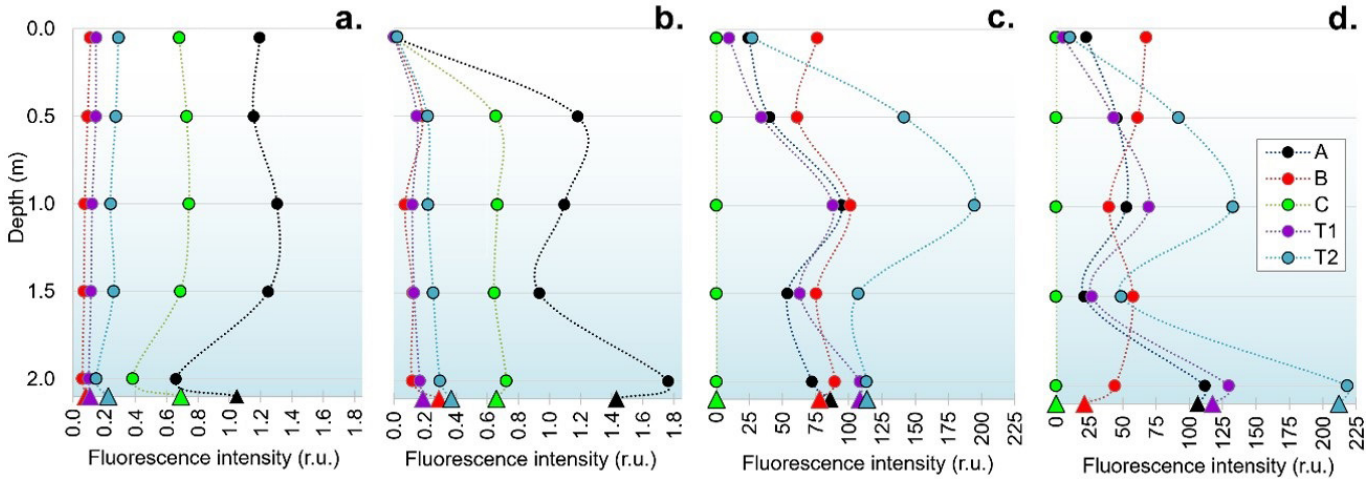

Figure 7. FI peaks (A, B, C, T1, and T2) of DOM at different depths in the Passaúna reservoir water intake area: (a) and (b), respectively, 2 and 7-days after starting incubation of water sample enriched with humic acid; (c) and (d), respectively, 2 and 7-days after starting incubation of water sample enriched with tyrosine and tryptophan. Points plotted on triangle form represent dark control, and circles the samples incubated exposed to solar radiation.

After 2-days, W+HA emitted fluorescence in peak T1, associated with tryptophan and/or analogous compounds and the other peaks' FIs were smaller than the initial values (sample before solar irradiation, i.e.: A=0.093, B=0.005, C=0.041, T1=0.000, and T2=0.015 r.u.). After 7-days of incubation, only peak A referring to the surface sample set did not exhibit higher FI. Such variations probably resulted from the transformations caused by photodegradation associated with biological activity (nanophytoplankton remaining of the filtration procedure).

Samples enriched with amino acids (W+Tyr+Trp) showed peak C minus expressive after 2 and 7-days of incubation on the reservoir, compared to the samples before incubation, whose peaks of FI were: A=87.3, B=103.6, C=6.1, T1=111.8, and T2=113.4 r.u.

To A, B, T1, and T2, there were insignificant differences between the incubation depths, including dark control. However, peak C (with dark control exception) the FI increased proportionally to the depth increase in the water column, demonstrating the vertical attenuation effect.

The results observed during the 1st field experiment emphasize the strong dependence on the balanced interaction of both microbiological agents and abiotic variables and the difficulty of identifying the weights of each component in the cycle of matter separately, according to report in the literature (Leenheer, 1994; Geller, 1986; Lindell et al., 1996; Jørgensen et al., 1998; Moran & Covert, 2002; Mostofa et al., 2013).

The results observed during the 2nd field experiment, especially those related to natural DOM enriched with DOM standard solutions, enabled the determination of DOM degradation in the aquatic environment. The results presented here highlight

the occurrence and influence of the DOM photodegradation process in a temperate oceanic climate reservoir.

FINAL CONSIDERATIONS

Reports on the dynamics of DOM with an emphasis on photoinduced reactions are recent and scarce in Cfb and Cfa climates (that have frequent interruptions in direct and abundant natural light), mainly in the southern hemisphere. Therefore, the variability in the amount of available solar radiation associated with the intrinsic characteristics of DOM can severely influence the respective rates of degradation in the water column.

Caution is essential when considering singly photochemical transformations, principally in waters with low organic matter levels, as the viability of degradation has been demonstrated under the condition of strict interdependence between photo and biochemical processes. This highlights the need to maintain the best possible conditions to favor the healthy functioning of the aquatic systems self-purification and the organic matter and nutrients cycling, especially in complex systems such as reservoirs.

Expanding the DOM contents at an experimental level allows viewing a part of the complex process of DOM degradation, demonstrating the feasibility of estimating the environment's response poor in nutrients and organic matter to possible – but undesirable – increases in the anthropic DOM-allochthonous input, given the proximity to urban, agricultural areas and important roads. Given this, it is possible to conclude that for higher degradation rates, in waters with high organic load, in reservoirs located in regions of humid temperate climate, or temperate oceanic climate, a longer time of exposure to solar radiation is necessary, also considering the contribution of the others conditioning factors for DOM photodegradation.

If the reservoir's particularities are known and respected, the contribution of DOM's photodegradation to the water quality of public supply reservoirs is satisfactory even in locations without a precise definition between the dry and rainy season, that is, with many cloudy and rainy days throughout of the year.

The application of spectroscopic techniques, of absorbance at wavelengths in the UV-Vis range and excitation and fluorescence emission, is a great tool for the management of water resources because, despite this study having used equipment residing in laboratories, several of the consulted works report the use of portable fluorimeters and photometers, as well other types of sensors to measure other variables in situ - some of them, similar to the monitoring system of vestments associated with quality, usually monitored, already implemented in the Passaúna Reservoir water intake and several other reservoirs.

The research developed so far brings a complementary point of view on the DOM dynamics in the reservoir in the place that can be considered the most important because its principal purpose is water supply to the population. Thus, the satisfactory responses obtained in this study make promising future studies focusing on the other facets of aquatic organic matter and their photochemical transformations upstream and downstream of the water intake region (in other usual points of main reservoir sampling, in the pre-reservoir and at critical points in the river section), as well as to evaluate the bioavailability photoproducts of Passaúna reservoir natural DOM for the microbial community.

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Carolina Ferreira de Souza: Experimental planning; *in situ* and laboratory analysis; data processing and processing; manuscript writing.

Heloise Garcia Knapik: Experimental planning; guidance technological support; manuscript review and writing.

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