

Origin, concentration, availability and fate of dissolved organic carbon in coastal lagoons of the Rio de Janeiro State

Origem, concentração, disponibilidade e destino do carbono orgânico dissolvido em lagoas costeiras do Estado do Rio de Janeiro

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Abstract: The coastal lagoons in the northern Rio de Janeiro State (Brazil) present a wide gradient of dissolved organic carbon (DOC) and water color, with the highest DOC concentrations reported in the literature for aquatic ecosystems. Thus, they represent a peculiar set of ecosystems for the study of the origin, processing and fate of DOC in inland waters. We reviewed data from 2 decades of studies on the carbon cycle in these coastal lagoons and discussed the fluctuations in the concentration and quality of DOC, factors affecting DOC microbial and photochemical degradation, CO₂ emission, as well as the role of humic and non-humic carbon to the energy flow through the trophic chains. We show that DOC quality, not its quantity, determines the rates of photochemical and microbial degradation both seasonally (within system) and spatially (among systems), with the exception of DOC photo-oxidation among lagoons, which is partially explained by DOC concentration at regional scale. In humic lagoons, there is a fairly predictable pattern of seasonal variation in DOC concentration associated to rainfall-induced inputs of allochthonous C. However, little is known about the exact timing of these allochthonous inputs and how they relate to the seasonal variation of DOC chemical properties (*i.e.* its quality). Depth-integrated photo-oxidation rates were less representative in highly humic lagoons, due to strong light attenuation in the water column. Nevertheless, the potential contribution of photo-oxidation and bacterial respiration to total CO₂ efflux (~11%) did not differ significantly when all lagoons were pooled together. Contrary to prevailing paradigms for humic waters, microalgae seem to be the main C source in humic lagoons, sustaining pelagic food webs through zooplankton, in spite of some contribution of allochthonous C. Thus, the predominant role of the microbial loop in the DOC recovery to food webs in such systems is to be questioned.

Keywords: coastal lagoons, dissolved organic matter, dissolved organic carbon, DOC, humic substances.

Resumo: As lagoas costeiras do norte do Estado do Rio de Janeiro apresentam um amplo gradiente de carbono orgânico dissolvido (COD) e coloração da água, com as maiores concentrações registradas na literatura. Portanto, representam um conjunto peculiar de ecossistemas para estudos sobre a origem, processamento e destino do COD em águas continentais. Neste trabalho, revisamos 2 décadas de estudos sobre o ciclo do carbono nas lagoas costeiras desta região e discutimos as flutuações na concentração e qualidade do COD, fatores afetando sua degradação microbiana e fotoquímica, a emissão de CO₂, assim como a contribuição do COD húmico e não húmico para o fluxo de energia através das cadeias tróficas. Nós mostramos que a qualidade, e não a quantidade do COD, determina as taxas de degradação fotoquímica e microbiana tanto sazonalmente (dentro dos sistemas) como espacialmente (entre sistemas), com exceção da foto-oxidação entre lagoas, a qual foi parcialmente explicada pela concentração de COD em escala regional.

Em lagoas húmicas, há uma variação sazonal razoavelmente previsível da concentração de COD associada a entradas de C orgânico induzidas pelas chuvas. Porém, pouco se sabe sobre a temporização exata destas entradas alóctones e os efeitos destas sobre a variação sazonal das propriedades químicas do COD (*i.e.* sua qualidade). As taxas de foto-oxidação integradas para a coluna d'água foram menos representativas nas lagoas altamente húmicas, devido à forte atenuação da luz. No entanto, as contribuições potenciais da foto-oxidação e da respiração bacteriana para o efluxo total de CO₂ (-11%) não diferiram significativamente quando todas as lagoas foram consideradas juntas. Contrariamente a paradigmas prevaletentes para ambientes húmicos, as microalgas mostram-se como a fonte predominante de C em lagoas húmicas, sustentando a teias tróficas pelágicas através do zooplâncton a despeito de alguma contribuição do C alóctone. Portanto, o papel predominante da alça microbiana na recuperação do COD para as teias tróficas nestes sistemas deve ser questionado.

Palavras-chave: lagoas costeiras, matéria orgânica dissolvida, carbono orgânico dissolvido, COD, substâncias húmicas.

1. Introduction

Inland aquatic ecosystems have been recently recognized as main players in the global carbon cycle once they mineralize most of the carbon fixed in terrestrial ecosystems, being responsible for the emission of great amounts of carbon dioxide (CO₂) to the atmosphere (Cole et al., 2007; Tranvik et al., 2009). Due to their predominantly low depths and perimeter:volume ratios, their metabolism is frequently dominated by decomposition of terrestrial organic matter in the form of dissolved organic carbon, (DOC, Wetzel, 1992; Cole et al., 1994; Downing et al., 2006). DOC represents a dynamic C pool, exceeding the amount of organic C contained in the aquatic biota in freshwaters (Steinberg, 2003). Within DOC, humic substances – which are dark-colored products of plant decomposition – represent a dominant fraction accounting for 50-80% of DOC in most aquatic ecosystems (Thomas, 1997; Steinberg, 2003). Thus, DOC (and in particular humic substances) is expected to play an important role in the pelagic carbon cycle in inland aquatic ecosystems.

The source of the organic matter is usually an important factor affecting its fate and the flow of energy in aquatic ecosystems (e.g., Farjalla et al., 2006). For instance, in humic-rich ecosystems, water color inhibits aquatic primary production and favors heterotrophic activity and CO₂ emission to the atmosphere (Thomaz et al., 2001). In the water column, DOC can basically be mineralized by microbes and by sunlight (del Giorgio and Cole, 1998; Moran and Covert, 2003) or it can be incorporated to the organisms' biomass along the trophic chain, through the microbial loop (Azam et al., 1983; Odum et al., 2004). It has been recently suggested that, in tropical humic

ecosystems, DOC is predominantly driven to respiration rather than to incorporation into the trophic chain (Farjalla et al., 2009), putting in question the supposed trophic importance of the microbial loop in humic-rich freshwaters. Moreover, a recent meta-analysis showed that bacterial respiration is favored in relation to bacterial production—i.e., lower bacterial growth efficiency—in tropical compared to temperate freshwaters (Amado et al., 2013), suggesting a lower relevance of carbon transfer through the microbial loop in the warmer, tropical aquatic ecosystems.

Coastal lagoons are aquatic ecosystems occupying a large part of the seacoast in most continents (Kjerfve, 1994). These ecosystems are surrounded by a sandy landscape, which may result in great inputs of terrestrial DOC to the water column (Esteves et al., 2008). In the north of Rio de Janeiro State (Brazil), there is a set of coastal lagoons with contrasting limnological characteristics, such as salinity, trophic status and, notably, contrasting humic DOC contents (Farjalla et al., 2001; Suhett et al., 2004; Caliman et al., 2010). Some of these ecosystems figure within the highest DOC concentrations registered in the literature (up to 18.33 mM), probably due to high leaching of allochthonous DOC from the permeable, sandy *restinga* soil (Farjalla et al., 2009; Suhett et al., 2011). This interaction is likely enhanced in small lagoons, with higher perimeter:area ratios, especially those with dendritic shape, such as Cabiúnas and Comprida (Table 1, Panosso et al., 1998). Due to these features, these coastal lagoons represent a very peculiar set of aquatic ecosystems for the study of the carbon cycle, in particular for issues related to DOC origin, dynamics, processing and fate. Thus, several questions arise which could be addressed in these ecosystems: (i) What are their main DOC

Table 1. Selected morphometric and limnological features of the surveyed coastal lagoons. Perimeter, area and perimeter:area ratios obtained from Caliman et al. (2010). Depth, salinity and pH data are the medians (minimum – maximum) values measured from Oct/2008 to Oct/2010 (unpublished data), except for Iriry lagoon, where data were available only for a single sampling on Dec/2003 (unpublished data). n.d. = not determined.

	Perimeter (km)	Area (km ²)	Perimeter: area ratio	Depth (m)	Salinity (ppt)	pH
Amarra Boi	0.22	2.56	11.82	0.7 (0.3-1.0)	0.1 (0.1-1.0)	3.83 (3.50-5.56)
Atoleiro	n.d.	n.d.	n.d.	0.6 (0.3-1.0)	0.1 (0.1-0.2)	3.53 (3.07-3.70)
Barrinha	0.28	2.32	8.29	0.8 (0.3-1.1)	4.1 (1.3-8.2)	7.88 (6.29-9.36)
Bezerra	0.02	0.86	53.25	0.7 (0.5-1.0)	0.8 (0.2-1.9)	5.86 (3.64-6.57)
Cabiúnas	0.34	14.61	42.67	3.4 (1.9-5.8)	0.4 (0.2-2.2)	6.65 (6.16-6.93)
Carapebus	4.11	42.52	10.34	0.9 (0.5-1.0)	3.0 (1.0-25.8)	7.50 (6.57-7.95)
Casa Velha	0.53	5.13	9.69	0.7 (0.4-1.1)	4.0 (1.3-9.2)	8.04 (6.67-9.45)
Catingosa	0.09	1.36	15.58	0.8 (0.6-1.0)	15.1 (7.1-20.7)	7.70 (7.19-8.25)
Comprida	0.11	3.61	31.75	2.5 (0.9-4.0)	0.1 (0.0-0.1)	4.22 (3.85-4.44)
Encantada	0.05	1.24	24.95	0.9 (0.6-1.3)	1.7 (0.8-7.5)	7.12 (6.82-7.84)
Garças	0.21	2.87	13.55	0.9 (0.5-1.2)	9 (1.3-19.4)	7.37 (5.17-8.00)
Imboassica	2.60	12.49	4.81	1.7 (0.6-2.3)	0.8 (0.2-21.2)	7.89 (5.94-9.60)
Iriry	n.d.	n.d.	n.d.	1.8	0.1	5.16
Maria Menina	0.60	4.32	7.16	0.6 (0.3-0.9)	14.2 (2.8-21.5)	7.78 (6.71-8.65)
Paulista	1.41	25.65	18.23	1.0 (0.6-1.4)	1.1 (0.1-3.8)	6.83 (3.82-7.50)
Pires	1.59	6.73	4.22	0.7 (0.5-1.0)	7.7 (2.9-10.5)	7.83 (5.21-8.47)
Piripiri 1	n.d.	n.d.	n.d.	0.7 (0.5-1.0)	4.9 (0.6-11.9)	6.75 (5.47-8.32)
Piripiri 2	n.d.	n.d.	n.d.	0.7 (0.4-1.0)	4.8 (0.8-9.4)	7.10 (5.96-7.71)
Preta	1.94	20.66	10.63	1.0 (0.6-1.8)	3.6 (1.0-6.8)	7.31 (5.86-8.41)
Robalo	1.25	8.97	7.18	0.9 (0.7-1.1)	19.9 (8.7-27.3)	8.00 (7.31-9.00)
Ubatuba	0.34	3.45	10.14	0.5 (0.1-1.1)	3.9 (1.7-11.7)	7.78 (6.82-9.71)
Visgueiro	1.21	5.43	4.49	0.8 (0.6-1.1)	22.4 (8.9-33.1)	7.99 (7.52-8.65)

sources and what is the dynamics of DOC inputs to these lagoons? (ii) What is the relationship between DOC concentration and microbial and photochemical mineralization rates? (iii) What is the relevance of terrestrial humic carbon to the coastal lagoons functioning? (iv) Which mineralization process (microbial or photochemical) is more important to overall C mineralization? (v) How relevant is humic DOC to the energy flow through the trophic chain?

In this work, we aimed to identify the origin and fate of DOC in the coastal lagoons of the northern Rio de Janeiro State. We revised papers from 2 decades of carbon cycle studies in the coastal lagoons of this region, as well as recent unpublished data from the database of the Laboratory of Limnology/UFRJ, focusing on DOC concentrations, sources and quality, microbial and photochemical degradation, trophic chain (through stable isotopes analysis) and CO₂ fluxes. Our review encompassed an 80 km section of the seacoast of the Rio de Janeiro State, comprising the municipalities of Rio das Ostras, Macaé, Carapebus and Quissamã (22° 08'-22° 30' S and 41° 15'-41° 55' W). A total of 22 lagoons were encompassed by our survey, with all but two of them (Iriry, in Rio das Ostras,

and Imboassica, in Macaé) being located inside the Restinga de Jurubatiba National Park. Maps and more detailed information of the geographical location of these lagoons may be found in Di Dario et al. (in press), in this issue. An overview of morphometric and limnological feature of the surveyed lagoons is presented in Table 1.

2. A Wide Gradient of DOC and Water Color

The surveyed lagoons reveal a wide range of DOC concentrations, both spatially and temporally (Figure 1a). The median DOC concentration ranged from 0.69 mM in Imboassica lagoon to 8.80 mM in Atoleiro lagoon. Temporally, DOC concentration varied up to 12-fold in the same lagoon, as shown for Visgueiro (Figure 1a). The vast majority of the DOC data surveyed here were above median (0.75 mM) and even the maximum (1.83 mM) values found in temperate lakes representative of a wide clear-water to humic gradient (Figure 1a) (Granéli et al., 1998; Bertilsson and Tranvik, 2000). It should be noted that even in humic Negro River in the Amazon, DOC seldom reaches 1 mM DOC (Granéli et al., 1998; Rodríguez-Zúñiga et al.,

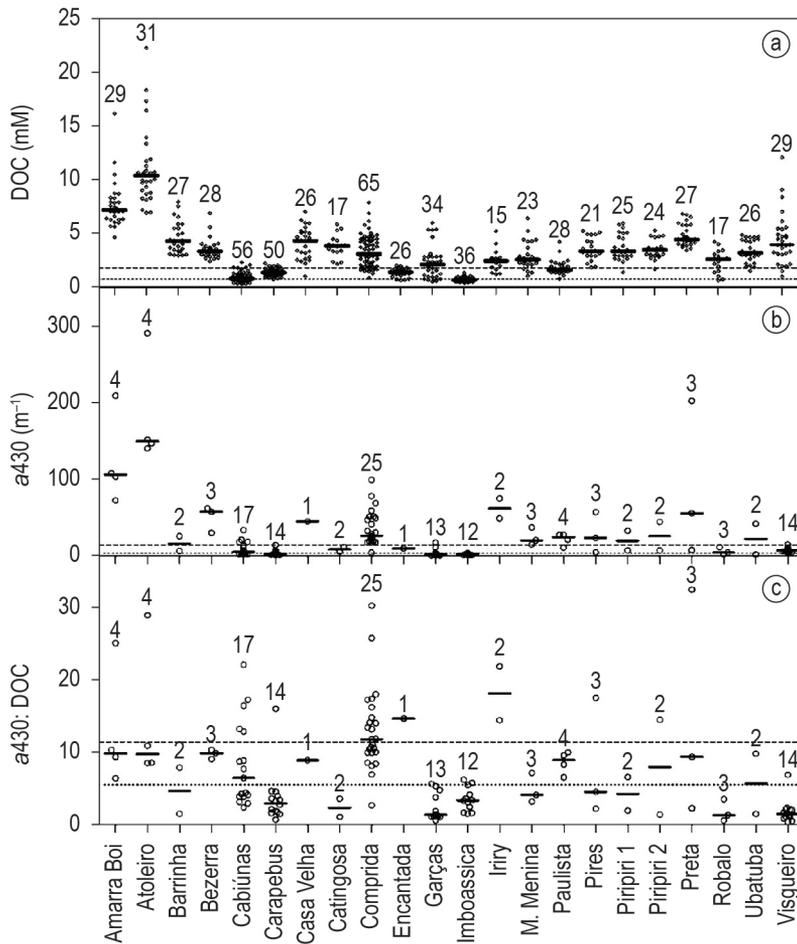


Figure 1. Dissolved organic carbon (DOC) concentration (a), water color (absorption coefficient at 430 nm, a_{430}) (b) and water color:DOC ratio (a_{430} :DOC) (c) for 22 coastal lagoons in the northern Rio de Janeiro State. Data obtained from the database of the Laboratory of Limnology/UFRJ and from Granéli et al. (1998). The short, horizontal solid lines represent the medians for each lagoon. The horizontal dashed and dotted lines represent the maximum and median values, respectively, for each variable considering data from temperate lakes over a wide range of DOC (Granéli et al., 1998; Bertilsson and Tranvik, 2000) and a_{430} and a_{430} :DOC (Granéli et al., 1998). The superscript numbers represent the number of data (n) for each variable/lagoon.

2008). DOC concentrations in Amarra-Boi and Atoleiro lagoons were notably high, reaching values one order of magnitude higher than these reference values (max. 22.5 mM, Figure 1a). These values reported for Amarra-Boi and Atoleiro are the highest ones reported in the literature for freshwater ecosystems, to our knowledge.

Water color also varies widely within (temporally) and among (spatially) these coastal lagoons (Figure 1b). Again, the majority of the surveyed water color values—measured as the absorption coefficient at 430 nm, a_{430} (Hu et al., 2002)—for the lagoons exceeded the median (4.15 m^{-1}) and maximum (14.51 m^{-1}) values for temperate lakes with varying humic content (Granéli et al., 1998). Atoleiro and Amarra-Boi lagoons are highlighted

by the highest a_{430} , reaching values close to 300 m^{-1} in the highly humic Atoleiro lagoon (Figure 1b). Thus, there is compelling evidence that most of these lagoons are predominantly humic, because the light absorption at low wavelengths (UV to blue, 240-500 nm) is typical of chromophoric structures of humic substances (Steinberg, 2003). However, there may be a confounding effect of DOC concentration on water color, because it can increase light absorption even if DOC quality (*i.e.*, specific absorptivity) is not changed. We calculated the DOC specific absorptivity at 430 nm (a_{430} :DOC) for every paired water color and DOC data available for a better assessment of the humic aspect of these lagoons. Most of the a_{430} :DOC values found here were above the median for temperate

lakes (5.53, Figure 1c). For some lagoons (*e.g.* Atoleiro, Comprida and Iriry), there were a_{430} :DOC exceeding the maximum for the reference temperate lakes (11.38, Figure 1c). The pattern was quite similar to that of water color, but it additionally highlighted the humic character of lagoons with relatively low DOC concentration (*e.g.*, Cabiúnas lagoon, Figure 1c).

These data reveal the high spatial and temporal heterogeneity of DOC quantity and quality in the coastal lagoons of the northern Rio de Janeiro State, with particular emphasis on the extremely high DOC concentrations found and on the predominant humic aspect of most of these lagoons. These features make those environments particularly interesting for studies involving the carbon cycle and carbon balance in tropical systems.

3. The Origin of DOC

Dissolved organic carbon may be of autochthonous origin, when it is produced inside the aquatic system, or allochthonous, when it is produced outside it. Allochthonous carbon may originate from inflowing water bodies, but the term is more commonly applied to terrestrial carbon, mostly humic substances, originated in the surrounding area (Kritzberg et al., 2004). Excretion by phytoplankton is a major source of autochthonous DOC (mostly labile bacterial substrates) in inland waters (Fogg, 1977). For the coastal lagoons surveyed here, it has been shown that phytoplanktonic excretion potentially contributes great amounts of DOC to the water column, ranging from 1.17 mM C d⁻¹ in the clear-water Imboassica to 1.50 mM C d⁻¹ in the humic Cabiúnas lagoon, representing 4 and 48% of phytoplankton production in those lagoons, respectively (Roland, 1998). Also, many coastal lagoons are largely colonized by aquatic macrophytes, which produce large amounts of organic carbon. A great fraction of this carbon is released to the water column during macrophyte senescence and decomposition, being a major source of DOC (Mann and Wetzel, 1996). Stepanauskas et al. (2000) showed that autochthonous DOC produced within macrophyte stands in Cabiúnas lagoon could be consumed by planktonic bacteria, but overall DOC bioavailability into the stands was relatively low. The authors suggested that DOC in this system should be mostly of terrestrial origin and more diagenetically changed (Stepanauskas et al., 2000).

Stable carbon isotope data available for two humic lagoons in Restinga de Jurubatiba National

Park (Cabiúnas and Comprida) demonstrate that DOC $\delta^{13}\text{C}$ bulk signature is an average of autochthonous (phytoplankton and aquatic macrophytes) and allochthonous (terrestrial CAM and C3 plants) components (Figure 2a and b). However, a strong contribution of terrestrial CAM plants—*i.e.*, the dominant *Clusia hilariana* Schltdl. from the surrounding *restinga*—to DOC is evident, because the range of values for DOC signature is comprised below the terrestrial CAM and above the other producers' signatures (Figure 2a and b). As shown in the previous section, most of the coastal lagoons in this region are predominantly humic (Figure 1c). In these lagoons, humic substances may account for 55 to 98% of DOC (Suhett et al., 2004). Thus, it seems reasonable that DOC in such lagoons is dominated by allochthonous humic substances originated by the decomposition of *C. hilariana* and other CAM plant leaves in the surrounding sandy soils.

An additional aspect of DOC of the humic coastal lagoons in the region is revealed by fluorescence analyses (unpublished data). Excitation-emission

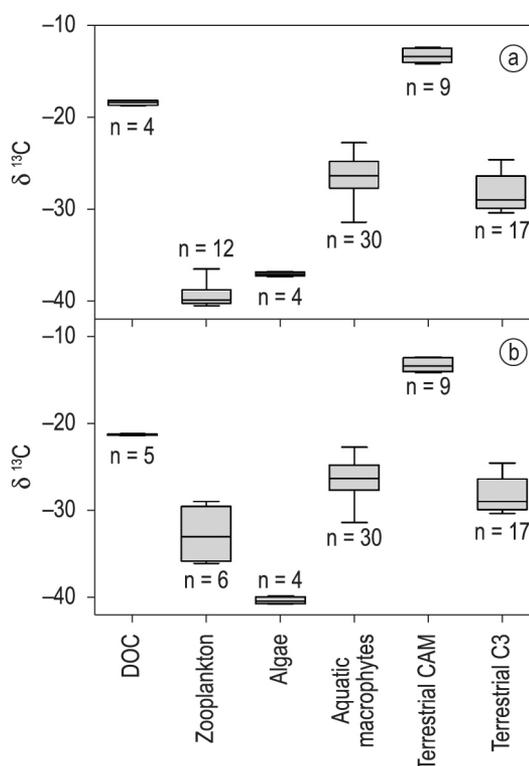


Figure 2. Carbon isotope signatures of planktonic organisms and carbon compartments in two humic lagoons in the northern Rio de Janeiro State: a) Cabiúnas (modified after Marinho et al. 2010), b) Comprida (F. Meirelles-Pereira, unpublished data).

matrices (EMM) of DOC from three humic lagoons in the Restinga de Jurubatiba National Park (Amarra-Boi, Atoleiro and Comprida) show very similar patterns, with emission peaks around 465 nm (excitation around 370 nm) (Figure 3a, b, and c). Also, these three lagoons presented higher fluorescence emission concentrated in the right upper quadrant, spreading toward the right upper corner (Figure 3a, b, and c). This indicates that humic DOC in these systems is similarly highly aromatic, which is a result of the continued humification process (Santos et al., 2010). This pattern is reinforced by the humification index (*sensu* Zsolnay et al., 1999), which presented relatively high and quite similar values to Amarra-Boi, Atoleiro and Comprida lagoons (Figure 3a, b and c). Iriy lagoon, on the other hand, has its fluorescence emission peak at a slightly lower wavelength (~450 nm, excitation at ~350 nm), with

emission more concentrated in the lower quadrants, with a fluorescence shoulder extending toward the lower left corner (Figure 3d). This pattern indicates a lower aromaticity of DOC in Iriy lagoon (lower humification), which is reinforced by the humification index, which was on average 38% lower compared to the other three lagoons (Figure 3d).

These discrepancies probably reflect geological and vegetational differences in the watersheds of those lagoons. Amarra-Boi, Atoleiro and Comprida are located in a reasonably continuous phytogeographic area comprised by the Restinga de Jurubatiba National Park. It is interesting to note the similarity of their DOC EMM in spite of the 20 km linear distance between Comprida and Atoleiro lagoons. Iriy lagoon, in turn, is located within a recently urbanized area c.a. 35 km far from the National Park. Since most of

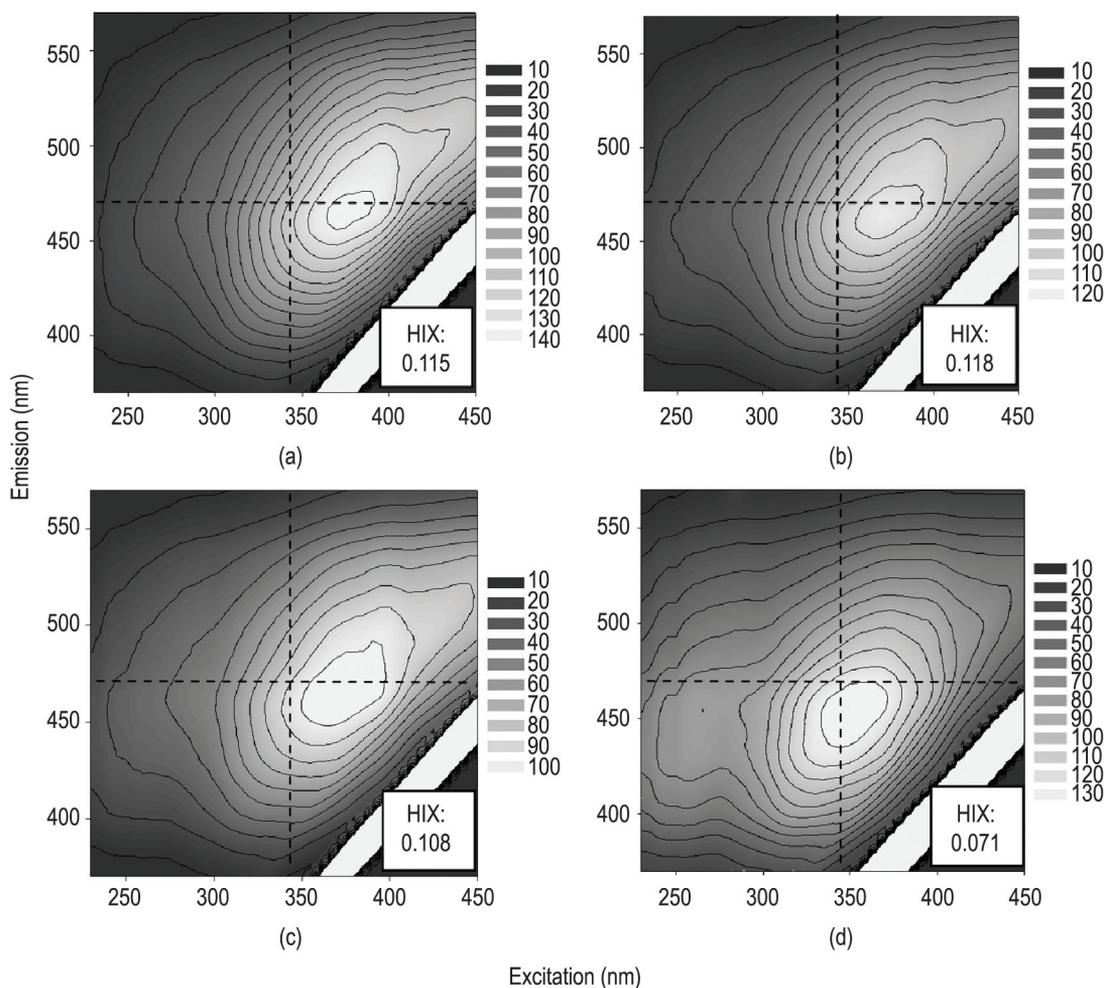


Figure 3. Fluorescence excitation-emission matrices of dissolved organic matter from four coastal lagoons in the northern Rio de Janeiro State: a) Amarra-Boi, b) Atoleiro, c) Comprida and d) Iriy. Fluorescence emission given by different shadings, measured in arbitrary units. The humification index (HIX) is also presented in the graphs (see text for more details. Data by A.L. Suhett (unpublished)).

native *restinga* vegetation has been removed from this area, it is probable that the chemical aspects of humic substances produced in the surrounding soils will also change according to the current source of plant material available for humification processes. Moreover, the possibility of domestic sewage release in Iriry lagoon cannot be discarded, and this would contribute non-humic DOC to this humic system, changing the DOC fluorescence signature.

Carbon isotope studies are still lacking in the clear-water lagoons in this region to a better knowledge of the main sources of DOC to these systems. Although phytoplankton and macrophytes do contribute to the DOC pool, as previously discussed, other primary producers—such as periphyton and micro-phytobenthos—may be highly productive and contribute considerable amounts of DOC in shallow aquatic ecosystems (Revsbech et al., 1981; Wetzel, 1990; Farjalla et al., 2005). This issue seems especially relevant for some shallow, clear-water lagoons with high DOC content (even higher than the typical 2 mM DOC threshold for humic systems), as is the case of Barrinha, Catingosa and Visgueiro lagoons (Figure 1a). The origin of the large amounts of non-colored DOC is not yet understood for these systems.

4. Seasonal Variation of DOC Concentration and Quality in Humic Lagoons

As mentioned above, the DOC concentration in these coastal lagoons may present a great temporal variation, particularly within a seasonal cycle. In the humic coastal lagoons of the region, a consistent seasonal pattern is usually found for the variation of DOC concentration, with peaks at the beginning or during the rainy season (late spring/early summer, October to February) (Farjalla et al., 2002; Suhett et al., 2007). As summarized in a conceptual model by Suhett et al. (2007), after peaking in the rainy season, DOC concentration in a humic coastal lagoon declines due to physical, chemical and biological processes. Besides being consumed by heterotrophic microbes, DOC may be also partially degraded or even mineralized by sunlight (Moran and Zepp, 1997). This photo-degradation process can produce labile bacterial substrates from biologically refractory compounds such as humic substances, enhancing total DOC removal in humic ecosystems (Amado et al., 2007). Along with these processes, some DOC fractions including insoluble humic substances may precipitate to the sediment under particular

conditions such as low pH, increasing salinity and high iron availability (Steinberg, 2003). As for pH and salinity, these conditions are very recurrent, often simultaneously, in most of the studied lagoons (Table 1, Caliman et al., 2010). All these processes acting together would be responsible for declining DOC concentrations throughout the year, until the beginning of a new rainy season (Suhett et al., 2007).

This pattern is less pronounced in some years and not perfectly synchronized between lagoons, even for those very close to each other (e.g., Comprida and Cabiúnas, Figure 4a and b, Pearson correlation not significant, $P > 0.05$). This may reflect differences in the yearly rainfall and in the morphometry (Table 1) of each lagoon. Nevertheless, the hydrological aspects of the transportation of allochthonous DOC from the surrounding *restinga* are still very poorly understood, but it seems plausible that the observed rainfall-induced DOC peaks are due to increased run-off and leaching of the surrounding sandy soil, or by the intrusion of overflowing, humic-rich water from the soaked water-table (personal field observations). In the case of the humic Comprida lagoon, Suhett et al. (2007) showed that DOC concentration was strongly correlated to cumulative rainfall in the last 60 or 90 days ($r=0.80$ and $r=0.90$, respectively), indicating that a time-lag is needed for terrestrial DOC to reach the lagoons. This time-lag is probably related to the time the water-table needs to reach a threshold water level or to the amount of water that is needed to reach saturation and an efficient organic matter leaching. It should be noted that DOC concentration increases in these humic lagoons in spite of water level increases in the rainy period, when a dilution effect could be expected, as commonly observed for salinity and other limnological variables (Laque et al., 2010). This means that the amounts of DOC entering these systems are really large, overwhelming the dilution effect.

Not only DOC concentration, but its quality also varies seasonally (Suhett et al., 2007) for Comprida lagoon. A DOC photoreactivity index, positively related to DOC specific absorptivity, increased consistently in the beginning of the rainy season, being positively related to DOC photo-oxidation rates and to cumulative rainfall in the last 30 days (Suhett et al., 2007). This is the only study which evaluated the seasonal variation of DOC quality to date in the coastal lagoons in this region. The only other seasonal study involving DOC in these coastal lagoons (Farjalla et al., 2002), investigated

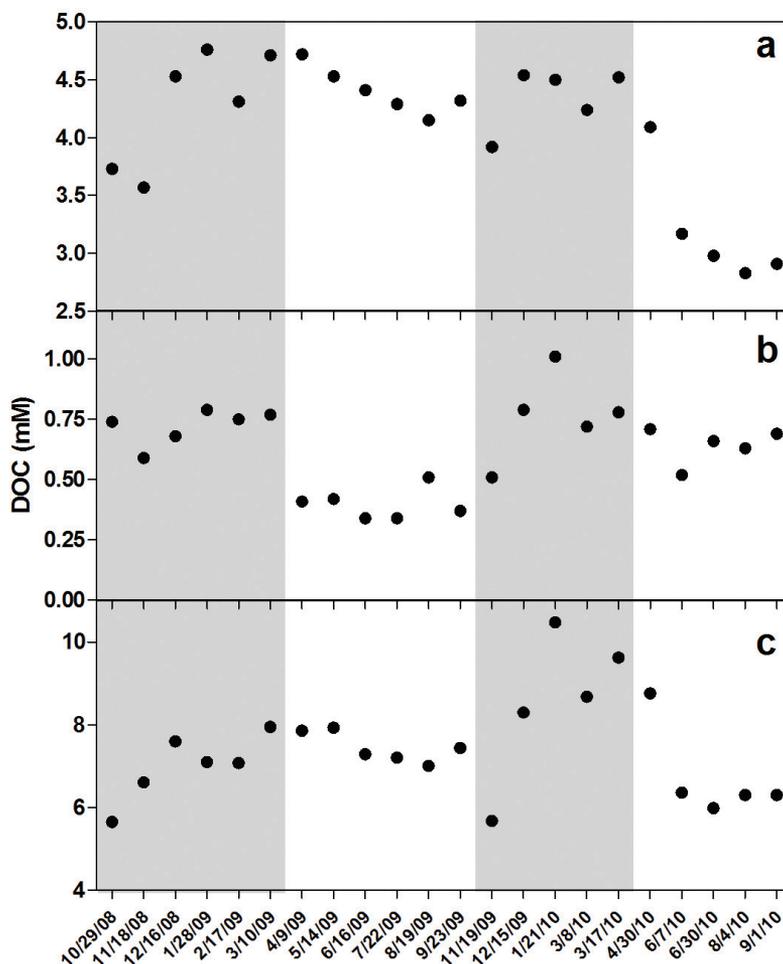


Figure 4. Temporal variation of dissolved organic carbon (DOC) in three humic lagoons between Oct/2008 and Sept/2010. a) Comprida, b) Cabiúnas and c) Amarra-Boi. Shaded areas in the graphs represent the rainy period for the region. A significant synchrony was found only between Comprida and Amarra-Boi (Pearson correlation, $r = 0.62$, $P = 0.002$).

the relationship between DOC concentration and bacterial production, but it did not assess any DOC-quality measure. Moreover, the approach used by Suhett et al. (2007) involved the calculation of an *a posteriori* photo-reactivity index, based on the liability of DOC to photochemical degradation by different light wavebands. Thus, a more thorough seasonal investigation of DOC quality is still needed in these systems, combining *a priori* DOC-quality measures—e.g. optical properties based on light absorption and fluorescence (Nieto-Cid et al., 2006)—with photochemical and microbial DOC processing rates.

5. The Relationships Between DOC Concentrations and the Rates of Microbial and Photochemical Processes

Although DOC is the substrate for the metabolism of planktonic bacteria, metabolic

rates such as bacterial production (BP), bacterial respiration (BR) and bacterial carbon demand ($BCD = BP + BR$) are not consistently related to DOC concentration. In a spatial perspective considering 16 coastal lagoons in the Restinga de Jurubatiba National Park (unpublished data), none of these bacterial parameters were related to DOC (Figure 5a, b and c, linear regressions, $P > 0.05$). Similar results were reported by Farjalla et al. (2002) in a seasonal perspective (monthly samplings during one year) for the humic Comprida, Iodada (synonym for Iriy) and Carapebus lagoons, as depicted in Figure 6a in the case of Comprida lagoon (linear regression, $P > 0.05$). Photo-oxidation rates were also unaffected by DOC concentration in a seasonal perspective, as described for Comprida lagoon, as consequence of huge seasonal variation of DOC photoreactivity (*i.e.* quality) over the seasonal cycle (Figure 6b, Suhett et al., 2007). In a spatial perspective, on the other hand, DOC is positively

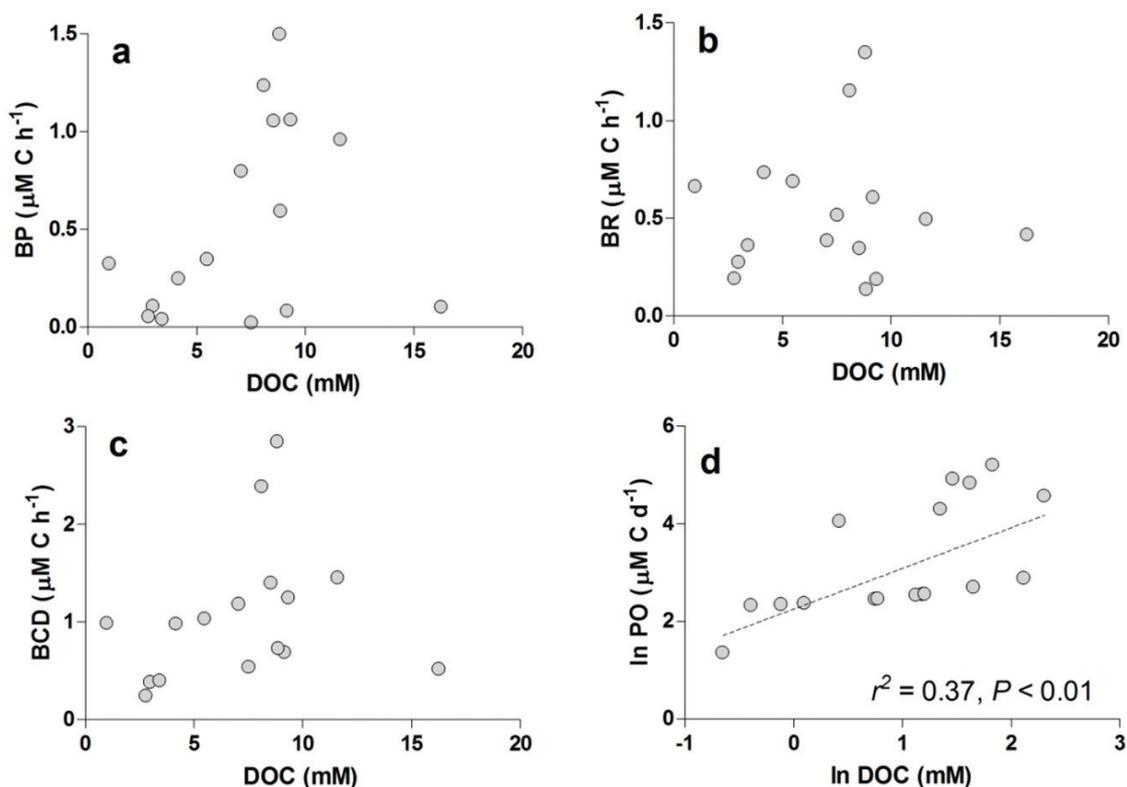


Figure 5. Relationships between DOC concentration and consumptive processes in coastal lagoons from the northern Rio de Janeiro State, in a spatial perspective (each lagoon was sampled only once and is represented by a single point in each graph). a) Bacterial production (BP, $n = 16$), b) bacterial respiration (BR, $n=16$), c) bacterial carbon demand (BCD = BP + BR, $n=16$) and d) photo-oxidation (PO, $n=20$). Data in (a), (b), and (c) by S.M.S. Jacques, V.S. Scofield and V.F. Farjalla (unpublished) and (d) by A.M. Amado, T.A.S. Ferraz, A.L. Suhett and V.F. Farjalla (unpublished). On graph (c), a significant positive relationship was found (linear regression, $r = 0.256$, $P = 0.023$), but it was mainly caused by an outlier (Atoleiro, 10.07 mM DOC), whose removal deemed the regression not significant.

related to photo-oxidation rates (Figure 5d, $r = 0.37$, $P < 0.01$), as was also previously shown for larger data-sets including aquatic ecosystems from all over the world (Suhett et al., 2006; Farjalla et al., 2009). This implies that DOC concentration is still a major determinant of photo-oxidation rates at regional scales, even though other factors—such as DOC photo-reactivity, sunlight incidence, iron availability—are responsible for the unexplained variation in the reported relationships (Suhett et al., 2006).

There are concurring explanations for the above cases in which DOC was not related to processing rates. First, DOC quality (*i.e.*, its reactivity) to microbial and photochemical processes may vary both spatially and temporally, as discussed in the previous sections (see also Amado et al., 2003; Rodríguez-Zúñiga et al., 2008). Thus, the amount of DOC *per se* may not reflect its actual bio- or photo-availability. This unrelatedness was demonstrated seasonally for DOC photo-oxidation by Suhett et al. (2007), with these rates

being determined by DOC optical properties (*e.g.*, DOC specific absorptivity), rather than just DOC concentrations. Second, for bacterial DOC consumption, nutrient (mainly P) limitation has been demonstrated in humic lagoons in the region (Farjalla et al., 2002). In the case of Comprida lagoon—and this is likely the case of other humic-rich lagoons—carbon limitation was also shown by increasing BP with glucose addition, indicating an excess of refractory DOC in the humic coastal lagoons. Thus, even under increasing nutrient availability, DOC quality may still limit its efficient consumption and processing by bacterioplankton in these coastal lagoons.

6. How Significant are Photo-Oxidation and Bacterial Respiration to CO_2 Efflux from the Water Column?

The surveyed data revealed that the magnitude of depth-integrated DOC photo-oxidation rates varied by one order of magnitude among the

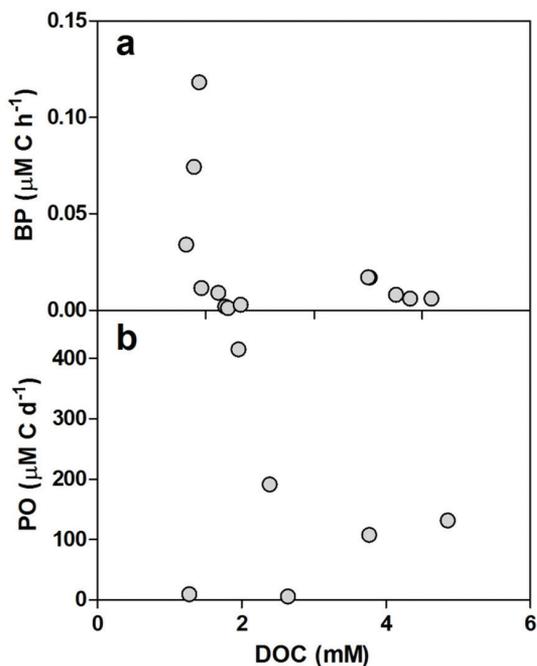


Figure 6. Relationships between DOC concentration and consumptive processes in Comprida lagoon on a seasonal perspective. a) bacterial production (BP, after Farjalla et al. 2002) and b) photo-oxidation (PO, after Suhett et al. 2007). No significant relationship was found.

coastal lagoons, ranging from 1.50 to 16.64 mmol C $\text{m}^{-2} \text{d}^{-1}$ (Imboassica and Visgueiro, respectively) (Table 2). These depth-integrated rates lie in a similar range as that found for Nordic lakes of different humic content (0.99 – 14.25 mmol C $\text{m}^{-2} \text{d}^{-1}$, Granéli et al., 1996; Vähätalo et al., 2000; Jonsson et al., 2001). It is worth noting that highly humic, DOC-rich lagoons, such as Atoleiro and Comprida (see Figure 1), presented depth-integrated photo-oxidation rates among the lowest ones registered here. In a recent review, Farjalla et al. (2009) have shown that these humic lagoons produce the highest volume-based DOC photo-oxidation rates reported in the literature. Nevertheless, light attenuation is very strong in these systems so that visible light may be attenuated by 90% at the top 20 cm and UV-B can be totally attenuated at the top 1 cm (data not shown). Thus, there is a counterbalancing effect of water color, drastically constraining depth-integrated photo-oxidation rates in highly humic lagoons, even though they present extremely high volume-based (potential) rates. This leads to a particularly low effective contribution of DOC photo-oxidation to total CO_2 efflux in the humic coastal lagoons (less than 5% in most cases), whilst a higher contribution

is found in clear-water lagoons (up to 48%), where light penetrates most of the water column (Table 2). However, the values for most coastal lagoons were higher than the 10% contribution of photo-oxidation to whole-lake mineralization reported for a Swedish humic lake (Jonsson et al., 2001).

The surveyed depth-integrated BR rates ranged from 3.06 mmol C $\text{m}^{-2} \text{d}^{-1}$ in Pires lagoon to 59.90 mmol C $\text{m}^{-2} \text{d}^{-1}$ in Cabiúnas lagoon (Table 2). The percent contribution of BR to total CO_2 efflux in the studied coastal lagoons ranged from 1.6% in the humic Atoleiro to 80.7% in the clear-water Barrinha lagoon (Table 2). In the case of the humic Cabiúnas and Comprida lagoons, a relatively large contribution of BR than photo-oxidation to total CO_2 efflux was observed (56.9 and 68.0%, respectively, Table 2). This was mostly an effect of their higher mean depth (~ 3 m), while most of the surveyed lagoons are generally shallower (< 1 m deep) (Table 1). This happens because BR takes place in the whole water column, while photo-oxidation is limited to the depth to which light penetrates. Also, in some humic coastal lagoons (e.g., Amarra-Boi and Atoleiro), DOC photo-oxidation and BR together account for a very low share of the total CO_2 efflux ($< 15\%$, Table 2). In these cases, sediment respiration may be the main component of C mineralization, particularly in these very shallow lagoons. The joint contribution of both processes to CO_2 efflux may sum up to more than 100% (Table 2), which may happen basically for two reasons. First, not all mineralized C on a daily basis is released from the water column: actually, the emission rates will depend on temperature, salinity, wind speed among other environmental variables (Cole and Caraco, 1998). Second, autotrophic processes with variable magnitude also take place at all lagoons, counterbalancing C mineralization and acting negatively to the net CO_2 efflux.

Overall, the surveyed data do not support different contributions of depth-integrated DOC photo-oxidation and BR to CO_2 efflux in the coastal lagoons in this region (Figure 7, *t* test, $P = 0.581$), although a considerably proportional contribution of BR was found in some particular cases (Table 2). This is rather surprising, given the strong depth-limitation of photochemical processes in most of the surveyed lagoons. However, this only happened because most of these coastal lagoons are shallow (< 1 m deep), also limiting the potential contribution of BR to C mineralization. In deeper humic systems, such as the Negro River in the Amazon, the proportional contribution of BR to whole-water

Table 2. Depth-integrated DOC photo-oxidation and bacterial respiration rates, and maximal CO₂ efflux in 20 coastal lagoons of the northern Rio de Janeiro State. Numbers into brackets are the potential (%) contribution of each process to the maximal CO₂ efflux in each lagoon. Maximal efflux refers to the highest values observed for each lagoon from Oct/2008 to Oct/2010 (unpublished data). Photo-oxidation rates measured by A.M. Amado, T.A.S. Ferraz, A.L. Suhett and V.F. Farjalla (unpublished data) and bacterial respiration rates by S.M.S. Jacques, V.S. Scofield and V.F. Farjalla (unpublished data). Note that the potential contributions of both processes may sum up to more than 100% (see the text for details). n.d. = not determined.

Lagoon	Photo-oxidation (mmol C m ⁻² d ⁻¹)	Bacterial respiration (mmol C m ⁻² d ⁻¹)	Maximal CO ₂ efflux (mmol C m ⁻² d ⁻¹)
Amarra-boi	1.82 (2.6)	6.37 (9.0)	70.61
Atoleiro	1.95 (0.4)	8.42 (1.6)	517.83
Barrinha	11.05 (36.8)	24.24 (80.7)	30.02
Bezerra	11.19 (42.6)	8.66 (32.9)	26.31
Cabiúnas	7.43 (7.4)	56.90 (56.9)	100.05
Carapebus	7.55 (13.7)	5.6 (10.1)	55.21
Casa Velha	13.08 (48.1)	nd	27.18
Catingosa	16.41 (18.8)	3.50 (4.0)	87.51
Comprida	3.94 (6.2)	43.11 (68.0)	63.37
Encantada	6.45 (9.8)	4.23 (6.4)	65.71
Garças	10.17 (10.6)	nd	95.96
Imboassica	1.50 (1.0)	nd	146.07
Maria Menina	15.80 (20.1)	5.19 (6.6)	78.44
Paulista	7.88 (10.6)	8.45 (11.3)	74.59
Pires	4.94 (5.6)	3.06 (3.5)	87.79
Piripiri 2	11.51 (16.4)	nd	70.33
Preta	5.25 (3.1)	16.16 (9.6)	168.74
Robalo	11.40 (21.2)	24.87 (46.3)	53.70
Ubatuba	14.74 (19.2)	nd	76.74
Visgueiro	16.64 (38.2)	9.82 (22.6)	43.57

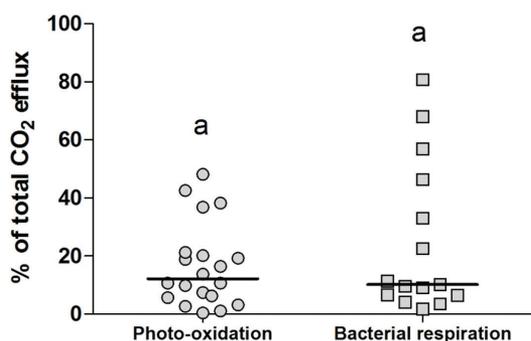


Figure 7. Potential contribution of DOC photo-oxidation (n=20) and bacterial respiration (n=15) to the maximal CO₂ efflux in the coastal lagoons, after data on Table 1. The horizontal lines indicate the medians and the superscript letters indicate that no significant difference was found between the contributions of the two processes (unpaired *t* test with ln-transformed data, *P* = 0.581, *t* = 0.693, d.f. = 33).

column C mineralization is certainly much higher than that of photo-oxidation, because BR takes place in the whole water column irrespective of light penetration (Amaral et al., 2013).

7. Does the Microbial Loop Sustain Food Webs in Humic Coastal Lagoons?

Once it enters the water column in its dissolved form (DOC), organic C can only be recovered to pelagic food webs through uptake and incorporation into biomass by heterotrophic bacterioplankton. This microbial loop would integrate DOC with higher trophic levels associated to bacterivorous organisms, such as protozoans and zooplanktonic metazoans (Azam et al., 1983). In humic aquatic ecosystems, where DOC is abundant and sunlight penetration is limited, this role of the microbial loop should be presumably larger than that of food chains based on phytoplankton (Jansson et al., 2000; Cotner and Biddanda, 2002). Additionally, the photochemical production of labile compounds after humic substances and its uptake by bacterioplankton (Wetzel et al., 1995) should enhance the contribution of the microbial loop to the carbon and energy transfer to higher trophic levels. This latter issue was evaluated in only one humic lagoon in this region (Comprida), without any support to a higher potential role of the microbial loop in carbon transfer to higher

trophic levels in these highly humic lagoons due to the interaction between DOC and sunlight (Amado et al., 2007).

In addition, carbon isotope data for the humic Cabiúnas and Comprida coastal lagoons (Figure 3) (Marinho et al., 2010, and unpublished data) reveal that zooplankton $\delta^{13}\text{C}$ signature is surprisingly deviated towards that of microalgae, indicating an important contribution of these organisms as carbon source for the pelagic food web even in humic coastal lagoons. As discussed above, the $\delta^{13}\text{C}$ of DOC in both lagoons is an average of autochthonous and allochthonous sources, but with an evident contribution of a terrestrial CAM plant species. The contribution of allochthonous C sources to zooplankton via both DOC and POC (data not shown) cannot be excluded in the case of Comprida lagoon, which is richer in DOC and has a more pronounced humic aspect (Figures 1 and 3b). However, in the case of Cabiúnas lagoon—which is less rich in DOC and less colored—phytoplankton seems to be the exclusive C source for zooplankton and, by extension, to pelagic food webs (Figures 1 and 3a). In humic freshwaters, mixotrophic flagellates may be major components of phytoplankton, due to nutritional advantages of this feeding mode in nutrient-poor waters (Jansson, 1998). Thus, mixotrophic phytoplankton might account for part of the C subsidies to zooplankton in Cabiúnas and Comprida lagoon, although this does not seem to be the case in Cabiúnas lagoon, because algae $\delta^{13}\text{C}$ signature is much deviated from the signature of DOC, which would be a major C source for mixotrophs.

In conclusion, there is no compelling evidence that pelagic food webs in the humic coastal lagoons of the studied region are heavily sustained by allochthonous DOC, nor is there evidence that humic DOC photodegradation makes its incorporation into bacterioplankton biomass more efficient. There is evidence in the literature of stimulation of protozoan and metazooplankton growth upon DOC exposure to sunlight in lakes with varying DOC content, some of which were humic (De Lange et al., 2003; Daniel et al., 2006). However, these studies are often restricted to lakes with DOC content lower than those found in the humic coastal lagoons studied here. Here, the excess of DOC and the nutrient limitation may hinder the efficient utilization of DOC by bacteria and its transfer to higher trophic levels. Nevertheless, we should note that both the carbon isotope analysis and the photochemical study were restricted to only

two humic lagoons in the region. A more thorough appreciation of these aspects over the whole DOC and water color range found in these lagoons would largely contribute to a more representative appraisal of this issue.

8. Conclusions

The coastal lagoons in the northern Rio de Janeiro state represent a very wide spatial gradient of DOC and water color, with values among the highest reported in the literature. Most of these lagoons are humic, and allochthonous C is their major DOC source. For humic lagoons, there is a fairly clear seasonal pattern of variation in DOC concentration associated to rainfall, but little is known about the exact timing of these allochthonous inputs. Photo-oxidation and bacterial respiration rates are not related to DOC concentration due to spatial and temporal variability in DOC quality and to nutrient limitation. Depth-integrated photo-oxidation rates were particularly less representative in highly humic lagoons, due to strong light attenuation in the water column. Even in humic lagoons, microalgae seem to be a major C source sustaining pelagic food webs through zooplankton, in spite of some contribution of allochthonous C. Thus, the predominant role of the microbial loop in such systems is to be questioned.

Acknowledgement

The authors are grateful to the financial support granted by CNPq (Universal Program - Projects 480232/2004-0, 475961/2007-2 and 479437/2010-6), FAPERJ (Prêmio Jovem Cientista do Nosso Estado - Project 103.316/2011) and CENPES/PETROBRAS (ANPETRO 8920 and ANPETRO 9803) to V.F.F. The authors also thank for a productivity research grant to V.F.F, a postdoc fellowship to F. Meirelles-Pereira (CAPES/FAPERJ PAPD Program), and PhD scholarships to T. Laque and V. Scofield by CAPES, and to S.M.S. Jacques by FAPERJ.

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Received: 08 June 2013

Accepted: 11 December 2013