

SHORT-TERM CHANGES AND LONGITUDINAL DISTRIBUTION OF CARBON METABOLISM IN THE PIAUÍ RIVER ESTUARY (SERGIPE, BRAZIL)

SOUZA, M. F. L. de^{1,2} and COUTO, E. C. G.³

¹Departamento de Química, Universidade Federal de Sergipe, São Cristóvão, CEP 49100-000, SE, Brazil

²Programa de Pós-graduação em Geoquímica, Universidade Federal Fluminense, Niterói, CEP 24020-007, RJ, Brazil

³Departamento de Biologia, Universidade Federal de Sergipe, São Cristóvão, CEP 49100-000, SE, Brazil

Correspondence to: Erminda C. Guerreiro Couto, Departamento de Biologia, Universidade Federal de Sergipe, CEP 49100-000, São Cristóvão, SE, Brazil, e-mail: minda@sergipe.ufs.br

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(With 1 figure)

ABSTRACT

Net pelagic metabolism (NPM) and net ecosystem metabolism (NEM) were assessed by ΣCO_2 changes in three sampling stations along Piauí River estuary. At the upper estuary station, sampling was carried out over 48 h. Samples exhibited high DIN:DIP ratios. Chlorophyll-*a* ranged from 0.2 to 2.5 $\mu\text{g}\cdot\text{l}^{-1}$, being higher at the upper estuarine station than marine ones. Net pelagic metabolic rates ranged from -13.2 to $61.2 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Presence of mucilaginous algal material can explain the net mineralization. In the photic period, NPM ranged from -0.05 to $3.04 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. NEM ranged from -7.77 to $6.65 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Bottom resuspension due to microphytobenthic flotation and a high turbidity plume inside de estuary reflected in negative metabolic rates (mineralization). Benthic metabolism was inferred by net system minus pelagic metabolism. Microphytobenthic community seems to be the main responsible for system metabolism, specially in the upper estuary, although the anthropogenic inputs exert strong long term influence.

Key words: estuary, short-term changes, primary production, mineralization, microphytobenthos.

RESUMO

Variações de curto prazo e distribuição longitudinal do metabolismo do carbono no estuário do Rio Piauí (Sergipe, Brasil)

O metabolismo pelágico líquido (MPL) e o metabolismo líquido do ecossistema (MLE) foram medidos pela variação do ΣCO_2 em três pontos de amostragem no estuário do Rio Piauí. Na estação a montante, a amostragem foi conduzida durante 48 h. As amostras apresentaram uma alta relação NID:PID. A clorofila-*a* variou entre 0,2 e 2,5 $\mu\text{g}\cdot\text{l}^{-1}$, com concentrações superiores na estação a montante àquelas de maior influência marinha. O MPL oscilou de $-13,2$ a $61,2 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. A presença de material mucilaginoso algal pode explicar os resultados de taxas metabólicas negativas (mineralização). Durante o período fótico, o MPL variou de $-0,05$ a $3,04 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. O MLE variou de $-7,77$ a $6,65 \text{ mgC}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$. Ressuspensão de sedimento e uma pluma de alta turbidez refletiram-se em episódios de mineralização. Uma estimativa do metabolismo bêntico foi realizada através da diferença entre MLE e MPL. A comunidade microfítobêntica parece ser a principal responsável pelo metabolismo do ecossistema, especialmente na cabeceira do estuário, embora o aporte antropogênico de matéria orgânica e nutrientes exerça forte influência a longo prazo.

Palavras-chave: estuário, mudanças de curto prazo, produção primária, mineralização, microfítobentos.

INTRODUCTION

Estuaries have been pointed out as highly productive areas, mainly based on the observed and measured autotrophic biomass (e.g., mangrove, macrophytes, seaweeds and even phytoplankton if compared with the oceans). Although this is really true, much of the photosynthetically fixed carbon is remineralized inside the estuary, instead of exported to coastal waters.

This autoctonous mineralization and alloctonous organic matter inputs turns the balance of autotrophic and heterotrophic processes to net heterotrophy (Hopkinson, 1985; Rowe *et al.*, 1986; Smith *et al.*, 1991).

Tropical water bodies respond to short-term environmental changes. Climatic and meteorological forces, such as anomalous episodes of intense precipitation or drought, river and tidal cycles, strong wind action, and front formation act physically or take an indirect role on the system's features, and can rapidly affect the biogeochemical processes (Knoppers, 1994).

These short term changes and the sum of measurement errors are additional obstacles to long term assessments of ecosystem's metabolism by individual component measurements (Nixon & Pilson, 1984; Smith & Hollibaugh, 1997). Nevertheless, they must be accounted for, at least as a key to understand estuarine biogeochemical processes. This work intended to be a preliminary survey on carbon metabolism and short-term changes in a Brazilian northern estuary, with the aim of minimize the lack of information about most of these systems.

Study area

Piauí River is the main tributary of the Piauí-Fundo-Real Estuarine Complex, a tropical estuary (Fig. 1) situated in northeast Brazil (11°09' to 11°30'S and 37°15' to 37°30'W). The river extends over 132 km, with a drainage basin covering 4,150 km². The estuarine area is about 60 km², with extensive marginal areas covered by mangrove. The average depth is about 5 m. The system is well mixed with great salt water entrance at dry season (October-May), turning to partially mixed during the wet season (June-September) (Souza, 1997).

In its lower estuarine area the river is almost unpolluted, but the upper river (upstream from the

dam, 12 km from study area) is subject to anthropic influence, with heavy domestic and industrial sewage from the city of Estância, with high organic content. A detailed characterization of the organic industrial effluents and estimate of the influence in water chemistry and metabolism are given in Andrade *et al.* (1998).

MATERIAL AND METHODS

The experiments were carried out during the dry season, when freshwater inputs become a less important driven force. The carbon metabolism was assessed by experiments of 24 h, carried out during November 17-20, 1994 at three points along the estuary. Water samples were incubated *in situ*, using light glass bottles (0.3 L) suspended on subsurface (~ 0.3 m) and bottom (~ 1.0 m above). Measurements were made in duplicate at dawn (~ 6:00 h), noon, sunset and at dawn again, for each station. At the same time, free water was collected four times from dawn to dawn, to assess the whole system metabolism over 24 h. Wind and water temperature were also measured. Surface water samples were filtered on 0.45 µ HA Millipore filters for further chlorophyll-*a* determinations (Strickland & Parsons, 1972), and dissolved inorganic nutrients (Grasshoff *et al.*, 1983) analyses.

Alkalinity and pH measurements were performed as soon as possible on a nearby field laboratory (Campus Avançado do Crasto, Fig. 1), within about 20 m after water sampling. The pH was measured on the NBS scale with a resolution of 0.01 pH units. Alkalinity was determined by HCl potentiometric titration, using a simplified Gran's function (Carmouze, 1994). The total dissolved carbonates (ΣCO_2) were calculated by the pH-alkalinity-S method (Carmouze, 1984, 1994).

The changes of ΣCO_2 content on the incubated bottles were used to calculate the production/mineralization rates in the water column during the daytime, and mineralization rates during the night. The sum of these rates are called the "net pelagic metabolism" (NPM \cong gross pelagic primary production [GPP_p] – total pelagic mineralization [M_p]) of water column (Carmouze, 1994). These measurements present the errors inherent to incubation procedures, that are detailed described by Hall & Moll (1975).

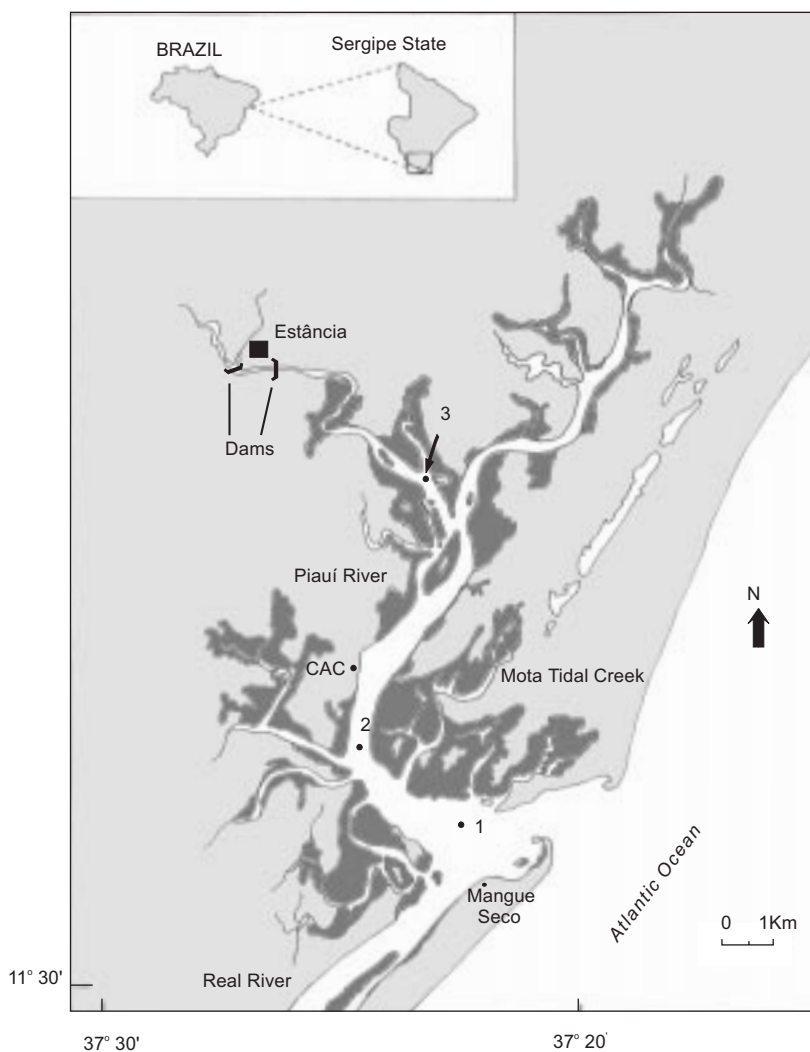


Fig. 1 — Study area, showing the sampling stations, and the location of the Campus Avançado de Crasto (CAC). Mangrove areas showed as darker areas.

In a similar way, the CO_2 changes in the free water furnish the “net ecosystem’s metabolism” (NEM; Carmouze, 1994), “whole or total system’s metabolism” (TSM; Nixon & Pilson, 1984), or “net ecosystem production” (NEP; Smith & Hollibaugh, 1997), which expresses the sum of all autotrophic and heterotrophic metabolic rates ($\text{NEM} = \text{TSM} = \text{NEP} \cong \text{gross primary production of ecosystem} [\text{GPP}_c] - \text{total ecosystem mineralization} [\text{M}_c]$) of the ecosystems compartments (pelagic, benthic, intertidal wetlands etc.). Both procedures can result in negative ($\Delta\text{CO}_2 < 0$; net autotrophy) or positive values ($\Delta\text{CO}_2 > 0$; net heterotrophy) to NPM and NEM (Carmouze, 1994; Smith & Hollibaugh,

1997). The inverted sign expressed in the results refers to organic matter production ($+C_{\text{org}}$) and mineralization ($-C_{\text{org}}$). Criticism on the second approach are well explained in Nixon & Pilson (1984), and are based on the high estuarine water advection and mixing, and gas exchange with atmosphere.

To minimize the errors of free water calculations, a correction was made for CO_2 exchange at the air/water interface, using the Fick’s Law and the whole system’s metabolisms was assessed only with the measurements of dawn and twilight, that almost match the semidiurnal tide cycle (Carmouze, 1994).

RESULTS AND DISCUSSION

Physical and chemical conditions and phytoplanktonic biomass

Salinity ranged from 31 to 35 S at station 1 and from 28 to 33 S at station 2. No thermal or saline stratification were observed at these stations (Table 1). At station 3, salinity ranged from 16 to 26 S along the time, with slight stratification (1-2 S) over depth (Table 1).

Dissolved inorganic nitrate concentrations were relatively high at all stations (Table 1). Compared with results obtained for other periods of the year (Souza, 1997), nitrate concentrations were about fifteenfold higher. Ammonia was also high at the upper reaches station. This ammonia can be released by floating microphytobenthic flocs from sediment surface observed in this site, exposing the ammonia and phosphate rich sub-superficial interstitial waters. The ammonia is rapidly

oxidized (nitrification) or absorbed and was not present in high concentrations in the downstream stations. The nitrogen abundance resulted in high DIN:DIP molar ratios (28-118), under usual coastal phosphate concentrations (Table 1).

So, these ratios express better the dissolved inorganic nitrogen abundance, rather than phosphorus limitation in the environment. Chlorophyll-*a* concentration were low, from 0.2 to 2.5 $\mu\text{g}\cdot\text{L}^{-1}$, being higher on the upper estuary station (St. 3), decreasing seaward.

The observed CO_2 supersaturation in most free water samples (Table 1), is enough to conclude that the estuary was under strong heterotrophic activity during the sampling period. The source of this heterotrophy is mainly placed in the upper estuarine areas (Tables 1 and 2), probably due to the anthropogenic organic inputs upstreams the dam that limits the estuary. The mangrove forests are another important source of organic matter (Fig. 1).

TABLE 1

Results from free water. Nutrients and chlorophyll-*a* data from November, 18 (St. 3) and 19, 1994 (St. 1 and 2), about 12:00 p.m.; other data are average and S.D. of sampled period (n = 4 samples for station 1 and 2 and n = 7 samples for station 3); s = surface waters, b = bottom waters.

Site	Mean depth (m)	$\text{NH}_3/\text{NH}_4^+$ μM	NO_2^- μM	NO_3^- μM	PO_4^{3-} μM	DIN:DIP molar	Chl- <i>a</i> $\mu\text{g}\cdot\text{L}^{-1}$	S p.s.u.	Temp. $^\circ\text{C}$	pH	sat. CO_2 %
1 s	9.0	1.14	0.13	15.0	0.20	81	0.9	33.0 \pm 2.2	27.8 \pm 1.9	8.22 \pm 0.15	130.9 \pm 68.2
1 b	-	0.54	0.11	10.2	0.12	89	0.2	33.2 \pm 2.0	27.7 \pm 2.1	8.31 \pm 0.13	97.4 \pm 42.5
2 s	8.5	1.21	0.15	14.8	0.30	54	1.4	30.8 \pm 2.5	27.8 \pm 1.9	8.19 \pm 0.16	142.8 \pm 68.2
2 b	-	1.53	0.10	11.0	0.45	28	0.9	31.0 \pm 2.7	27.8 \pm 1.9	8.20 \pm 0.17	146.6 \pm 77.5
3 s	3.0	17.6	0.13	15.2	0.28	118	2.4	22.7 \pm 3.9	28.8 \pm 1.6	7.81 \pm 0.09	464.5 \pm 157.5
3 b	-	19.0	0.09	12.0	0.53	58	2.5	23.5 \pm 3.6	28.9 \pm 1.7	7.82 \pm 0.11	455.9 \pm 154.5

TABLE 2

Physical and chemical properties of water in St. 3, surface layer, along the tidal cycles. Dawn and twilight almost at the same tidal stage.

	Tidal stage	pH	S	$^\circ\text{C}$	% CO_2
Dawn	Flood	7.86	24	28.0	400.2
Noon	Ebb	7.71	20	30.0	634.7
Twilight	Flood	7.87	25	28.0	328.4
Dawn	Flood	7.82	25	27.5	394.3
Noon	Ebb	7.69	16	31.5	690.7
Twilight	Flood	7.90	26	28.0	334.5
Dawn	Flood	7.87	24	28.0	403.5

Net pelagic metabolism (NPM)

Table 3 synthesizes the net pelagic metabolism (NPM) results in the three studied stations. St. 3 exhibited net mineralization in the surface during the day ($-1.04 \text{ mgC.m}^{-3}.\text{h}^{-1}$) in 17 November, and net production ($1.54 \text{ mgC.m}^{-3}.\text{h}^{-1}$) in 18 November. The bottom layer was more productive in the first than in the second day. This can also be explained by the releasing of benthic algal layer, due to the winds (Beaufort scale 2–3 NE) that blowed during almost all day (17 November), and intense solar radiation.

This floating microphytobenthic layer covered a significant surface area. The decay of the detrital organic matter can be responsible for the net mineralization in surface. After decay and disaggregation, the benthic producers are spread in the water column. Allied with the abundance of nitrate, this increased the organic matter production in the water column in the bottom ($3.04 \text{ mgC.m}^{-3}.\text{h}^{-1}$) and bottom and surface in the second day, resulting in an average rate 2 fold higher ($61.2 \text{ mgC.m}^{-2}.\text{d}^{-1}$) than the first day ($31.5 \text{ mgC.m}^{-2}.\text{d}^{-1}$).

The low rates of mineralization at night in stations 1 (bottom and surface) and 2 (bottom) reflect the influence of seawater, with low organic matter concentration, as supported by the salinity data (Table 1).

Mineralization rates in the night and at the surface during the day (st. 2), that resulted in an area weighed average of $-13.2 \text{ mgC.m}^{-2}.\text{d}^{-1}$, might be product of the high turbidity plume that cha-

racterize the confluence of Mota tidal creek and R. Piauí (Fig. 1; Souza, 1997).

Net ecosystem metabolism

Table 2 shows the behavior of the physical and chemical features and % saturation of CO_2 in St. 3 surface, along the tidal cycles. These results clearly formed two groups with distinct characteristics, in the ebb and flood tide, independent of the period of the day. Since the net ecosystem metabolism was measured by the CO_2 concentrations in the dawn and twilight, and the tidal regime is semidiurnal, both are coupled in about 12 hour time intervals.

This means that approximately the same water mass was monitored, since freshwater flow was very low ($\sim 1.5 \text{ m}^3.\text{s}^{-1}$), and the main influence of advection is to subject the bottom communities to different abiotic conditions, which can affect physiological responses.

Moreover, the salinity near the dam (about 7 Km upstream) remains near zero even in the drought, but still with a significant tidal range (pers. obs.), revealing that despite the horizontal motion, there is little horizontal and vertical mixing in the shallow and narrow upper estuary. Therefore, due to the presumably high water residence time at the upper estuary, the upstream dam anthropogenic inputs do not have a fast response in the estuarine conditions, though certainly exert a great influence in longer term, as observed in the saturation of CO_2 (Tables 1 and 2).

TABLE 3

Results from water incubations (net pelagic metabolism = NPM) in the day (GPP – M), night (M) and sum over 24 hours, in a volume and areal basis. Positive values = production, negative values = mineralization.

Site	Day	Night	Σ 24 hs	
	$\text{mgC.M}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-2}.\text{h}^{-1}$
1 s	0.68	> -0.01	8.55	35.60
1 b	-0.05	> -0.01	-0.65	–
2 s	-0.09	-0.20	-3.41	-13.20
2 b	0.06	-0.04	0.30	–
3 s (17/11)	-1.04	-0.06	-13.20	31.50
3 b	3.04	-0.19	34.20	–
3 s (18/11)	1.54	-0.06	17.80	61.20
3 b	2.11	-0.19	23.00	–

The rates measured by the free water approach were very low (Table 4), revealing a balance between autotrophic and heterotrophic processes. Despite the high NPM rates obtained in station 3 (Table 3), the NEM measured rates were low, with little net production in an area basis during the first day ($6.65 \text{ mgC.m}^{-2}.\text{d}^{-1}$). The second day showed a net mineralization ($-7.77 \text{ mgC.m}^{-2}.\text{d}^{-1}$), in spite of the higher average NPM, considering na areal basis (Table 3). Although the data required to obtain integrated values for 24 hs were not available (Table 4), was observed a

net mineralization in the photic period at St. 1 ($-8.01 \text{ mgC.m}^{-2}.\text{d}^{-1}$).

These results suggest an active participation of the benthic system (including intertidal wetlands) in the ecosystem metabolism, with rates that reach and even surpass the greatest NPM rates.

Estimate of benthic metabolic rates (BMR)

Despite the associated errors involved in this estimate, the Table 5 presents the values that must be reached by benthic metabolism to justify and support the obtained NEM rates ($\text{BMR} \equiv \text{NEM} - \text{NPM}$).

TABLE 4

Results from free water (net ecosystem metabolism = NEM) in the day (GPP - M), night (M) and sum over 24 hours volume and area weighed. Positive values = production, negative values = mineralization.

Site	Day	Night	Σ 24 h	
	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{d}^{-1}$	$\text{MgC.m}^{-2}.\text{d}^{-1}$
1 s	-0.08	-	-0.89^*	-8.01^*
1 b	-0.01	-	-0.02^*	-
2 s	0.05	-	0.57^*	4.85^*
2 b	-0.05	-	-0.59^*	-
3 s (17/11)	0.36	-0.17	-0.14	6.65
3 b	0.13	-0.03	4.57	-
3 s (18/11)	-0.07	-0.11	-5.46	-7.77
3 b	0.05	-0.15	0.28	-

* Results only from the photic period (11.4 h); night metabolism not measured.

TABLE 5

Estimate of the effects of benthic metabolism rates ($\text{BMR} \equiv \text{NEM} - \text{NPM}$), volume and area weighed. Positive values = production, negative values = mineralization.

Site	Day	Night	Σ 24 h	
	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{h}^{-1}$	$\text{mgC.m}^{-3}.\text{d}^{-1}$	$\text{MgC.m}^{-2}.\text{d}^{-1}$
1s	-0.76	-3.24	-	-
1f	0.04	-	-	-
2s	0.14	0.13	-	-
2f	-0.11	-	-	-
3s (17/11)	1.40	-2.27	13.06	-24.86
3f	-2.91	-	-29.63	-
3s (18/11)	-1.61	-5.51	-23.26	-68.97
3f	-2.06	-	-22.72	-

Except by St. 2 in the photic period ($0.13 \text{ mgC.m}^{-2}.\text{h}^{-1}$), all averages in areal basis or integrated over 24 h. were negative, as a result of the intense mineralization processes. Benthic community appears to be an important component of the ecosystem metabolism. Microphytobenthic floating flocs (mainly *Lyngbya cf. confervoides*, with presence of *Nitzschia* spp. and *Coscinodiscus* spp.) were observed abundantly at first day noon. Flotation occurs when microphytobenthic production is high, forming molecular oxygen bubbles over the superficial sediment layer. The disaggregation and decay of this material can explain the measured mineralization rates on water column. Moreover, the exposed subsurface sediment layer, rich in dead organic matter and presumably previously anaerobic, could become an important decomposition site and source of dissolved nutrients. The removal of this thin microphytobenthic layer allow aerobic decomposition of the organic matter, with enhanced mineralization rates. This process, as also observed in a hypersaline, phosphorus limited coastal lagoon (L. Araruama, RJ), may sharply modify the water biogeochemistry (Souza, 1993). *Lyngbya* mats spreading over water column can produce both decaying organic matter, ammonia, and nitrate high concentrations over the estuary, releasing the nitrogen once fixed (Phlips *et al.*, 1992; Rysgaard *et al.*, 1994; Paerl & Pinckney, 1996). This non-heterocystous cyanobacteria may present nitrogen fixation, even in the floating flocs, despite the O_2 saturation, since they maintain the mat structure, with the existence of low oxygen microzones (Wetzel, 1993; Paerl & Pinckney, 1996). The high biomass of *Enteromorpha* spp., another N_2 fixing algae (Owens & Stewart, 1983) observed on the upper estuarine areas, can also contribute for the enhancement of dissolved inorganic nitrogen stock.

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