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Photochemical mineralization of DOM in high humic tropical aquatic ecosystems: ambiguous regulation by watercolor

Mineralização fotoquímica da MOD em ecossistemas aquáticos tropicais húmicos: efeito ambíguo da coloração da água

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Abstract: Aim: Photochemical mineralization is a significant pathway for the total oxidation of Dissolved Organic Carbon (DOC) in aquatic ecosystems. The concentration of DOC, watercolor, solar radiation intensity, diagenetic state of DOC, and oxygen availability are known regulating factors influencing the DOC photochemical mineralization process. However, these studies have not yet assessed the importance of these regulatory factors under extreme conditions of DOC concentration and watercolor. The aims of this study were: (1) to optimize methodological parameters for investigating the photo-degradation process in tropical humic/super-humic aquatic ecosystems; (2) to evaluate the relative importance of regulatory factors influencing photochemical mineralization in tropical humic/super-humic ecosystems; and (3) to measure photochemical mineralization rates in 20 coastal tropical humic/super-humic ecosystems and comparing them with available data worldwide. **Methods:** Three types of DOC exposure experiments were conducted: (i) exposing water samples to different solar radiation intensities, (ii) exposing water samples of the same origin but with different DOC concentrations (dilutions) to sunlight and (iii) exposing water samples from a gradient of 20 environments with distinct characteristics to sunlight. **Results:** Our results revealed that oxygen concentration became limiting for the photochemical mineralization process in experiments investigating super-humic ecosystems. Watercolor exhibited ambiguous effects on photochemical mineralization; in environments with colored-DOC, increased DOC watercolor favored higher potential photochemical mineralization rates, whereas in super-humic environments, increased DOC watercolor reduced the photochemical mineralization potential due to DOC self-shading. **Conclusions:** We emphasize that the measured results in this study represent the highest values of photochemical mineralization ever recorded in the literature.

Keywords: DOC; coastal lagoons; photo-oxidation; carbon cycling; self-shading.

Resumo: Objetivo: A mineralização fotoquímica é uma via significativa para a mineralização de carbono orgânico dissolvido (COD) em ecossistemas aquáticos. A concentração de COD, cor da água, intensidade da radiação solar, estado diagenético do COD e disponibilidade de oxigênio são fatores reguladores conhecidos que influenciam o processo de mineralização fotoquímica do COD. Porém, esses estudos ainda não avaliaram a importância desses fatores reguladores sob condições extremas de concentração de COD e coloração da água. Os objetivos deste estudo foram: (1) otimizar parâmetros metodológicos para investigação do processo de fotodegradação em ecossistemas aquáticos húmicos/super-húmicos tropicais; (2) avaliar a importância relativa dos fatores reguladores que influenciam a mineralização fotoquímica em ecossistemas húmicos/super-húmicos tropicais e (3) medir as taxas de mineralização fotoquímica em 20 ecossistemas húmicos/super-húmicos tropicais costeiros e compará-los com dados disponíveis em todo o mundo. **Métodos:** Foram realizados três tipos de experimentos de exposição ao COD: (i) exposição de amostras de água a diferentes intensidades de radiação solar, (ii) exposição de amostras de água da mesma origem, mas com diferentes concentrações (diluições) de COD e, (iii) exposição de amostras de água de um gradiente de 20 ambientes com características distintas à luz solar. **Resultados:** Nossos resultados revelaram que a concentração de oxigênio foi limitante para o processo de mineralização fotoquímica em experimentos que investigam ecossistemas super-húmicos. A coloração da água exibiu efeitos ambíguos na mineralização fotoquímica; em ambientes com COD colorido, o aumento da coloração da água favoreceu maiores taxas de mineralização fotoquímica potencial, enquanto em ambientes superhúmicos, o aumento da coloração da água reduziu o potencial de mineralização fotoquímica devido ao auto-sombreamento do DOC. **Conclusões:** Enfatizamos que os resultados medidos neste estudo representam os maiores valores de mineralização fotoquímica já registrados na literatura.

Palavras-chave: COD; lagoas costeiras; foto-oxidação; ciclagem de carbono; auto-sombreamento.

1. Introduction

Over the last decades, science and society have been giving special attention to climatic global changes issues (Erickson III et al., 2000; Craine et al., 2003; IPCC, 2023), particularly focusing on studies related to the carbon cycle in response to the accumulation of greenhouse gases, such as carbon dioxide (CO_2), in the atmosphere. Consequently, research efforts have been significantly devoted to understanding the natural release of carbon from terrestrial and aquatic ecosystems into the atmosphere, as well as processes that could facilitate the uptake of atmospheric carbon by these ecosystems (Reich et al., 2001; Grace & Malhi, 2002; Craine et al., 2003; Sobek et al., 2003; Rantakari & Kortelainen, 2005).

Aquatic ecosystems play a central role in the global carbon cycle, as they contain a significant portion of the Earth's carbon and act as important pathways for carbon flux between terrestrial ecosystems and the atmosphere, mainly through the processing of DOC (e.g. Cole et al., 2007; Tranvik et al., 2009; Abril et al., 2014). The processing of DOC in the water column mainly occurs through two fundamental processes: bacterial degradation and photochemical degradation. Bacterial degradation involves the utilization of DOC by bacteria as a source of nutrients and/or energy. Photochemical degradation, on the other hand, is the process of total or partial decomposition of DOC by solar radiation (PAR and ultraviolet A and B) acting on light-absorbing organic molecules (e.g., humic substances; for a review, see Suhett et al., 2006). As a result, molecules of O_2 are consumed to form inorganic carbon compounds (e.g., CO_2, CO), more oxidized organic compounds than the initial ones, organic peroxides, hydrogen peroxide (H_2O_2), singlet oxygen ($^1O_2$), among other reactive oxygen species (Cory et al., 2010; Amado et al., 2015).

Photochemical degradation processes are regulated by several factors: (1) the reactivity of DOC with solar radiation, (2) the amount of radiation reaching the DOC, (3) the concentration of DOC in the ecosystem, (4) the quality or origin of DOC, and (5) the availability of oxygen (O_2) in the water (Granéli et al., 1996, 1998; Andrews et al., 2000; Bertilsson & Tranvik, 2000; Farjalla et al., 2001a; Amado et al., 2003, 2006; Biddanda & Cotner, 2003). The photochemical degradation process can be responsible for approximately 10% of total mineralization in deep temperate lakes and can contribute to a similar extent as bacterial respiration to the total mineralization in tropical lakes (Granéli et al., 1996; Jonsson et al., 2001; Amado et al., 2006). Besides directly promoting the mineralization of DOC, the photochemical degradation process also affects the availability of DOC for bacterial degradation, either enhancing or decreasing it (Amado et al., 2015). Thus, photochemical degradation is a key process in the carbon cycling of continental aquatic ecosystems.

Most lakes on the planet are shallow with a high surface-to-volume ratio, which means

their DOC is mainly composed of organic compounds of terrestrial origin, predominantly humic substances (Wetzel, 1992; Downing et al., 2006). Humic substances constitute a stock of numerous organic molecules that exhibit a yellow to brown coloration, depending on their concentration and composition (for a review on humic substances, see Steinberg et al., 2006). Due to their dark color, humic substances are highly reactive to solar radiation and, therefore, undergo photochemical degradation at greater scales compared to other substances (e.g., algal origin; Amado et al., 2006, 2007).

Tropical coastal lagoons present a wide variation in physicochemical characteristics. In the northern part of the State of Rio de Janeiro, coastal lagoons exhibit a large range of DOC concentrations, varying between 1.0 and 7.0 mM, watercolor (Absorbance at 430 nm) between 0.005 and 0.315, and chlorophyll *a* between 0.83 and 136.44 µg L-1 (Farjalla et al., 2001b). The variation in the last two parameters indicates alternation between terrestrial (allochthonous) and aquatic (autochthonous) sources of DOC in these environments. When compared with the global literature, coastal lagoons in northern Rio de Janeiro have generally much higher DOC concentrations and can be considered super-humic (Farjalla et al., 2009). Thus, Farjalla et al. (2004) emphasized the need for studies aiming at understanding how these parameters affect photochemical degradation rates in coastal lagoons of northern Rio de Janeiro. Despite five articles being published on photochemical degradation in these environments, none of them evaluated the effects of each parameter on photochemical degradation rates, nor did they cover more than four ecosystems (Granéli et al., 1998; Farjalla et al., 2004; Suhett et al., 2004, 2007; Amado et al., 2007). Additionally, because of the high solar radiation incidence rates in tropical regions it could expected that photochemical degradation rates should be extremely high in the tropical humic/super-humic coastal lagoons.

Coastal lagoons also display a wide range of salinity, from oligohaline to hypersaline conditions (e.g., 0.1-130 ppt; Farjalla et al., 2001b, e.g., 0.1-130 ppt; Enrich-Prast et al., 2004). The marine influence on salinity results in high concentrations of carbonate forms in the water, elevating pH, and alkalinity. The photochemical degradation process is typically studied by observing variations in the concentrations of dissolved inorganic carbon (DIC) between samples exposed to solar radiation and non-exposed (control) samples. However, the high alkalinity in some saline coastal lagoons results in high carbonate forms concentration and, consequently high DIC concentrations (Esteves, 1998), making it challenging to detect small variations in DIC concentration due to photochemical mineralization. Consequently, it is not straightforward to evaluate photochemical mineralization in some of these environments (for a review, see Suhett et al., 2006).

Given the unique biogeochemical characteristics of the coastal lagoons in the northern Rio de Janeiro State and their potential impacts on the magnitude and detectability of the photochemical mineralization process, the aims of this study are: (1) to adjust methodological parameters for the study of the photochemical mineralization process in tropical coastal lagoons with marine influence; (2) to assess the relative importance of different regulatory factors (DOC concentration, watercolor, sunlight incidence, and oxygen concentration in the water) in the photochemical mineralization process in tropical coastal humic/super-humic ecosystems and (3) to estimate the DOC photochemical mineralization rates in 20 tropical coastal humic/super-humic ecosystems and compare them to other tropical and temperate ecosystems.

2. Material and Methods

2.1. Study area

The photochemical mineralization process was investigated in 20 coastal ecosystems located in the northern part of the State of Rio de Janeiro, Brazil, encompassing the municipalities of Rio das Ostras, Macaé, Carapebus, and Quissamã. Nineteen coastal lagoons (Amarra-boi, Barrinha, Bezerra, Carapebus, Cabiúnas, Casa-Velha, Catingosa, Comprida, Encantada, Garça, Imboassica, Maria Menina, Paulista, Pires, Piripiri II, Preta, Robalo, Ubatuba, and Visgueiro) and a groundwater spring (Atoleiro) were evaluated. All these ecosystems are located within a conservation unit, the Restinga de Jurubatiba National Park (Parque Nacional da Restinga de jurubatiba), except for Imboassica lagoon (22° 08'-22° 30' S and 41° 15'-41° 55' W), which is situated in an urban area between the municipalities of Rio das Ostras and Macaé and receives domestic effluents. The remaining environments inside the national park are well-preserved, surrounded by a shrub vegetation and sandy soil. These coastal ecosystems encompass gradients of several limnological parameters, ranging from oligotrophic to eutrophic, clear

water to highly humic conditions, oligohaline to hypersaline conditions, and varying concentrations of DOC, nitrogen (N), phosphorus (P), among others (Farjalla et al., 2001b; Enrich-Prast et al., 2004). The highly humic ecosystems are the ones with DOC concentration above 1-2 mM (Suhett et al., 2013).

2.2. General experiments set up

All samples in this study were collected from the subsurface (approximately 20 cm depth) of each ecosystem and stored in polyethylene bottles previously washed with 10% HCl and deionized water and rinsed with water from the respective environment. In the laboratory, all samples were pre-filtered through 0.7 µm pore size glass fiber filters (GF75, Advantec), and then filtered through 0.2 µm pore size membrane filters to exclude bacteria (95%). The samples were then placed in quartz tubes (24.5 cm length; 2.2 cm diameter) and sealed with glass caps, without internal atmosphere. The samples were incubated under sunlight for up to 6 hours, between 9:00 and 17:00, according to the experiments described below, immersed in water in a plastic pool to keep samples temperature (29 °C; ± 1). Every 30 minutes (in Experiment 1 described below) or every hour (in Experiments 2 and 3 described below), the incident radiation was measured with a radiometer (IL 1400 - International Light Inc.) equipped with three sensors for PAR, UV-A, and UV-B radiation (280-700 nm). The total incident radiation on the samples was calculated by integrating the radiation values for each radiation band over the time intervals in which they were measured, as described by Granéli et al. (1998) and Amado et al. (2007). Before incubation, the following parameters were measured in the samples: DOC and DIC concentrations, absorbance at 430 nm, and dissolved oxygen concentration (O_2). At the end of the incubations, the concentrations of O_2 and DIC were measured.

We set up three photochemical degradation experiments, as follow:

(1) Photochemical mineralization experiments with different incubation times:

These experiments were conducted with samples from three ecosystems: Atoleiro, Cabiúnas Lagoon, and Imboassica Lagoon. For each ecosystem, 25 quartz tubes were incubated with 0.2 µm filtered samples, as described above, and 5 of the tubes were wrapped in aluminum foil and used as dark controls. In these experiments, all tubes were incubated simultaneously, as described above, but each ecosystem had samples exposed for different incubation times: Atoleiro – 1, 2, 3, 4, 5, and 6 hours of incubation; Cabiúnas Lagoon – 2, 4, and 6 hours of incubation; and Imboassica Lagoon – 2, 3, 4, 5, and 6 hours of incubation. At each time interval, at least one control tube and four exposed tubes were removed from the incubation and had their O_2 and DIC concentrations measured immediately. To compare the photochemical mineralization rates between different incubation times of samples from the same ecosystem, normalizations were performed based on the incident radiation, as described ahead (Analytical Methods and Calculations section).

(2) Sample dilution experiments:

These experiments were conducted with samples from three environments: Atoleiro, Comprida lagoon, and Cabiúnas lagoon. The DOC concentration was determined for each sample, and they were then diluted with Milli-Q water to the concentrations presented in Table 1. Each dilution was placed in 8 quartz tubes and sealed with glass caps, with no internal atmosphere. Out of these 8 tubes, 4 were wrapped in aluminum foil as dark controls, and all the tubes were incubated under sunlight, as described before. Incubations were carried out on different days to cover all samples and dilutions. The Atoleiro samples were incubated for 3 hours and 30 minutes, except for the dilutions of 15, 10, and 5 mg C L^{-1}, which were incubated for 6 hours, similar to the samples and dilutions from the other two ecosystems. Based on experiments with different incubation times, samples with high

Table 1. Initial DOC concentrations and dilutions made in experiment 2 for Atoleiro, Comprida lagoon, and Cabiúnas lagoon.

	Initial DOC ($mg.L^{-1}$)	Dilution DOC ($mg.L^{-1}$)												
		110	100	90	80	70	60	50	40	30	20	15	10	5
Atoleiro	122	X	X	X	X	X	X	X	X	X	X	X	X	X
Comprida	50								X	X	X	X	X	X
Cabiúnas	18											X	X	X

Spaces marked with X show effectively diluted samples.

DOC concentrations should be exposed to radiation below 20 mW cm^{-2} to prevent limitations in the photochemical mineralization process due anoxic conditions (see results and discussion). Therefore, the samples were incubated for different times according to their chemical characteristics. At the end of each incubation, measurements of O_2 and DIC concentrations were taken.

(3) Photochemical mineralization experiments from the 20 ecosystems:

These experiments were carried out with samples from the twenty previously mentioned coastal aquatic ecosystems. All samples were incubated under sunlight, following the procedures described above. The samples from Ubatuba, Casa-Velha, Preta, and Atoleiro lagoons were incubated for only 4 hours to keep the total sunlight incidence below 20 mW cm^{-2}, as mentioned earlier. The remaining samples were incubated for a total of 6 hours. The photochemical mineralization rates were normalized by the incident radiation on the samples to make them comparable, as they were exposed to the sunlight under different solar radiation intensities.

To compare the DOC photochemical degradation rates in coastal lagoons with other ecosystems in the tropical and temperate regions, we conducted a survey of global literature to encompass a wide variety of environmental types, including rivers, clearwater lakes, and dark water (humic-rich) lakes. We used data from 6 studies conducted in tropical ecosystems (Amon & Benner, 1996; Granéli et al., 1998; Amado et al., 2003, 2006; Suhett et al., 2004, 2007) and 4 studies conducted in temperate ecosystems (Salonen & Vähätalo, 1994; Granéli et al., 1996, 1998; Reitner et al., 1997). These studies were chosen because they used solar exposure or artificial light sources with similar intensity in experiments lasting one or a few days. It is important to note that the studies on photochemical mineralization in tropical ecosystems found in the literature were concentrated in Brazil, but as previously mentioned, the sampled ecosystems represented various types, enhancing the representativeness of this analysis for tropical ecosystems in general. The data were divided into three groups: (1) Temperate ecosystems; (2) Tropical ecosystems; and (3) Tropical coastal lagoons. In this third group, data from the literature and data from the 20 coastal lagoons studied in the present work were included.

All photochemical mineralization rates were expressed in μM C d^{-1} (micromoles of Carbon per day). When exposures were performed for only 6 hours, as was the case for most of the data for tropical ecosystems (e.g. Granéli et al., 1998; e.g. Amado et al., 2003), the presented photochemical mineralization values were considered as the total for the entire day, hence being underestimated. Values expressed in oxygen consumption were converted to carbon considering a 1:1 molar ratio between consumed O_2 and produced CO_2. In some studies, multiple values for the same ecosystem are presented.

2.3. Analytical methods and calculations

The term "photochemical mineralization rate" was used in this study to refer to the quantity of DIC produced or O_2 consumed in the exposed samples relative to the control samples during the incubation period under sunlight.

For DIC analysis, the samples were acidified with phosphoric acid (25%), converting all DOC to CO_2, which was then quantified using an infrared detector in a TOC 5000 Shimadzu carbon analyzer. Standard solutions were prepared using sodium carbonate and sodium bicarbonate (Na_2CO_3 and $NaHCO_3$, respectively) at concentrations of 0, 1, 2, and 5 mg C l-1 for the standard curves.

For DOC analysis, the samples were combusted at 680 °C, converting all dissolved carbon forms into CO_2, which was quantified using a similar procedure as for DIC analysis. The standard solution was prepared using potassium hydrogen phthalate ($C_8H_5KO_4$) at concentrations of 0, 1, 5, 10, 20, 50, 100, 150, and 200 mg C l^{-1} for the standard curves. For both DIC and DOC analyses, at least three injections were made per sample, and coefficients of variation equal to or less than 2% were accepted (e.g. Granéli et al., 1998). Photochemical mineralization rates based on CO_2 production were calculated as the differences in DIC concentrations between the exposed and control samples at the end of the incubations.

The concentration of O_2 in all tubes was measured using a gold microelectrode connected to a picoammeter (Unisense©, see Briand et al., 2004). Photochemical mineralization rates based on O_2 consumption were calculated as the differences in O_2 concentrations between the exposed and control samples at the end of the incubations. The values were presented as positive consumption values.

The absorbance at 430 nm was measured using a spectrophotometer (Beckman DU 560),

with a 1 cm quartz cuvette and Milli-Q water as a reference (blank). The values were transformed into absorption coefficients according to Hu et al. (2002) (Equation 1):

$$a430 = (A430 \times 2.303) / L \quad (1)$$

where *a430* is the absorbance at 430 nm, and *L* is the optical path length of the cuvette (in meters). The absorption coefficient at 430 nm (*a430*) was used as an estimate of watercolor (Strome & Miller, 1978).

For the normalization by incident radiation, it was assumed that photochemical mineralization rates increase linearly with the total intensity of incident radiation on the samples. Therefore, the normalized rates were calculated using the following Equation 2:

$$Tn = Ta \times (Ra / R\max) \quad (2)$$

where: *Tn* is the normalized photochemical mineralization rate; *Ta* is the photochemical mineralization rate of a specific sample, *a*; *Ra* is the incident radiation on the same specific sample, *a*; *Rmax* is the highest radiation that was incident on any of the samples being compared.

2.4. Statistical analyses

Linear regression analyses, whether simple or multiple, were performed to evaluate the relationship between photochemical mineralization rates measured by DIC production and O_2 consumption, with using the JMP IN 5.0 software.

Analysis of Variance (ANOVA) tests with Tukey-Kramer post hoc tests were used to compare the photochemical mineralization rates between the literature and the present study. These analyses were conducted using GraphPad Prism 4.0 software.

The photochemical mineralization rates in temperate, tropical, and coastal lagoon environments were compared using the non-parametric Kruskal-Wallis test with Dunn's post hoc test. The minimum accepted level of significance for the statistical tests was $p < 0.05$.

3. Results

The photochemical mineralization rates based on O_2 consumption and DIC production, including all data (20 lagoons plus the dilution experiments), showed a significant positive relationship with an average conversion rate of approximately 100% ($R^2 = 0.80$, $p < 0.0001$; Figure 1).

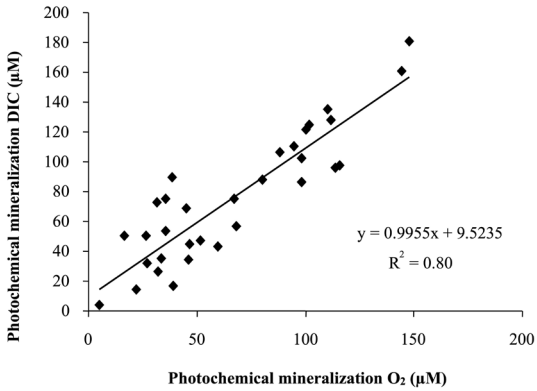

Figure 1. Correlation between photochemical mineralization rates by O_2 consumption and photochemical mineralization rates by DIC production. The analysis includes data from the 20 lagoons, as well as all data from the Atoleiro, Comprida lagoon, and Cabiúnas lagoon dilutions (N = 32).

3.1. Photochemical mineralization experiments with different durations

Both DOC concentration, watercolor and photochemical mineralization rates (based on O_2 consumption and DIC production) were higher at Atoleiro than in Cabiúnas and Imboassica lagoons samples, respectively (Tables 2, 3 and 4). The three studied ecosystems exhibited similar patterns in the dynamics of photochemical mineralization during the incubation time. Atoleiro and Cabiúnas lagoon showed increasing photochemical mineralization rates over time, both in terms of O_2 consumption and DIC production (Tables 2 and 3). Imboassica lagoon exhibited a trend of increasing rates over time, but the patterns were less evident (Table 4). When the photochemical mineralization rates were normalized by the received radiation intensity in each time interval, the three environments showed different behaviors. Atoleiro displayed a decreasing trend in the normalized photochemical mineralization rates with increasing incubation time (Figure 2a). Cabiúnas lagoon exhibited stability in the normalized photochemical mineralization rates over time, with similar values in most intervals, especially for DIC production (Figure 2b). Imboassica lagoon did not show variation in the rates of O_2 consumption but displayed a slight decrease in the normalized rates of DIC production over time (Figure 2c).

After 3 hours of incubation, the concentration of O_2 in the exposed Atoleiro samples had already been reduced by more than 80%, reaching a total reduction of over 90% after 6 hours of incubation (Figure 3). On the other hand, the concentration of O_2 in the exposed Cabiúnas lagoon samples

Table 2. DOC concentration, a_{430}, photochemical mineralization rates (by O_2 consumption and DIC production) at indicated time intervals, and incident radiation intensity during incubation in Atoleiro samples.

	Atoleiro					
DOC (mM)	15.58					
a_{430} (m^{-1})	175.0					
	Incubation time (hours)					
	1	**2**	**3**	**4**	**5**	**6**
Photochemical mineralization						
O_2 consumption (µM)	0,033 (0.001)	0.129 (0.002)	0.125 (0.009)	0.184 (0.031)	0.218 (0.008)	0.230 (0.009)
DIC production (µM)	0.034 (0.006)	0.095 (0.012)	0.136 (0.019)	0.170 (0.005)	0.190 (0.021)	0.217 (0.007)
Accumulated radiation (mW cm^{-2})	2.305	6.984	12.783	18.937	24.275	25.634

Standard deviations are shown in parentheses.

Table 3. DOC concentration, a_{430}, photochemical mineralization rates (by O_2 consumption and DIC production) at indicated time intervals, and incident radiation intensity during incubation in samples from Cabiúnas Lagoon.

	Cabiúnas L.		
DOC (mM)	1.24		
a_{430} (m^{-1})	12.0		
	Incubation time (hours)		
	2	**4**	**6**
Photochemical mineralization			
O_2 consumption (µM)	0.007 (0.004)	0.024 (0.002)	0.045 (0.007)
DIC production (µM)	0.013 (0.004)	0.028 (0.004)	0.038 (0.007)
Accumulated radiation (mW cm^{-2})	10.568	16.909	27.562

Standard deviations are presented in parentheses.

Table 4. DOC concentration, a_{430}, photochemical mineralization rates (by O_2 consumption and DIC production) at indicated time intervals, and incident radiation intensity during incubation in samples from Imboassica Lagoon.

	Imboassica L.					
DOC (mM)	1.27					
a_{430} (m^{-1})	7.8					
	Incubation time (horas)					
	1	**2**	**3**	**4**	**5**	**6**
Photochemical mineralization						
O_2 consumption (µM)	ND	0.005 (0.005)	0.011 (0.001)	0.009 (0.003)	0.012 (0.004)	0.007 (0.002)
DIC production (µM)	ND	0.010 (0.003)	0.010 (0.002)	0.015 (0.001)	0.014 (0.001)	0.009 (0.004)
Accumulated radiation (mW cm^{-2})	ND	6.049	10.508	13.448	14.733	16.038

Standard deviations are presented in parentheses. ND = not determined.

underwent a reduction of less than 25% after 6 hours of incubation, and in the Imboassica lagoon, it experienced a reduction of less than 9% after 6 hours of incubation (Figure 3).

3.2. Dilution experiments

Data from simple linear regressions between the variables for Atoleiro and lagoons Comprida and Cabiúnas are presented in Table 5. All correlations for Atoleiro samples were positive and significant, with the strongest correlation observed between photochemical mineralization (O_2) and a_{430} (watercolor). In Comprida lagoon, the correlations with photochemical mineralization (O_2) were not significant, and the main correlation was observed between photochemical mineralization (DIC) and a_{430}. In this lagoon, stronger

Table 5. Simple linear regression data between parameters in experiments with DOC dilutions in Atoleiro, Comprida Lagoon, and Cabiúnas Lagoon.

N	Atoleiro	Comprida L.	Cabiúnas L.
	14	7	4
DOC *vs.* Photochemical mineralization (O_2)	$R^2 = 0.89$	$R^2 = 0.45$	$R^2 = 0.98$
	$p < 0.0001$	$p = 0.0968$	$p = 0.0096$
DOC *vs.* Photochemical mineralization (DIC)	$R^2 = 0.78$	$R^2 = 0.86$	$R^2 = 0.99$
	$p < 0.0001$	$p = 0.0026$	$p = 0.0006$
a_{430} *vs.* Photochemical mineralization (O_2)	$R^2 = 0.92$	$R^2 = 0.52$	$R^2 = 0.83$
	$p < 0.0001$	$p = 0.0662$	$p = 0.0901$
a_{430} *vs.* Photochemical mineralization (DIC)	$R^2 = 0.88$	$R^2 = 0.92$	$R^2 = 0.88$
	$p < 0.0001$	$p = 0.0007$	$p = 0.0610$
DOC *vs.* a_{430}	$R^2 = 0.86$	$R^2 = 0.98$	$R^2 = 0.86$
	$p < 0.0001$	$p < 0.0001$	$p = 0.0739$
Photochemical mineralization O_2 *vs.* DIC	$R^2 = 0.87$	$R^2 = 0.48$	$R^2 = 0.98$
	$p < 0.0001$	$p = 0.0860$	$p = 0.0122$

N = number of observations (number of different DOC concentrations generated by dilutions) for each ecosystem. Presented R^2 (degree of correlation) and p (degree of significance) of the correlations.

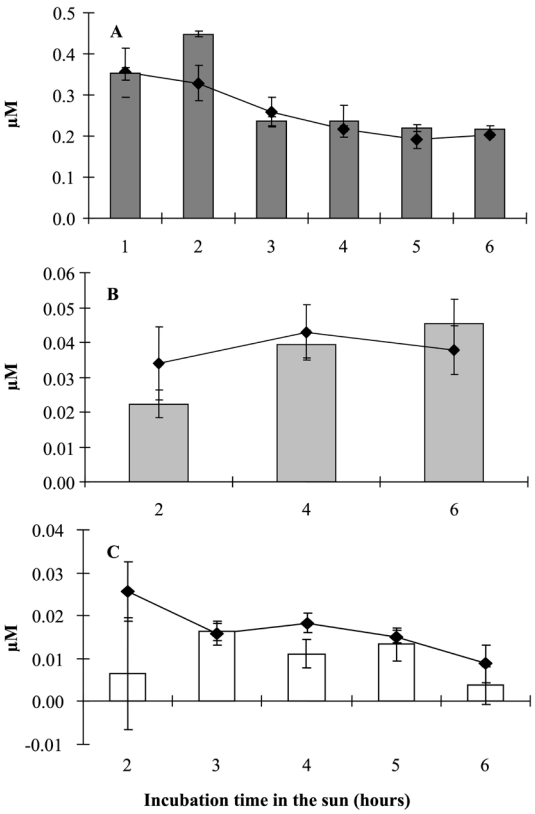

Figure 2. Photochemical mineralization rates normalized by radiation at different incubation times in (A) Atoleiro; (B) Cabiúnas lagoon; and (C) Imboassica lagoon. The bars represent the mean rates of photochemical mineralization by O_2 consumption, and the dots represent the mean rates of photochemical mineralization by DIC production. Error bars indicate the standard deviation. Note the differences between the scales.

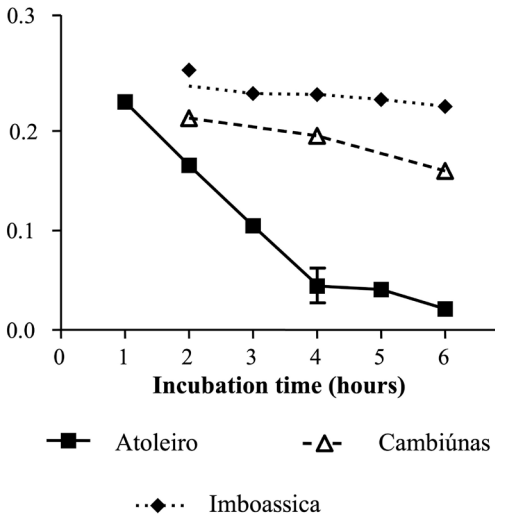

Figure 3. Concentration of O_2 in exposed samples from Atoleiro, Cabiúnas lagoon, and Imboassica lagoon incubated in sunlight at different incubation times. Error bars indicate the standard deviation.

correlations were observed when multiple regressions were performed with all parameters (Table 6). Unlike Atoleiro, the photochemical mineralization process in Comprida lagoon was determined by a balance between DOC concentration and watercolor and the incident radiation. In Cabiúnas lagoon, the correlations between photochemical mineralization rates and DOC concentrations were high and significant, while the correlations with a_{430} were not significant, despite presenting high R^2 values (Table 5).

Analyzing the parameters of the correlations between DOC and photochemical mineralization (DIC) in the three lagoons, it was observed that Atoleiro, the environment with the highest in situ DOC concentration, had the lower slope of the fitted linear model, followed by Comprida and

Table 6. Multiple regression data between parameters in Comprida Lagoon (N = 7).

Comprida Lagoon		
Photochemical mineralization (O_2) *vs.* a_{430} + DOC	$R^2 = 0.59$	$p < 0.168$
Photochemical mineralization (DIC) *vs.* a_{430} + DOC	$R^2 = 0.93$	$p < 0.004$
Photochemical mineralization (O_2) *vs.* a_{430} + DOC + Rad	$R^2 = 0.91$	$p < 0.047$
Photochemical mineralization (DIC) *vs.* a_{430} + DOC + Rad	$R^2 = 0.93$	$p < 0.028$

Cabiúnas lagoons, which had the lowest *in situ* DOC concentration. On the other hand, the linear coefficient exhibited an opposite pattern, being higher at Atoleiro (Figure 4).

3.3. Photochemical mineralization experiments with samples from 20 ecosystems

DOC concentration in the 20 studied ecosystems ranged from 0.522 mM to 10.067 mM, and a_{430} varied from 0.014 to 1.261 in Imboassica lagoon and Atoleiro, respectively (Table 7). The incident radiation on the samples ranged from 10.833 to 21.682 mW cm^{-2} (Table 7). The photochemical mineralization rates, both based on O_2 consumption and DIC production, were the highest in Preta lagoon and the lowest in Imboassica lagoon (Table 7).

Photochemical mineralization based on O_2 consumption showed a positive relationship with the DOC concentration in the 20 studied environments ($R^2 = 0.42$, $p = 0.0019$; Figure 5a). On the other hand, photochemical mineralization based on DIC production did not show a significant relationship with the same parameter ($R^2 = 0.36$, $p = 0.1569$, Figure 5b). However, when outliers were excluded in both analyses, the correlation became even more significant for O_2 consumption ($R^2 = 0.70$, $p < 0.0001$; Figure 5c) and became significant for DIC production ($R^2 = 0.90$, $p = 0.0037$, Figure 5d).

The literature review of photochemical mineralization data revealed higher rates in tropical environments compared to temperate regions ($p < 0.05$). The photochemical mineralization rates of coastal lagoons were not significantly higher than the other tropical environments (Figure 6).

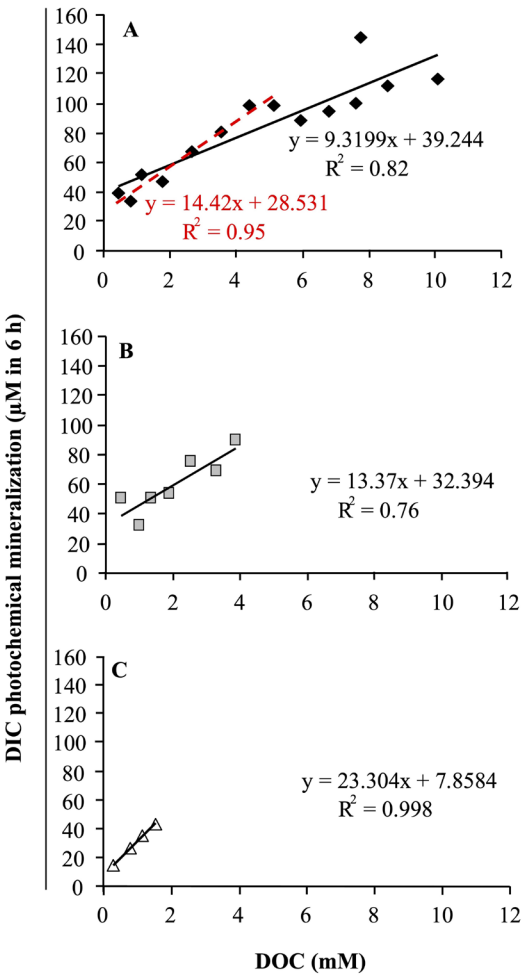

Figure 4. Correlation between rates of photochemical mineralization by DIC production and DOC concentration in (A) Atoleiro; (B) Comprida lagoon; and (C) Cabiúnas lagoon. The solid line represents the regression with all values, and the red dashed line represents the regression with only DOC values less than 6 mM. The red equation corresponds to the regression of the red dashed line.

4. Discussion

Photochemical degradation of the dissolved organic carbon (DOC) is an important pathway to degradation of the dissolved organic matter in inland aquatic ecosystems, either as a direct mineralization process or by facilitating microbial degradation, mainly in humic substances-rich ecosystems (Amado et al., 2007, 2015; Suhett et al., 2013). Tropical coastal aquatic ecosystems are among the most humic-rich aquatic ecosystems in the world and are key components of the global carbon cycling (Farjalla et al., 2009). Measuring DOC

Table 7. DOC concentration, a_{430}, radiation, photochemical mineralization by O_2 consumption, and photochemical mineralization by DIC production in the 20 studied lagoons.

Lagoons	Amarra-boi	Atoleiro	Barrinha	Bezerra	Cabiúnas	Carapebus	Casa Velha	Catingosa	Comprida	Encantada	Garça	Imboassica	Mª Menina	Paulista	Pires	Piri Piri II	Preta	Robalo	Ubatuba	Visgueiro
DOC (mM)	8.349	10.067	3.307	3.086	1.526	0.894	5.082	3.348	3.862	0.678	2.120	0.522	5.236	1.107	3.281	3.088	6.247	3.347	4.328	2.172
a_{430}	0.907	1.261	0.113	0.132	0.146	0.062	0.196	0.052	0.431	0.043	0.049	0.014	0.162	0.048	0.249	0.194	0.8784	0.051	0.184	0.065
Radiation (mW cm^{-2})	15.221	18.930	18.930	17.480	18.930	18.930	17.876	10.833	18.930	21.361	10.833	21.682	10.833	17.480	21.361	18.93	17.876	10.833	17.876	10.833
Photochemical mineralization (μM O_2 $6h^{-1}$)	54.861	113.983	63.628	70.857	68.397	26.030	101.765	64.973	31.478	16.496	33.736	4.771	122.718	22.881	48.084	102.673	147.856	39.621	110.435	70.904
SD	10.12	19.15	5.49	6.00	10.31	3.66	8.73	13.03	6.84	2.64	3.41	6.52	18.03	2.95	3.20	5.78	10.33	8.67	6.072	8.91
Photochemical mineralization (μM C $6h^{-1}$)	ND	95.635	ND	ND	57.190	ND	124.613	ND	73.033	ND	ND	3.870	ND	ND	ND	ND	181.052	ND	135.231	ND
SD		26.63			2.92		10.69		7.35			2.31					12.64		7.44	

ND = not determined due to methodological issues with high salinity. All presented photochemical mineralization rates were normalized by the total radiation of 21.361 $mWcm^{-2}$.

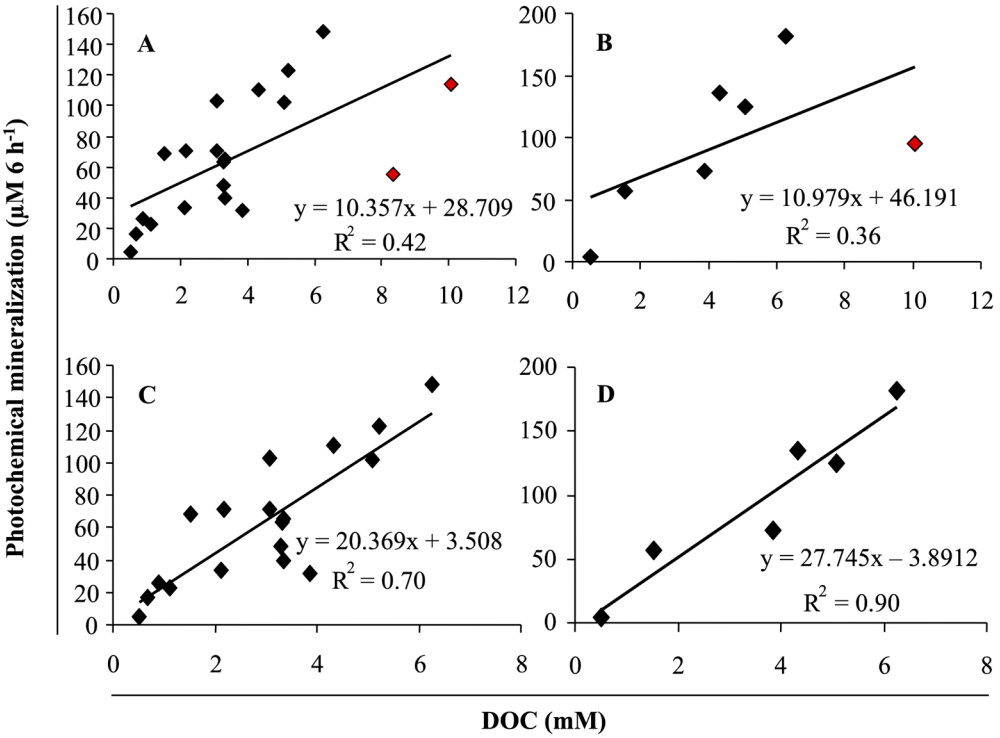

Figure 5. Correlations (A) between rates of photochemical mineralization by O_2 consumption and DOC concentration; (B) between rates of photochemical mineralization by DIC production and DOC concentration; (C) between rates of photochemical mineralization by O_2 consumption and DOC concentration without "outliers"; and (D) between rates of photochemical mineralization by DIC production and DOC concentration without "outliers." The "outliers" are highlighted in red and correspond to Atoleiro and Preta lagoon in graph A and Preta lagoon in graph B. (A) $p = 0.0019$; (B) $p = 0.1569$; (C) $p < 0.0001$; (D) $p = 0.0037$.

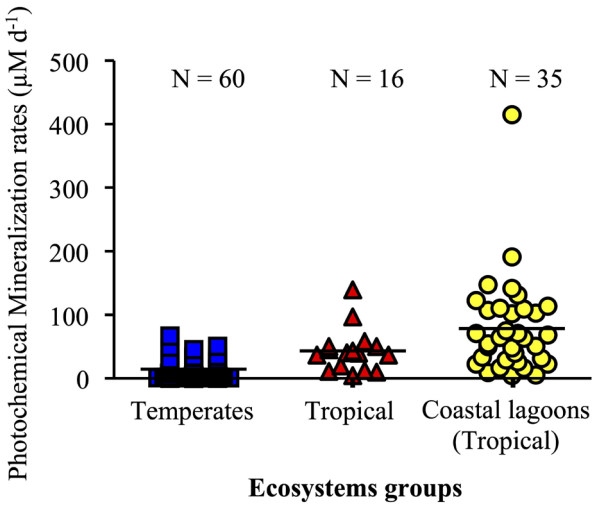

Figure 6. Photochemical mineralization rates in temperate, tropical, and tropical coastal lagoon ecosystems. Data extracted from the literature and the present study. Blue squares represent daily rates of photochemical mineralization in temperate ecosystems, red triangles represent daily rates of photochemical mineralization in tropical ecosystems, and yellow circles represent daily rates of photochemical mineralization in tropical coastal lagoons. The mean values of temperate ecosystems differ from the other two data groups ($p < 0.01$; Kruskal-Wallis and Dunn's post hoc test). The mean values of tropical ecosystems do not differ from those of tropical coastal lagoons (Kruskal-Wallis and Dunn's post hoc test). The lines represent the mean values of each data group.

photochemical mineralization as dissolved inorganic carbon (DIC) in coastal aquatic ecosystems may be challenging because of methodological interferences of marine carbonates influences. Our results showed that it is reliable to measure these processes by high resolution dissolved oxygen consumption in a 1:1 ration to DIC production. In addition, the DOC color (by humic substances) presented an ambiguous role to DOC photochemical mineralization rates: increasing colored DOC in clear waters stimulated DOC photochemical mineralization by increasing the sunlight interaction with the DOC. On the other hand, in darker humic ecosystems it decreased photochemical mineralization due to self-shading. Even considering the self-shading, the humic tropical coastal lagoons presented the highest photochemical mineralization rates ever recorded in the literature. Here we discuss the mechanisms behind the mentioned patterns.

4.1. The methodological approach of measuring photochemical mineralization by O_2 consumption or DIC production

The process of photochemical mineralization results in the consumption of O_2 to produce numerous more oxidized organic compounds than the originals, as well as inorganic compounds (e.g., carboxylic acids, CO_2, H_2O_2, $^1O_2$, etc). Among the most used methodologies to detect photochemical mineralization rates are O_2 consumption and DIC production (e.g., Amon & Benner, 1996; Granéli et al., 1998; Amado et al., 2007). O_2 consumption is typically measured using highly sensitive methods such as mass spectrometry and gold micro-electrodes. On the other hand, DIC production is commonly measured using carbon analyzers (e.g., TOC Shimadzu) by acidification with phosphoric acid and reading in an infrared detector. Both methodologies have advantages and disadvantages. The O_2 consumption method can be used for environments with diverse physicochemical characteristics. However, it may not be the best estimative method for photochemical mineralization rates, as O_2 can be consumed for the partial oxidation of organic compounds, making it not representative for CO_2 formation, i.e. it can form more oxidized but organic compounds. On the other hand, DIC production, although resulting in a good estimate of carbon mineralization, cannot be used for measurements in ecosystems with high alkalinity. High alkalinity leads to a chemical equilibrium favoring the existence of carbonates, making the water extremely rich in DIC (Esteves, 2011), thereby preventing the detection of small variations in DIC concentration due to photochemical mineralization.

Coastal lagoons are ecosystems that exhibit a wide variation in alkalinity, pH, and salts (Esteves, 1998; Enrich-Prast et al., 2004). Some lagoons have acidic pH (often pH < 4) due to the presence of humic substances from surrounding vegetation (restinga). Others present high salinities due to proximity to the ocean, with seawater entering during storm events or through sandbar openings that separate the lagoons from the ocean (Genovez et al., 2024). Some lagoons are even hypersaline, formed by the damming of seawater, with some water undergoing evaporation, resulting in high salt concentrations (e.g., Lagoa das Garças may have salinities above 100 ppm; Farjalla et al., 2001a; Enrich-Prast et al., 2004). The marine influence makes the water in these environments rich in DIC, mainly as carbonates and bicarbonates. Therefore, conducting experiments to measure DOC mineralization rates in all coastal lagoons, as discussed further, becomes challenging, despite being extremely relevant for the carbon cycle in these coastal regions.

With the aim of validating the method of measuring photochemical mineralization rates based on O_2 consumption for estimating CO_2 formation through photochemical decomposition, we performed a simple regression analysis with all the data from the present study, comparing photochemical mineralization rates based on O_2 consumption and DIC production. It is worth noting that data from lagoons with high alkalinity/salinity were not included in the analysis, as we did not obtain DIC production measurements for these environments. As a result of this analysis, we found that the photochemical mineralization rates based on O_2 consumption can be extrapolated to DIC production with a coefficient of 100% (1:1), as the relationship was significant ($P < 0.05$; $r^2 = 0.80$; Figure 1) and the slope of the linear model fitted to the data points was very close to 1 (0.9955). Therefore, we suggest that even in coastal lagoons with high salinity, using the O_2 consumption method should produce reliable estimates of DOC mineralization through the photochemical mineralization process. Although they were not included in the analyses, these lagoons are located near the analyzed lagoons and have similar characteristics in terms of dissolved organic matter. This result is fundamental for enabling future more specific studies in this type of environment and

validating the rates of photochemical mineralization based on O_2 consumption in the saline coastal lagoons of this study.

4.2. Precursors and limiting factors of photochemical mineralization process

Numerous studies have already shown that the photochemical mineralization process represents a significant pathway for the mineralization of DOC in aquatic ecosystems (e.g., Granéli et al., 1996; Jonsson et al., 2001; Amado et al., 2006; Suhett et al., 2013). It is also well-established that features such as DOC concentration and color, O_2 concentration, and the intensity of radiation incident on DOC are regulating factors in these ecosystems (e.g., Granéli et al., 1996; Andrews et al., 2000; Bertilsson & Tranvik, 2000; Farjalla et al., 2001b; Amado et al., 2003). In the literature, environments commonly classified as humic or super-humic lakes present high dissolved organic matter (DOM) concentration with a dark color, and the DOC concentration is around 20 mg C L^{-1} (e.g., LeBreton et al., 2000; Gutseit et al., 2007). According to Steinberg et al. (2006), most lakes on the planet have DOC concentrations between 1 and 100 mg L^{-1}, and some of the coastal lagoons of Northern Rio de Janeiro have extremely high DOC concentrations, reaching up to 160 mg C L^{-1}. In addition to high concentrations of humic substances, the tropical coastal lagoons are also subjected to high intensities of solar radiation year-round (Granéli et al., 1998). Therefore, coastal lagoons are under geographical, geochemical, and environmental characteristics that provide extreme conditions for the photochemical degradation process, which has not yet been investigated.

Our results showed an expected pattern of increasing photochemical mineralization rates with increased solar radiation incidence (Tables 2, 3 and 4). However, the high DOC concentrations and a_{430} values in the Atoleiro, a high-humic ecosystem, resulted in extremely high energy utilization efficiency of solar radiation for photochemical mineralization. Therefore, a significant amount of dissolved O_2 was consumed by photochemical mineralization only after 4 hours of incubation (Figure 3), making low O_2 concentrations a limiting factor for the process (stoichiometric limitation, where one of the reactants, O_2, becomes scarce). This explains the decline in photochemical mineralization rates over longer incubation periods in this environment and implies that long exposures (more than 4 hours) to solar radiation may underestimate the photochemical mineralization rates. Consequently, when normalized by incident radiation on the samples, photochemical mineralization rates were higher for samples exposed for shorter time periods (1, 2, and 3 hours) in the Atoleiro (Figure 2a). However, this limitation is not expected to occur *in situ*, as these environments are subject to wind action (especially coastal lagoons) and natural diffusion of atmospheric O_2 into the water, further enhancing the relevance of the photochemical mineralization process in tropical super-humic ecosystems.

The colored DOM in the water of coastal lagoons can also be extreme in some cases, offsetting light incidence. Atoleiro, in particular, showed an extremely high a_{430} value (almost 3 times higher) compared to other tropical super-humic environments such as Comprida lagoon (Atoleiro = 175 m^{-1}; Comprida = 60 m^{-1}, Suhett et al., 2007). In the Atoleiro, DOC is strongly related to watercolor (Table 4) due to the predominance of humic substances from surrounding vegetation, which represent more than 95% of the DOC in this environment (Suhett et al., 2004). However, at higher DOC concentrations, the extremely dark coloration of DOM absorbs light energy, resulting in reduced energy reaching deeper layers of the water (self-shading). This phenomenon becomes limiting for photochemical mineralization at DOC concentrations above 6 mM (Figure 5). In these extremely dark-colored environments, the photochemical mineralization process may be limited to only a few millimeters at the water surface (Granéli et al., 1998). However, in coastal lagoons, this may not significantly reduce the overall photochemical mineralization rates, as they are shallow ecosystems subject to strong coastal winds, which usually maintain constant water column mixing.

The Atoleiro, Comprida and Cabiúnas lagoons form a decreasing gradient of DOC concentration and a_{430} values (see Table 7). In Atoleiro, the variation in photochemical mineralization rates was best explained by a430, which became a limiting factor in this ecosystem (Table 5). In Cabiúnas lagoon, photochemical mineralization rates were best explained by DOC concentration, indicating that substrate availability is the limiting factor instead of the self-shading effect (Table 5). Comprida lagoon had photochemical mineralization rates best explained by multiple regressions by DOC concentration, a_{430}, and sunlight radiation (Table 6).

This suggests that photochemical mineralization may be co-limited by DOC concentration and a_{430}, as both parameters have intermediate values in this environment. The specific DOC color (a430/DOC) showed that the photochemical reactivity of the bulk DOC in Atoleiro is higher than in Comprida and Cabiúnas lagoons (0.125, 0.112, and 0.096, respectively). Examining the equations of linear regressions between photochemical mineralization rates and DOC concentration, we observed that the linear coefficient increases with DOC concentration, and the angular coefficient decreases with increasing DOC. However, in Atoleiro regression, excluding points with DOC concentrations above 6 mM C (self-shading trigger of DOC concentration to photochemical mineralization), the model's explanation becomes stronger, and the angular coefficient becomes similar to that of Comprida lagoon (Figure 4a). This demonstrates that darker DOC is more available for photochemical mineralization, but the strong effect of self-shading in super-humic environments with extreme DOC color (dark color) concentrations reduces the potential for photochemical mineralization. Thus, the DOM color results in ambiguous effects on the photochemical mineralization process. Increasing coloration in environments with clearer water increases the DOC availability for photochemical mineralization. Conversely, in environments with darker water, increasing DOC color may reduce the potential for photochemical mineralization due to intense self-shading of DOM.

It is now well-stablished that the photochemical degradation of DOM, especially from humic-rich ecosystems, results in the instantaneous consumption of oxygen (Cory et al., 2009) and resulting in the formation of reactive oxygen species (ROS), such as singlet oxygen, hydrogen peroxides, among others. These ROS are short-live compounds that rapidly decay and are known by negatively affecting the microbial metabolism causing its temporary inhibition (for instance see Amado et al., 2015). One could argue whether during the sunlight incubations in this work, it is likely or not that ROS have been generated consuming part of the available oxygen in the tubes and thus, speeded up the oxygen limitation in the most humic-rich ecosystems. As a result, the ROS formation could be competing with DOC mineralization process in some extent, which could affect (reducing) the photochemical coefficient of oxygen to carbon dioxide conversion (Figure 1). However, it is likely that it did not cause important changes in this relationship at the time of the measurements once the conversion coefficient was close to 1:1 (as show in Figure 1).

4.3. The patterns of photochemical mineralization rates in a humic lagoons gradient

As predicted in the previous section, the darkest DOM (high a_{430}) had ambiguous effect on the photochemical mineralization rates in the coastal lagoons. This pattern became evident when assessing photochemical mineralization rates in a natural DOC and a_{430} gradient in these lagoons. Preta lagoon and Atoleiro, where we recorded the highest DOC and a_{430} concentrations, drastically decreased correlation parameters between DOC concentrations and photochemical mineralization rates, likely due to the self-shading effects. This resulted in lower photochemical mineralization rates than expected by the linear model. However, when these environments were excluded from the analysis, the correlations parameters greatly improved ($p < 0.01$; Figure 5). Thus, it was observed that the photochemical mineralization measurements from natural super-humic ecosystems may be methodologically under-estimated due to DOC watercolor limitation, as experimentally predicted. The studied tropical coastal lagoons present a wide range of DOC concentration, humic contents, watercolor, Secchi disk depth and sunlight attenuation (Enrich-Prast et al., 2004; Suhett et al., 2013). Thus, the 10% radiation depth varies from 0.1 to 1.8 m (Enrich-Prast et al., 2004; Granéli et al., 1998) which also limits the DOC photochemical mineralization to the top water layer in the most DOC-rich ecosystems. However, as these coastal lagoons are shallow and subjected to coastal winds, neither oxygen nor watercolor limitation may strongly decrease photochemical mineralization *in situ* due to constant water column mixture, except for some short spatial and temporal specific conditions such as marine water intrusion (Genovez et al., 2024).

Despite the effects of self-shading reducing the potential for DOC photochemical mineralization in super-humic coastal environments, they still displayed extremely high photochemical mineralization rates (Table 6). Farjalla et al. (2009) conducted a review on DOC degradation in humic ecosystems, demonstrating that photochemical mineralization rates in tropical environments are, on average, higher than in temperate environments. In this study, a similar analysis was performed, but tropical coastal lagoons were grouped separately from other tropical and temperate

ecosystems. Our results confirmed that the highest photochemical mineralization rates occurred in the tropics compared to temperate environments, even after excluding the coastal lagoons from the first group of data (Figure 6). Moreover, the coastal lagoons alone, although presenting average data similar to other tropical ecosystems, exhibited extremely high values, representing the highest photochemical mineralization rates ever recorded in the literature (Figure 6).

The DOC in coastal lagoons showed to be less reactive than in small Amazonian rivers, which are protected from radiation by forest cover. The Amazonian environments display higher photochemical mineralization rates per DOC unit than coastal lagoons (Amado et al., 2003). However, a seasonal study by Suhett et al. (2007) recorded extremely high photochemical mineralization rates in a coastal humic lagoon in Rio de Janeiro state at the beginning of the rainy season. Thus, a synergy between high photochemical reactivity of freshly leached DOC from the Restinga and high solar radiation incidence in coastal lagoons during summer resulted in extremely high photo-degradation rates. However, this synergy is expected to dissipate rapidly as intense degradation reduces this photo-reactivity promptly.

Reviews on tropical ecosystems have shown that carbon concentrations in soils are lower than in temperate and boreal ecosystems (Silver et al., 2000). This is due to higher rainfall carrying organic matter into water bodies, suggesting higher DOC concentrations in tropical aquatic ecosystems. Suhett et al. (2006) demonstrated that, in addition to higher concentrations, DOC is also more photochemical reactive in tropical ecosystems. Therefore, the higher photochemical mineralization rates in this study compared to other data from the tropical region should be attributed to higher DOC concentrations and darker coloration in these environments, which are at similar latitudes (tropics) and subject to similar radiation intensities.

5. Conclusions

We conclude that the method for estimating photochemical mineralization rates through oxygen consumption was efficient for assessing DOC mineralization via photochemical mineralization in the studied coastal lagoons. Furthermore, we found that the conversion of oxygen consumption to DIC production follows a 1:1 ratio. However, it is essential to note that in experiments involving super-humic ecosystems with high DOC concentrations, such as tropical coastal lagoons, excessive oxygen consumption by the photochemical mineralization process may lead to oxygen becoming a limiting factor within a few hours.

The water coloration also played a role, showing an ambiguous effect on photochemical mineralization rates in ecosystems with varying DOC and color gradients. In environments with clearer DOM, increasing coloration favored higher potential rates of photochemical mineralization due to increased substrate availability. In contrast, in environments with very dark waters (super-humic), higher watercolor reduced the potential for photochemical mineralization due to intense self-shading of the DOM. These patterns were confirmed through the study of 20 coastal lagoons forming a gradient of DOC and coloration.

Finally, the tropical coastal humic lagoons in the northern part of Rio de Janeiro state exhibited extremely high rates of DOC photochemical mineralization, making them the highest recorded in the literature. This underscores the importance of these environments in the carbon cycle of coastal regions. The high photochemical mineralization rates observed in these environments, combined with elevated DOC concentrations and intense solar radiation, contribute significantly to the mineralization of DOC and may play a vital role in the dynamics of tropical coastal ecosystems.

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