

## Methane Concentration in Water Column and in Pore Water of a Coastal Lagoon (Cabiúnas Lagoon, Macaé, RJ, Brazil)

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### ABSTRACT

The aim of this study was to evaluate methane concentration in water column and pore water at limnetic and littoral regions of a coastal lagoon. At the littoral region samples were taken from three monospecific macrophytes stands (*Typha domingensis*, *Eleocharis interstincta* and *Potamogeton stenostachys*). The methane concentration in the pore water at the littoral region was higher than the concentration found at the limnetic region in each fraction of the sediment. The higher methane concentration in the superficial fraction of the sediment (0-2 cm) was shown at the *P. stenostachys* stand (3.7 mM). It was the only significantly different ( $p < 0.05$ ) from the limnetic region. The pore water methane concentration increased with depth at the aquatic macrophytes stands. The methane concentration in the water column did not vary significantly among the sampling sites ( $p > 0.05$ ). It could be concluded that there was a high influence of aquatic macrophytes on the pore water methane concentration.

**Key words:** Methane, water column, sediment, aquatic macrophytes, coastal lagoons

### INTRODUCTION

*Methanogens* are strictly anaerobic microorganisms that produce methane as the final product of their metabolism. Their most common habitats are freshwater and saline sediments, the digestive tract of animals and anaerobic digesters (Jones, 1991). The importance of *methanogens* in carbon cycling has been widely known (Boone, 1991). At aquatic ecosystems, the sediment is the main site of methanogenesis so, when the water column is anaerobic, it can support a significant methanogenesis (Kiene, 1991). *Methanogens* can use a short amount of substrates, mainly acetate, formate and hydrogen (Fenchel et al., 1998, Segers

and Kengen, 1998). Hence, the conversion of many organic molecules into methane needs interactions between non-methanogenic organisms and *methanogens*. The former can use a great variety of organic molecules that result in final metabolic products, which can be used by *methanogens*, resulting in methane production (Boone, 1991).

The majority of the coastal aquatic tropical ecosystems are shallow, allowing a wide development of aquatic macrophytes (Esteves, 1998). The aquatic macrophytes influence directly on methane dynamics at wetlands, once they are source of organic matter to the methanogens (Neue et al., 1997). The organic matter from aquatic

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macrophytes can be more resistant to decomposition, like the one from the emergent aquatic macrophytes *Typha domingensis* Pers. and *Eleocharis fistulosa* Schult., which have most of their carbon in support tissues. Otherwise, it can be more labile like the one from *Potamogeton stenostachys* K. Schum, a submergent aquatic macrophyte (Farjalla et al., 1999). Aquatic macrophytes can also act as a route to release methane to the atmosphere, through the aerenchyma (Boon and Sorrell, 1995, Kulshreshtha et al., 2000, Yavitt and Knapp, 1995), but it can also be released from the sediment to the atmosphere through diffusion of dissolved methane and ebullition of gas bubbles (Neue et al., 1997). The aquatic macrophytes play an important role in methane oxidation because their roots and rhizomes promote the sediment oxygenation, which allows the development of methanotrophic bacteria responsible for the oxidation of CH<sub>4</sub> into CO<sub>2</sub> (King, 1994).

The wetlands are considered the main source of atmospheric methane (Cicerone and Oremland, 1988) that currently contributes with about 20% to the global warming effect (Neue et al., 1997), because of its capacity to absorb infrared radiation. Considering the role of aquatic macrophytes community to the methane dynamics in wetlands, it is of great importance to study the influences of this community upon the methane biogeochemical processes at coastal aquatic tropical ecosystems. The alarming global changes attributed to methane, have raised questions about how these changes had already affected the climate and biogeochemical cycles on earth and how it will continue to affect them (Kiene, 1991).

The aim of this work was to evaluate the methane concentration in the water column and in pore water in a 10 cm sediment profile, at two sampling sites at Cabiúnas lagoon: littoral region (aquatic macrophytes stands) and limnetic region.

## MATERIALS AND METHODS

Cabiúnas Lagoon is located on the Restinga de Jurubatiba National Park at Macaé in the Northern region of Rio de Janeiro State (22°24' S and 41°42' W), one of the sites of the Long Term Ecological Research program (LTER) in Brazil. Cabiúnas is a shallow lagoon (mean depth of 2.37

m) and with a dendritic shape, which supports the establishment of aquatic macrophytes. The area of the lagoon is about 0.35 km<sup>2</sup> and it has a 10 km perimeter (Panosso et al., 1998). The pH of the water is near to neutral (Petruccio, 1998).

The water and sediment samples were collected at the limnetic region (site 1) and at the littoral region (site 2) at Cabiúnas lagoon (Fig. 1), during September 2000. The littoral region was divided into three distinct sub-sites according to the macrophytes stands: *Typha domingensis* stand, *Eleocharis interstincta* stand and *Potamogeton stenostachys* stand.

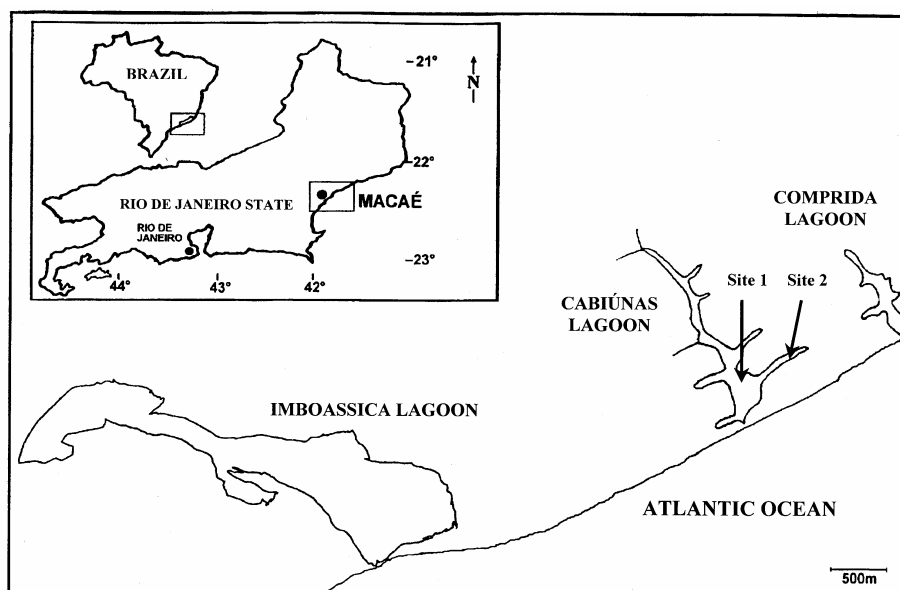
### Methane Concentration Evaluation

Five mL samples were collected both on the surface and on the bottom of water column, using plastic syringes and needle (n=5). The samples were stored in 10 mL glass flasks with rubber stoppers, with 0.1 mL of ZnCl<sub>2</sub> 4M to inhibit biological activity, and kept under refrigeration until the laboratory analyses.

Only the ten superficial centimeter fraction of the sediment (0-10 cm) was considered and it was divided at every 2 cm. Four mL of each fraction from the same sampling site (n=5) were stored in 25 mL glass flasks with rubber stoppers. To this, was added 4 mL of NaOH (4%) to expel the methane from the pore water (Casper, 1992). After shaking all the samples, 0.2 mL of gas was taken from the headspace using plastic syringes and needle and, than injected in a gas chromatograph (VARIAN Star 3400 - Varian Co., EUA). The operating conditions were FID detector temperature 220°C, injector temperature 120°C and a 1m Poropak-Q column (60/100 mesh) at 85°C and nitrogen as the carrier gas.

### Abiotic Variables

The abiotic variables from water measured in the field were temperature, salinity and water conductivity using a portable salinity, conductivity and temperature analyzer (YSI model 30/10 FT). The concentration of dissolved oxygen was evaluated according to Winkler methodology, modified by Golterman et al. (1978). The pH was determined using a digital pHmeter (Micronal model B278). These variables were measured both on the surface and on the bottom of water column only when it was deeper than 1 meter.



**Figure 1** - Schematic localization map of Cabiúnas Lagoon. The arrows indicate the two sampling sites.

**Table 1** - Abiotic variables of Cabiúnas Lagoon water column: depth, temperature, dissolved oxygen, electric conductivity, salinity and pH.

		Limnetic region	<i>P. stenostachys</i>	<i>T. domingensis</i>	<i>E. interstincta</i>
depth (m)		2.8	1.4	0.6	0.4
temperature (°C)	surface	25.2	26.3		
	bottom	25.4	26.4	25.9	26.6
O <sub>2</sub> (mg L <sup>-1</sup> )	surface	6.46	6.20	3.39	0.41
	bottom	6.52	6.32		
conductivity (μS cm <sup>-1</sup> )	surface	610	578		
	bottom	609	580	606	491
salinity (‰)	surface	0.3	0.3	0.3	0.2
	bottom	0.3	0.3		
pH	surface	7.35	7.30	6.68	5.99
	bottom	7.20	7.20		

For the sediment, the same samples fractions used to determine the methane concentration were used to evaluate Kjeldahl nitrogen, (Allen et al., 1974), total phosphorus (Fassbender, 1973) and organic carbon concentrations (using a TOC-5000 Analyzer Shimadzu Co., Japan).

### Statistical Analysis

The results for methane concentrations were statistically analyzed through nonparametric ANOVA with Dunn's post-hoc test. Methane concentration and organic carbon correlation was

analyzed through Spearman correlation. Software GraphPad InStat 3.00 was used for all statistical analyses. The other variables were not statistically analyzed.

### RESULTS AND DISCUSSION

The water column temperature varied from 25.2°C (limnetic region) to 26.6°C (*E. interstincta* stand). The conductivity and salinity results were similar among the sampling sites. The lower pH (5.99) was found in the *E. interstincta* stand and the

higher (7.30) in the *P. Stenostachys* stand and at limnetic region. The variables measured in the field were quite similar among the sampling sites and between the surface and the bottom. These results showed the homogeneity on the water column at Cabiúnas lagoon except for the lower concentration of dissolved oxygen in the water (0.41mg/L) registered in the region colonized by *E. interstincta* (Table 1).

The amount of nutrients (Kjedahl nitrogen, total phosphorus and organic carbon) in the sediment at the limnetic region was lower than that at the littoral region. The higher amount of nutrients was found at *T. domingensis* and *E. interstincta* stands, while intermediate amounts of nutrients were found in the *P. stenostachys* stand (Table 2).

**Table 2** - Contents of organic carbon (C - % DW), Kjedadhl-nitrogen (N - % DW) and total phosphorus (P - % DW) in the sediment of Cabiúnas lagoon, (---) data not obtained.

fractions	Limnetic region			<i>T. domingensis</i>			<i>E. interstincta</i>			<i>P. stenostachys</i>		
	C	N	P	C	N	P	C	N	P	C	N	P
0-2	0.71	0.06	0.00	12.85	1.64	0.07	18.20	2.34	0.06	7.96	0.50	0.06
2-4	0.46	0.06	0.00	13.00	1.42	0.06	17.09	1.74	0.05	7.66	0.50	0.03
4-6	0.58	0.15	0.01	14.63	1.42	0.06	15.55	1.35	0.04	5.48	0.42	0.02
6-8	1.24	0.11	0.03	13.78	1.43	0.06	16.80	1.58	0.03	5.39	0.24	0.01
8-10	3.37	0.17	---	13.86	1.36	0.07	16.49	1.45	0.04	4.36	0.28	0.02

On the other hand, the low organic matter deposition at the limnetic region was attributed to the low densities of phytoplankton at Cabiúnas Lagoon (Roland, 1998). Faria and Esteves (2001) studying other coastal lagoons also at northern of Rio de Janeiro State, suggested that the organic matter from the aquatic macrophytes at the littoral region was decomposed at its origin site, so when it reached the limnetic region it was more resistant for decomposition. Besides its concentration, the quality of the organic matter is another important factor to be considered (Kiene, 1991).

At the littoral region, the methane concentration in the pore water increased along the sediment profile (Fig. 2), as observed in other ecosystems (Benstead and Lloyd, 1996; Van der Nat and Middelburg, 2000). Despite this, the corresponding increase in carbon concentration along the sediment profile was not observed ( $r = 0.3985$ ,  $n=20$ ,  $p>0.05$ ). It can be due to the sediment structure that can support different microbial communities. In steady state, undisturbed sediments show a characteristic stratification. The availability of O<sub>2</sub>, nitrate, ferric iron and sulfate typically decreases with the

## Methane Concentration in Pore Water

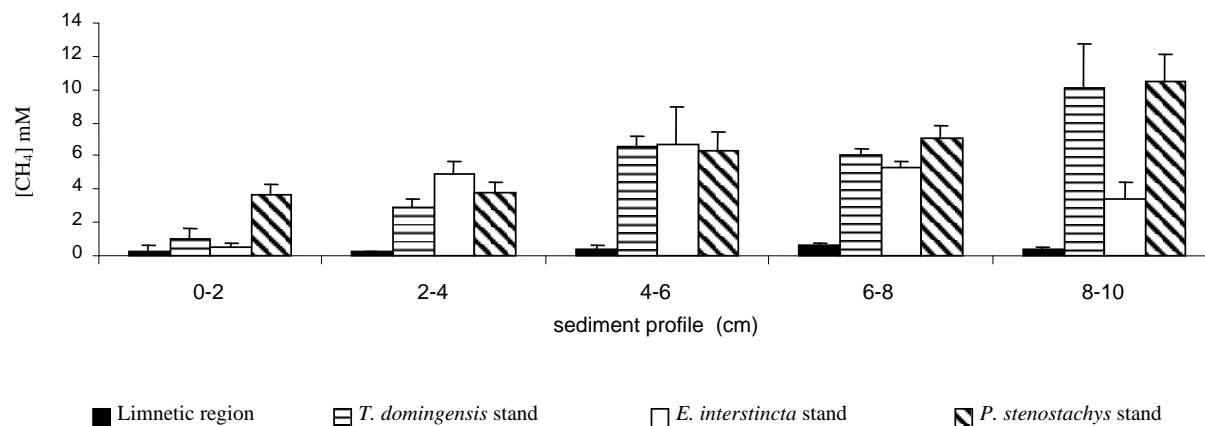
The methane concentration found in the pore water at the littoral region was higher than that at the limnetic region, both at all aquatic macrophytes stands and all fractions of the sediment profile (Fig. 2). This pattern could be explained by the greater accumulation of organic matter at the littoral region, attributed to the detritus from the aquatic macrophytes and to the surrounding restinga vegetation that promoted changes in the sediment, which could facilitate methanogenesis.

distance from the anoxic-oxic interface, so that in the end there is the zone where CH<sub>4</sub> production becomes the dominant final step in organic matter degradation (Conrad, 1989).

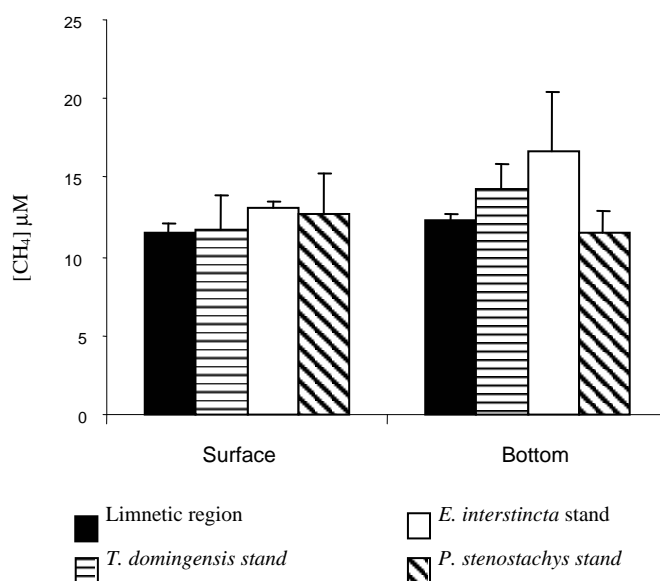
In relation to the methane concentration at the superficial fraction of the sediment (0-2cm) (Fig. 2), only the area colonized by *P. stenostachys* (3.7 mM) was significantly higher ( $p<0.05$ ) than the limnetic region (0.3 mM), contrary to the lower amounts of nutrients found in the sediment at this site (Table 2). According to Brum (2000) the *P. stenostachys* detritus decomposed five times faster than that observed for *E. interstincta*. According to Farjalla et al. (1999), the emergent aquatic macrophytes *T. domingensis* and *E. fistulosa* have a potential decomposition rate slower than *P. stenostachys*, because of the high percentage of supporting tissues that are more resistant to microorganisms decomposition. Submerged aquatic macrophytes, such as *P. stenostachys*, have a great reduction in their supporting tissues, since they are sustained by the water column and by aerenchyma tissue (Esteves, 1998). It enables the release of more labile substrate that can be easily used by the microbial

community in the water column and in the superficial fraction of the sediment, while the more refractory substrate is in the deeper layers of the sediment. It is possible that the nutrient

concentration on sediment at the *P. stenostachys* stand was lower because of its high decomposition rate and low contribution of particulate detritus from this macrophyte species.



**Figure 2** - Vertical concentrations profiles of pore water methane.



**Figure 3** - Surface and bottom water column methane concentration ( $p > 0.05$ ).

Comparing the higher methane concentration found in the sediment at Cabiúnas lagoon to the higher concentrations found in other ecosystems, (Table 3), It was observed that the methane concentration at the limnetic region of Cabiúnas lagoon was similar to irrigated rice fields in Italy, coastal basin of North Carolina (USA) and

Ellergower Moss site of New Galloway (Scotland). However, compared to other ecosystems, the methane concentration in the sediment at the macrophytes stands at Cabiúnas lagoon (Table 3) could be considered an important site of methane production.

### Methane Concentration in Water Column

In the water column, there were no significant differences ( $p > 0.05$ ) among the macrophytes stands and between those and the limnetic region, both at the surface and the bottom ( $p > 0.05$ ) (Fig. 3). Considering the influences of the pore water upon the water column through the nutrients release and gas diffusion (Fenchel et al., 1998), we could expect higher methane concentration at the

littoral region of Cabiúnas lagoon. However, Cabiúnas lagoon and other shallow coastal lagoons are submitted to water mixture due to wind action that avoid water column stratification (Ecolagoas project reports, 1991-1996, unpublished data). It explained the methane concentration similarity observed both between limnetic and littoral region and between surface and bottom (Fig. 3) and, among the abiotic variables shown in Table 2.

**Table 3** - Methane concentrations in water column (lowest and highest concentrations) and the highest concentrations in pore water and the respective sediment depth, (---) data not obtained.

Location	[CH <sub>4</sub> ] water (µM)	Higher [CH <sub>4</sub> ] pore water (mM)	Sediment depth (cm)	References
irrigated rice fields northern Italy coastal basin	---	~0.40	7.0	Frenzel et al., 1999
North Carolina, USA Eckernforde Bay	---	~2.00	10.0	Martens et al., 1998
Kiel Bight, Baltic Sea	---	~7.00	100.0	Martens et al., 1998
Ellergower Moss site New Galloway, Scotland	---	~0.35	20.0	Benstead and Lloyd, 1996
Baltic Sea	0.05 to 1.2	~4.00	22.5	Schmaljohann, 1996
Open ocean surface waters	0.0018 to 0.0031	---	---	Heyer, 1990
Diogo Lake Open Water, São Paulo, Brazil	0.73 to 1.35	---	---	Ballester, 2001
Diogo Lake Macrophytes stands, São Paulo, Brazil	0.84 to 2.60	---	---	Ballester, 2001
Cabiúnas Lagoon Limnetic region	11.46 to 12.32	0.61	6.0-8.0	this research
Cabiúnas Lagoon Littoral region	11.43 to 16.70	10.52	8.0-10.0	this research

Compared to other ecosystems, the methane concentration found at Cabiúnas lagoon (Table 3), was at least four times higher than Diogo Lake, (SP, Brazil), about 300 times higher than the Baltic Sea and 9000 times higher than superficial oceanic waters. These results suggested that the aquatic macrophytes species studied at Cabiúnas lagoon had a positive influence on methanogenesis. However, it was not possible to evaluate the influence of these species on the methane concentration in the water column.

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### RESUMO

O objetivo dessa pesquisa foi determinar a concentração de metano na coluna d'água e na água intersticial do sedimento nas regiões

limnética e litorânea de uma lagoa costeira (Lagoa Cabiúnas, Macaé, RJ). Na região litorânea as amostras foram coletadas em três estandes de macrófitas (*Typha domingensis*, *Eleocharis interstincta* e *Potamogeton stenostachys*). A concentração de metano na água intersticial na região litorânea foi maior do que aquela encontrada na região limnética em cada fração do sedimento. A maior concentração de metano na fração superficial do sedimento (0-2 cm) foi observada no estande de *P. stenostachys* (3.7 mM). Este resultado foi o único significativamente diferente ( $p < 0.05$ ) da região limnética. A concentração de metano na água intersticial aumentou com a profundidade nos estandes de macrófitas. A concentração de metano na coluna d'água não variou significativamente entre os pontos de coleta ( $p > 0.05$ ). Os resultados sugerem que há uma considerável influência das macrófitas aquáticas estudadas na concentração de metano na água intersticial do sedimento.

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