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Carbon and oxygen metabolism in a densely vegetated lagoon: implications of spatial heterogeneity

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ABSTRACT

Carbon and oxygen metabolism in a densely vegetated lagoon: implications of spatial heterogeneity

Ecosystem metabolism is an integrated descriptor of lake functioning. In systems dominated by submerged vegetation, as in many coastal environments, estimates of whole-system metabolism that are calculated through free-water diel techniques can be compromised by the high spatial heterogeneity of the metabolic signal. We investigated the spatial variability in the dissolved inorganic carbon (DIC) and dissolved oxygen (DO) concentrations and in the derived ecosystem metabolism in a coastal lagoon dominated by dense meadows of canopy-forming macrophytes. We analysed the gross primary production (GPP), respiration (R) and net ecosystem production (NEP) from diel variations of both DIC and DO at different sites during the period of maximum activity of the meadows.

Our results showed high spatial variability in the DIC and DO concentrations in the vertical and horizontal dimensions as a result of the intense metabolic activity of macrophytes in the littoral surface waters. High heterogeneity in metabolism was also observed in the lagoon, with a mean coefficient of variation of up to 48 % for GPP and R rates. Most of this variability occurred within the littoral areas with macrophytes. The DIC-derived metabolic rates were systematically higher than the DO-derived rates (slope 2.074), indicating the existence of strong inorganic carbon fluxes. Our results stress the need for high sampling efforts based on multiple sampling sites and coupling of DIC and DO estimates to allow accurate quantification of ecosystem metabolism in shallow lakes and lagoons that are dominated by submerged vegetation.

Key words: Ecosystem metabolism, Dissolved Inorganic Carbon, Submerged macrophytes, *Ruppia cirrhosa*, Western Mediterranean, Albufera des Grau.

RESUMEN

Metabolismo del carbono y el oxígeno en una laguna dominada por macrófitos: implicaciones de la heterogeneidad espacial

El metabolismo acuático es un descriptor fundamental del funcionamiento ecosistémico. En sistemas dominados por vegetación sumergida, como muchos sistemas costeros, las estimas de metabolismo a escala ecosistémica mediante técnicas de cambio de concentración en aguas libres se pueden ver limitadas por una elevada variabilidad espacial en la señal metabólica. En este trabajo se estudió la variabilidad horizontal en las concentraciones de carbono inorgánico disuelto (DIC) y de oxígeno disuelto (DO), así como en las tasas metabólicas derivadas de estos dos elementos, en una laguna costera dominada por densas praderas de macrófitos sumergidos. Durante el período de máxima actividad de los macrófitos se analizaron las tasas de producción primaria bruta (GPP), respiración (R) y producción neta ecosistémica (NEP) a partir de variaciones nictemerales de DIC y DO en distintas localidades de la laguna.

Se observó una elevada variabilidad espacial en las concentraciones de DO y DIC en las dimensiones vertical y horizontal. El patrón de variación espacial resulta de la intensa actividad metabólica de los macrófitos en el agua superficial de la zona litoral de la laguna. Los descriptores metabólicos mostraron una muy elevada variabilidad, con un coeficiente de variación de 48 % para las tasas de GPP y R. Una parte considerable de esta variabilidad se observó dentro de las zonas litorales con vegetación. Las tasas metabólicas estimadas por DIC fueron sistemáticamente mayores que las estimadas por DO (pendiente 2.074), indicando la presencia de importantes flujos de carbono inorgánico. Nuestros resultados ponen de manifiesto la necesidad de estimar el metabolismo sistémico a partir del análisis simultáneo de DIC y DO en múltiples puntos de muestreo en sistemas someros dominados por macrófitos sumergidos.

Palabras clave: *Metabolismo ecosistémico, Carbono Inorgánico Disuelto, Macrófitos sumergidos, Ruppia cirrhosa, Mediterráneo Occidental, Albufera des Grau.*

INTRODUCTION

Coastal ecosystems are amongst the most biogeochemically active areas of the biosphere and have a major role in shaping land-ocean carbon interactions (Gattuso *et al.*, 1998). In the last decade, considerable attention has been paid to carbon cycling in coastal ecosystems, which are now acknowledged to play a significant role in the global carbon cycle despite their comparatively small surface area (Thomas *et al.*, 2004); however, there is still a good deal of uncertainty regarding the quantitative role of coastal ecosystems, much likely due to their inherent high heterogeneity and dynamic behaviour (Borges *et al.*, 2005). Estuaries, embayments and coastal lagoons are highly productive ecosystems that are frequently dominated by submerged vegetation, which plays fundamental functional and structural roles in all aquatic environments in which it is found (Carpenter & Lodge, 1986, Jeppesen *et al.*, 1998). Submerged vegetation is involved in nutrient cycling (Nielsen *et al.*, 2004), sedimentation rates (James *et al.*, 2004), water-column stability and circulation (Herb & Stefan, 2004), food-web interactions (van Donk & van de Bund, 2002), and population dynamics (Burks *et al.*, 2002), and it is believed to play a major role in carbon-processing, -emission and -storage processes in coastal ecosystems (Fourqurean *et al.*, 2012).

Ecosystem metabolism (i.e., the balance between the major carbon pathways, primary production and respiration) is an integrated approach to ecosystem function that allows a better understanding of the processes controlling organic-carbon balances in coastal ecosystems (Kemp & Testa, 2011). The balance between gross primary production (GPP) and community respiration (CR) is the net ecosystem production (NEP), which defines the metabolic status of the system, i.e., autotrophic or heterotrophic for positive or negative NEP, respectively. Apart from the traditional enclosure approach (in which a fraction of the ecosystem is incubated and the carbon fluxes are measured), research is increasingly relying on techniques that favour the measurement of metabolic rates at a whole-system level. This is the case for the free-water diel method (FWDM), which was proposed several decades ago (Odum, 1956) and is currently growing in popularity due to the development of more reliable sensor technologies. Briefly, it is based on diel variations in open-water dissolved-oxygen (DO) concentration, accounting for the differences between the night-time (when only CR occurs) and daytime (when there is a balance between GPP and CR) rates of change after correcting for atmospheric exchange. The FWDM can also be applied directly to carbon by monitoring the dissolved-inorganic-carbon (DIC) concentration throughout the diel cycle (Staehr *et al.*, 2012a).

In coastal lagoons, submerged vegetation can attain high biomass densities and exhibit considerable micro-scale heterogeneity (de Biasi *et al.*, 2003), which can result in substantial spatial differences in the concentration of chemical water components (e.g., Lee & McNaughton, 2004). This heterogeneity may imply substantial horizontal variability in the diel DO signal and may thus have profound implications for estimates of ecosystem metabolism based on open-water measurements. One fundamental assumption of the FWDM is that the analysed system is homogenous or well mixed; the signal at a single station located in the central area of the system is usually assumed to be representative of whole-ecosystem processes (Staehr *et al.*, 2010). Few studies have analysed spatial variability in the DO signal in lakes in either the vertical (Coloso *et al.*, 2008; Staehr *et al.*, 2012b) or horizontal (Lauster *et al.*, 2006; van de Bogert *et al.*, 2007)

dimensions, but to the best of our knowledge, there are no studies on the spatial variability in DO diel variations in densely vegetated systems. Another feature of coastal ecosystems is their shallow depth, which results in intense sediment-water interactions. Thus, potential anaerobic metabolic processes could invalidate the use of the traditional Redfield oxygen-to-carbon stoichiometry when estimating aquatic metabolism from DO series, which would make the combined use of DIC and DO highly desirable (Torgersen & Branco, 2007). While numerous works deal with the metabolism of benthic macroalgae or phanerogams (e.g., Barrón *et al*., 2004) and the analysis of sediment fluxes in vegetated and unvegetated sediments (e.g., Viaroli *et al*., 1996), most rely on incubation techniques, and few papers report diel free-water variations in both DIC and DO in dense macrophyte meadows in either coastal ecosystems or lakes (see Ziegler & Benner (1998) for an exception).

Here, we investigate the spatio-temporal variability in the DIC and DO concentrations and in the derived estimates of ecosystem metabolism in a highly productive coastal lagoon dominated by dense meadows of submerged vegetation. Our specific questions were as follows: 1) are the DIC and DO concentrations spatially homogeneous in the lagoon throughout summer diel cycles; 2) what is the degree of spatial heterogeneity in estimates of ecosystem metabolism based on the FWDM; and 3) how well do the carbon- and oxygen-based estimates of ecosystem metabolism agree?

METHODS

Study site

The studied system (Albufera des Grau, Balearic Islands, Western Mediterranean, Fig. 1) is an enclosed lagoon containing dense and extensive macrophyte meadows that are almost exclusively dominated by *Ruppia cirrhosa*, which attains biomass as dense as 1760 gDW/m^2 (Obrador *et al*., 2007). The meadows cover more than 50 % of the lagoon surface and are distributed along the entire depth gradient, but the highest densities are located in littoral areas shallower than 1 m (see Obrador & Pretus (2010) for details). The lagoon is enclosed; water exchange with the sea

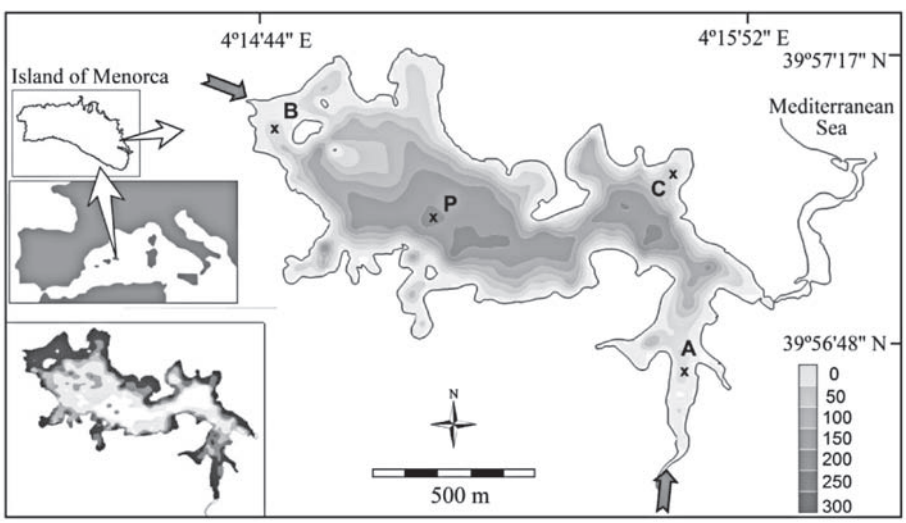

Figure 1. Location and bathymetric map (50-cm isobaths) of the Albufera des Grau coastal lagoon in the island of Menorca (Western Mediterranean). The sampling sites (crosses) and the freshwater inputs (arrows) are shown. The map in the inset shows the distribution of the macrophyte meadows during the studied period with the percent cover in quartiles (data from Obrador & Pretus, 2010). *Localización y mapa batimétrico de la laguna costera de s'Albufera des Grau (Menorca, Islas Baleares). Se indican los puntos de muestreo (cruces) y las entradas de agua dulce (flechas). El mapa inferior corresponde a la distribución espacial de las praderas de macrófitos durante el período de estudio (datos de Obrador & Pretus, 2010).*

is irregular and does not represent an important mechanism of water renewal in the system (water residence time of 8 months; Obrador *et al*., 2008). Previous studies have shown very fast carbon turnover in this system (carbon residence time of 4-19 days; Obrador & Pretus, 2012). See Table 1 for a summary of the basic features of the lagoon and the range in the limnological descriptors during the studied period.

Table 1. Morphometric descriptors and limnological features of the Albufera des Grau coastal lagoon during the studied period. *Características morfométricas y limnológicas de la Albufera des Grau durante el periodo de estudio.*

Morphometric descriptors	
Surface area (Ha)	78
Surface of littoral areas (< 1 m depth)	28
Water volume (hm^3)	1.0
Mean depth (m)	1.37
Maximum depth (m)	3.0
Limnological features	Mean ± s.d.
Temperature (°C)	24.4 ± 2.3
Salinity (g L^{-1})	16.2 ± 1.5
Alkalinity (meq L^{-1})	2.755 ± 0.306
DIN (μM)	5.7 ± 2.8
TP (μM)	5.2 ± 2.4
DOC (mg L^{-1})	14.5 ± 1.3
Calcite saturation index	1.25 ± 0.13
Chlorophyll-*a* (μg L^{-1})	8.0 ± 3.1

Field and laboratory work

Weekly samplings were carried out during the summer of 2002 (from 3 July to 9 September) at three littoral and shallow sites located beneath the dense macrophyte meadows (sites A, B, C; Fig. 1) and one pelagic site located in the macrophyte-free area of the lagoon (site P; Fig. 1). The depth of the sampling sites ranged from 0.5-0.7 m at the littoral sites to 2-2.5 m at the open-water pelagic site. Each survey consisted of three water measurements over a complete diurnal cycle (at dusk, dawn and dusk). At each sampling, the four sites were sampled within 45 min, and water samples were taken every 50 cm from surface to bottom. All samples were taken in duplicate. After some diel cycles were discarded due to intense rainfall or equipment malfunction, a total of 36 diel cycles were analysed.

Water salinity (practical salinity scale), pH (NBS scale), temperature (°C) and oxygen concentration (mM) were determined *in situ* with field sensors (WTW Multiline P3 and WTW Cond315i). The oxygen sonde was calibrated in vapour-saturated air before each deployment. The mean error of the oxygen and pH measurements was below 0.003 mM (0.9 %) and 0.01 pH units (0.1 %), respectively (determined from replicated measurements of reference samples). Water samples for chemical analyses were filtered and analysed in the laboratory as soon as possible. Total alkalinity (TA) was determined by potentiometric titration with H_2SO_4 (Stumm & Morgan, 1996), with a reproducibility of 0.03 meq/L (1.1 %). The concentrations of the DIC species were calculated from the pH and alkalinity values. The dissociation constants of Millero *et al*. (2006) at the measured salinity and temperature were used with CO2SYS software (Lewis & Wallace, 1998). The total DIC concentration, i.e., $CO_2 + HCO_3^- + CO_3^{2-}$, was measured with a precision of 0.087 mM (4 %). This precision includes the analytical reproducibility and the variability of the duplicate water samples and thus partially includes the micro-scale chemical heterogeneity, which is expected to be high in macrophyte-dominated systems (Barker *et al*., 2010). In this study, the TA of bottom-water samples was not determined, as previous observations during the thermally stratified hours of days in the same period showed that vertical variations in TA are below 4 % (n = 10, authors' unpublished data). Thus, the concentration of DIC for bottom waters was calculated from the TA of the corresponding surface-water sample, assuming that bottom TA equalled surface TA. We estimated the error in DIC associated with this assumption to be 0.064 mM and 0.004 mM for the littoral and pelagic sites, respectively, or less than 1 % and 3 %, respectively, of the mean concentrations. These estimates were performed at the same sites by comparing the DIC concentrations calculated from the measured bottom and surface alkalinities to those calculated assuming surface alkalinity at bottom in different summer samplings.

Numerical and statistical methods

We evaluated differences in the concentration of DIC and DO between sampling sites through the Mann-Whitney U test. The difference between surface and bottom waters was evaluated with the paired Wilcoxon test. All statistical analyses were evaluated to a significance level of 0.01 and performed in STATISTICA v.9 software.

The change in the concentration of DIC or DO during the night (from dusk to dawn) was attributed to night-time community respiration and exchange with the atmosphere. The change in DIC or DO during the day (from dawn to dusk) was attributed to gross primary production, daytime respiration and exchange with the atmosphere. Thus, the night community respiration (R_n) and the daytime net ecosystem production (NEP_d) were estimated from the following equations:

$$R_n = \Delta C_n - F \quad (1)$$

$$NEP_d = \Delta C_d - F \quad (2)$$

where ΔC_n and ΔC_d are the changes in the concentration of DIC or DO during the night and day, respectively (mmol L^{-1} h^{-1}), and F is the flux of CO_2 or O_2 across the air-water interface (mmol L^{-1} h^{-1}).

Daytime community respiration, R_d, was assumed to equal night-time R_n, although it is likely to be higher (Cole *et al.*, 2000). This widely used assumption can yield underestimates of gross primary production and R but would not have an effect on estimates of *NEP* (Cole *et al.*, 2000). Gross primary production (*GPP*) was then calculated as the sum of R_d and NEP_d. Finally, the estimates of *NEP* for the 24-hour period were calculated from the following equation:

$$NEP = GPP - R \quad (3)$$

where R is the daily community respiration, which is defined as the sum of R_n and R_d. For the bottom waters, F was set to zero.

Ideally, free-water estimates of metabolism should be based on high-frequency measurements to prevent the errors associated with inflections in the gas curves near dawn and dusk (Hanson *et al.*, 2003). In the absence of the equipment needed to perform continuous gas measurements and given the high spatial variability previously observed in the lagoon (Obrador, 2009), our sampling strategy was designed to favour replication and spatial coverage over sampling frequency. The main source of error in our sampling design may be that the time of sampling was not exactly coincident with dusk and dawn at all sites. To assess this potential source of error, on 21 August, we performed a complete diel cycle at site B, with water measurements every 2 hours. With the smoothed rate of change observed for DO and DIC, we estimated the error in sampling within 45 minutes around dawn and dusk. The errors of the metabolic parameters estimated in this way were 39 mmol m^{-2} d^{-1} for DO and 116 mmol m^{-2} d^{-1} for DIC. We discuss the effect of these errors later in this paper.

Air-water gas fluxes

The flux of CO_2 or O_2 across the air-water interface was calculated from the following equation:

$$F = \varepsilon k (C_{\text{atm}} - C_w) \quad (4)$$

where F is the flux (mmol m^{-2} h^{-1}); ε is the chemical enhancement factor for CO_2 (dimensionless); k is the gas transfer velocity (m h^{-1}); and C_w and C_{atm} are the concentrations of gas (CO_2 or O_2) in surface water and in atmospheric equilibrium, respectively (mmol m^{-3}). The concentration of CO_2 in atmospheric equilibrium was calculated from Henry's law ($CO_{2_{\text{atm}}} = \alpha \cdot pCO_2$), where α is the solubility constant for CO_2 at given salinity and temperature (mol m^{-3} atm^{-1}), obtained from Weiss (1974), and pCO_2 was assumed to be constant at 379 μatm (IPCC, 2007). The concentration of DO in atmospheric equilibrium was calculated from salinity and temperature, following Weiss (1970). We calculated k following the parameterisation of Borges *et al.* (2004) for microtidal estuaries with low influence of water current on k. A specific k-wind slope for the lagoon was calculated from the lagoon surface area (0.78 km^2), following the equations in Borges *et al.* (2004). The values of

k were corrected for the observed *in situ* salinity and temperature with the Schmidt numbers (ratio between the kinematic viscosity and the diffusion coefficient) for each gas (CO_2 and O_2). The Schmidt numbers for freshwater and seawater were calculated from water temperature, following the formulations of Wanninkhof (1992). A linear relationship with salinity was assumed to calculate the Schmidt numbers at the observed water salinity (Borges *et al.*, 2004). Daily values of wind speed (m s^{-1}) were obtained from the closest meteorological station (7 km away; Spanish Meteorological Institute). The chemical-enhancement factor for CO_2 was calculated for the *in situ* values of salinity, temperature and pH after the theoretical model of Hoover and Berkshire (1969), as described by Wanninkhof & Knox (1996).

RESULTS

Variability in DIC and DO concentrations

During the studied period, the biomass of macrophytes was approximately 600 gDW/m^2 but showed high spatial variability at each site (Table 2; mean coefficient of variation in biomass (CV) = 35 %).

The concentration of DIC and DO ranged from 0.57-2.89 mM and 0.02-0.61 mM, respec-

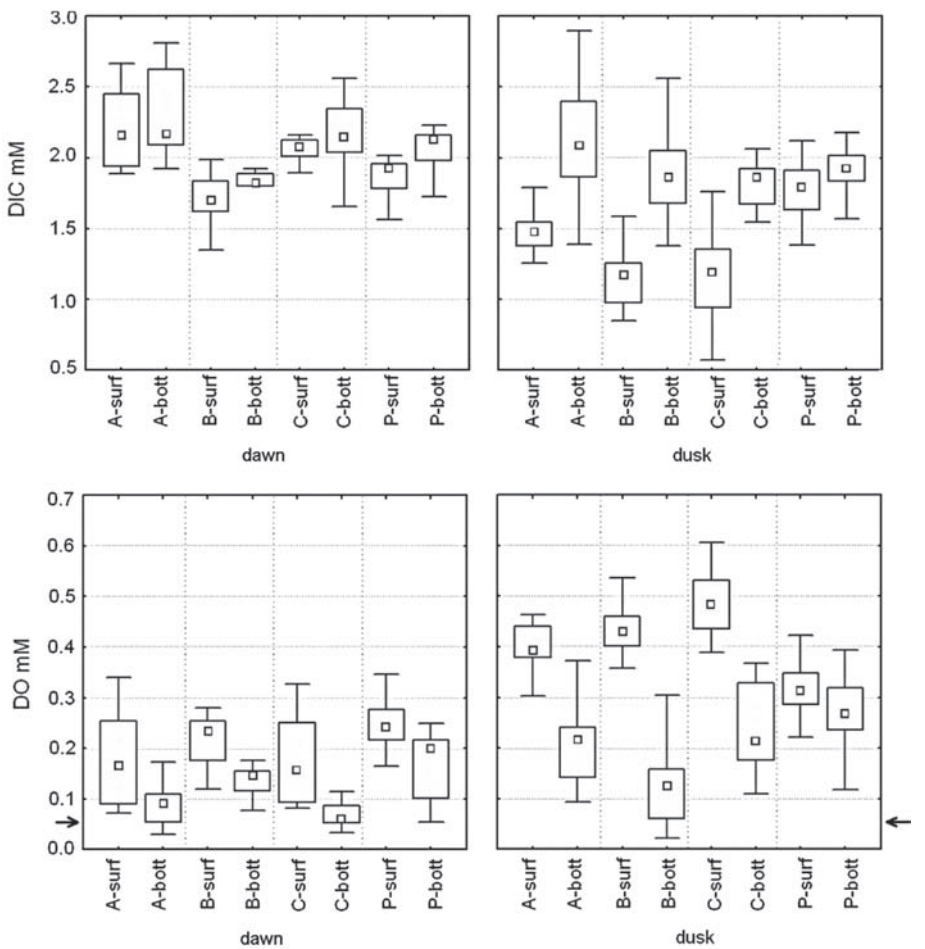

Figure 2. Variability in DIC and DO concentrations. The median (point), range (whiskers), and 25 % and 75 % percentiles (box) are shown for each site and depth and for the dawn and dusk samplings. The arrows indicate the 2 mg L^{-1} definition of hypoxia. *Variabilidad en la concentración de DO y DIC para cada localidad, profundidad y momento del día (mediana, rango y 25-75 % percentiles). Las flechas indican el umbral hipóxico de 2 mg* L^{-1}.

Table 2. Vertical gradients (bottom-surface) of temperature, DIC and DO at each sampling site (mean ± s.d.). Only the significant values ($p < 0.01$, Wilcoxon matched-pairs test for differences between the surface and the bottom) are shown. The depth and the mean biomass of *R. cirrhosa* are also shown for each site (data from Obrador & Pretus, 2010). *Gradientes verticales de concentración de DO, DIC y temperatura para cada punto de muestreo (media ± s.d.). Sólo se muestran los valores significativos (*p < *0.01, test de Wilcoxon para las diferencias entre superficie y fondo). Para cada punto se muestra también la profundidad y biomasa media de* R. cirrhosa *(datos de Obrador & Pretus, 2010).*

		Biomass (gDW m^{-2})	Temperature gradient (°C)		DIC gradient (mmol L^{-1} m^{-1})		DO gradient (mmol L^{-1} m^{-1})	
Site	Depth (cm)		dawn	dusk	dawn	dusk	dawn	dusk
A	50	576 ± 165	n.s.	−4.11 ± 2.49	n.s.	1.20 ± 0.68	n.s.	−0.38 ± 0.20*
B	50	606 ± 209	n.s.	−5.32 ± 2.46	n.s.	1.21 ± 0.48	n.s.	−0.52 ± 0.25*
C	50	621 ± 258	n.s.	n.s.	n.s.	1.19 ± 0.45	n.s.	−0.48 ± 0.23*
P	250	n.d.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

tively, and high spatial and temporal variability was observed (Fig. 2). Significant differences in DIC and DO were observed with respect to sampling time (dusk or dawn), type of site (littoral or pelagic) and depth (surface or bottom).

Vertical gradients in DIC and DO (mmol L^{-1} m^{-1}) were observed at the three littoral sites, but they were significant only at dusk (Wilcoxon test $p < 0.001$; Fig. 2; Table 2). These vertical gradients were positive for DIC (i.e., higher concentration at the bottom than at the surface) and negative for DO (lower concentrations at the bottom than at the surface). No significant differences between surface- and bottom-water concentrations were observed at the pelagic site. A significant vertical gradient in temperature was observed at littoral sites A and B at dusk (Fig. 3, Table 2), while the water column was always thermally homogenous at the pelagic site and at all littoral sites at dawn. During the studied period, no significant vertical gradients in salinity were observed.

Horizontal differences in DIC and DO concentrations were observed, but only at dusk and in surface waters (Table 3a). Surface DIC was significantly lower at the littoral sites than at the pelagic site (Fig. 2), and the reverse pattern was observed for DO (higher surface concentrations

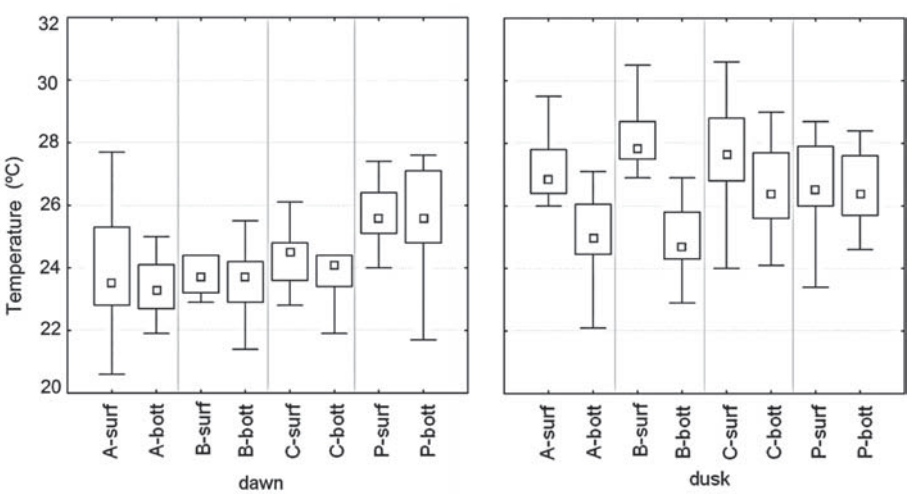

Figure 3. Variability in temperature during the studied period. Symbols are as in Figure 2. *Variabilidad térmica durante el periodo estudiado (símbolos como en la Figura 2).*

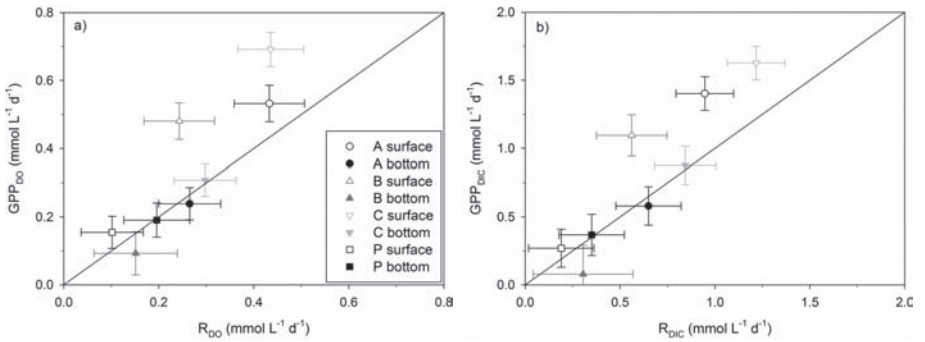

Figure 4. Estimates of respiration (R) against gross primary production (GPP) based on DO (a) and DIC (b). *Tasas de respiración (R) y producción primaria bruta (GPP) estimadas a partir de DO (a) y DIC (b).*

at the littoral sites than at the pelagic site). Bottom concentrations never showed significant differences between sites at $p < 0.01$ for DIC or DO.

Metabolic estimates

The daily air-water flux of CO_2 was always positive (invasion) and ranged from 0.017-0.580 mmol L^{-1} d^{-1}. For DO, positive and negative fluxes were observed, but oxygen evasion was the most common (89 % of the surveys). The daily flux of oxygen ranged from −0.088 to 0.077 mmol L^{-1} d^{-1}. These air-water fluxes were below 10 % of the diel change in DO concentration, and below 6 % of the diel change in DIC concentration, on average.

All diel cicles showed the expected variation in DIC, with higher concentrations at dawn than at dusk, and the reverse trend was observed for DO (lower values at dawn than at dusk; Fig. 2). The highest metabolic rates were measured in the surface waters of the three littoral sites (Fig. 4), which always showed positive NEP rates (Fig. 5). Lower GPP and R rates were measured in the bottom waters of the littoral sites and in both the surface and bottom waters of the pelagic site (Fig. 4). In these cases, GPP and R were nearly balanced, yielding NEP rates that were close to zero or slightly negative. The same spatial pattern observed for the DO-derived rates was also observed in DIC-derived rates.

A summary of the differences in metabolism between the littoral and pelagic sites is shown in Table 3. Higher metabolic rates (GPP, R and NEP) were measured in the surface littoral waters than in the surface pelagic waters (Fig. 4 and Fig. 5). No

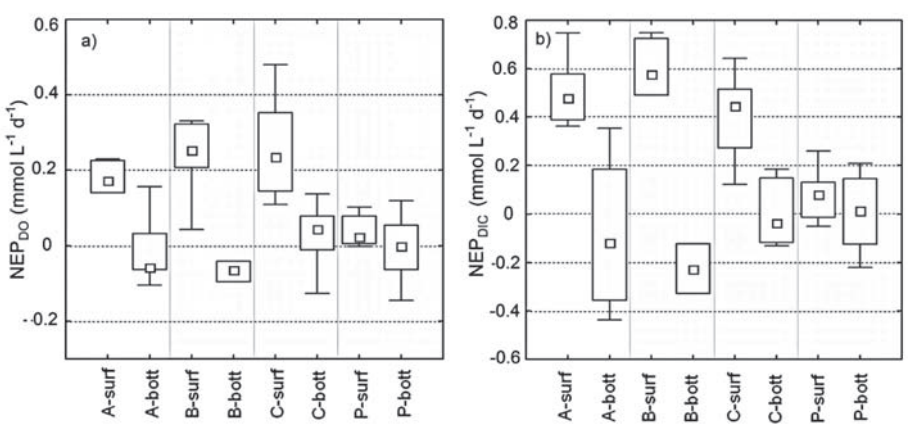

Figure 5. Net Ecosystem Production (NEP) rates for each sampling site and depth based on DO (a) and DIC (b). Note the different axis scale in each case. Symbols are as in Figure 2. *Tasas de producción neta ecosistémica (NEP) para cada localidad y profundidad estimadas a partir de DO (a) y DIC (b) (símbolos como en la Figura 2).*

significant differences in metabolic rates between littoral and pelagic sites were observed in bottom waters for DO-derived or DIC-derived rates.

The DIC-derived GPP and R rates were between two and three times higher than the DO-derived rates (Fig. 4). A strong linear relationship was observed between the diel rates of change of DO and DIC (corrected for atmospheric exchange) (Fig. 6). A least-squares fitted equation explained 77 % of the variance in the DIC rates, with a significant slope of -2.074 ± 0.096 ($p < 0.001$). All the diel rates fitted the regression line independent of the site (littoral/pelagic) and the depth (surface/bottom).

DISCUSSION

Spatial variability in DIC and DO concentrations

High variability was observed in the DIC and DO concentrations. The main driver of spatiotemporal variability was the metabolic activity of macrophytes in the littoral waters, as evidenced by our data. Firstly, vertical differences in concentration were observed only at the littoral sites and only at dusk. Such end-of-day vertical gradients are related to the vertical distribution of the dominant biological activity in the meadows. This pattern, with surface and bottom waters dominated by photosynthetic and respiratory processes, respectively, is expected in systems dominated by canopy-forming macrophytes like *R. cirrhosa*, which reaches the surface, resulting in intense self-shading (Carpenter & Lodge, 1986; Duarte *et al*., 2002). A different pattern would be expected in meadows of non-canopy-forming macrophytes or bottom macroalgae (D'Avanzo & Kremer, 1994). Furthermore, the physical structure of the water column enhances the vertical pattern created by biological processes. The vertical heterogeneity in DIC and DO at the littoral sites at dusk was supported by a vertical gradient in temperature (observed in two littoral sites, Table 2, Fig. 3). No such thermal gradient was observed at dawn. This gradient, with whole-water-column respiration at night, was responsible for the vertical homogeneity in DIC and DO concentration at dawn in the littoral areas of the lagoon. At the pelagic site, the water column was always vertically homogenous in terms of DIC and DO because there were no macrophytes to structure the metabolism of the water column and no vertical thermal stratification to promote vertical concentration gradients.

Secondly, horizontal differences in DIC and DO concentrations were limited to surface waters and occurred only at dusk (Fig. 2 and Table 3a), following the period of light-driven carbon uptake and oxygen release by photosynthetic activity in the macrophyte canopy. Such differences suggest a physical compartmentalisation of the lagoon into littoral and pelagic areas as a result of reduced horizontal mixing within the high-density macrophyte beds (Herb & Stefan, 2004);

Table 3. Summary of the Mann-Whitney U tests for the differences between the littoral (L) and pelagic (P) sites. The tests for the differences in a) temperature (°C) and concentrations (mM) and b) the metabolic rates derived from DO and DIC are shown. Significance levels are as in Table 2. *Resumen de las diferencias (test U de Mann-Whitney) entre localidades del litoral (L) y de la zona pelágica (P). Diferencias en temperatura (°C) y concentraciones (mM) (a), y en las tasas metabólicas basadas en DO y en DIC (b).*

a)	Temperature		DIC		DO	
	dawn	dusk	dawn	dusk	dawn	dusk
Surface water	n.s.	n.s.	n.s.	L < P	n.s.	L > P
Bottom water	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

b)	DO-derived rates			DIC-derived rates		
	GPP	R	NEP	GPP	R	NEP
Surface water	L > P	L > P	L > P	L > P	L > P	L > P
Bottom water	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

however, we did not observe significant horizontal gradients in temperature at dusk or dawn (Table 3a, Fig. 3). Thus, the differences in surface-water concentrations between sites (higher DO and lower DIC at the littoral sites compared to the pelagic site) are attributed to primary production by the meadows in surface littoral waters.

The lack of horizontal differences in bottom-water concentrations between the shallow littoral and deeper pelagic sites suggests that common processes take place at the bottom of the lagoon independent of depth and the presence of macrophytes. Interestingly, this homogeneity was observed for both DIC and DO (Table 3a), indicating that the pattern was not caused by inaccuracies in DIC or DO estimates. Moreover, we also found horizontal homogeneity in metabolic rates in bottom waters (Table 3b). These results are surprising given the expected biological activity of the macrophytes in bottom waters and especially because of the importance of submerged vegetation to sediment biogeochemistry (Viaroli *et al*., 1996; Azzoni *et al*., 2001). Although the littoral sites had denser macrophyte cover, the deeper pelagic site also had short sparse macrophyte shoots that only rarely reached the top of water column (Obrador & Pretus, 2010). The macrophytes in pelagic and littoral areas maintain oxygenated sediments throughout the lagoon. Furthermore, bottom irradiance levels were generally below the light requirements for *R. cirrhosa* (Obrador & Pretus, 2008), and this would favour respiratory oxygen consumption in pelagic and littoral bottom waters. Indeed, most of the bottom waters were heterotrophic (Fig. 5), showing no differences in NEP between littoral and pelagic sites (Table 3b), as will be discussed later.

In summary, the lagoon shifted from homogeneous conditions at dawn to vertical and horizontal heterogeneity in the daytime, with differences between surface and bottom waters in the littoral areas and between pelagic and littoral sites in the surface water. This pattern of vertical

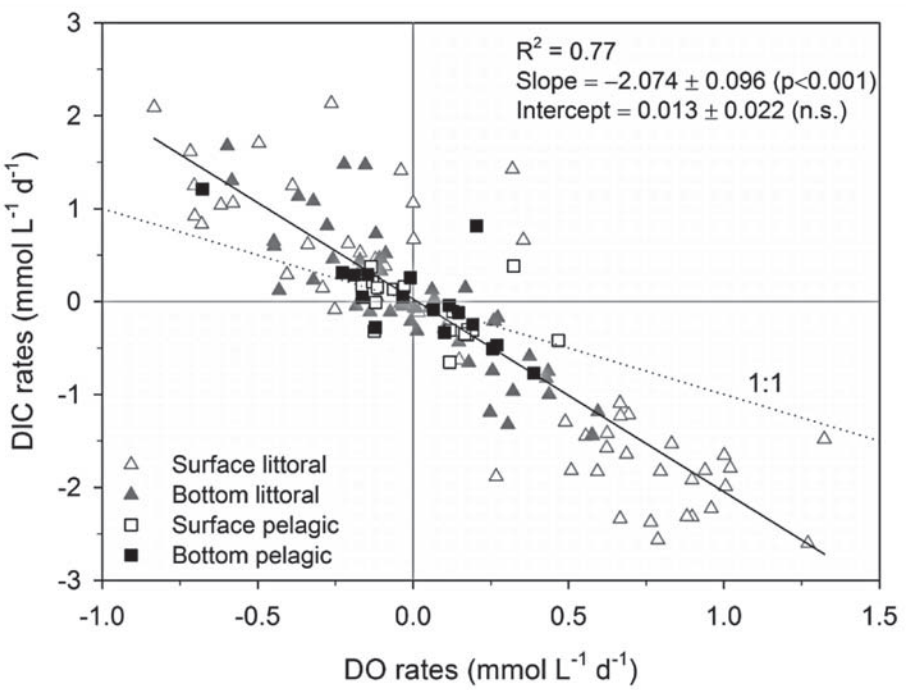

Figure 6. Relationship between the diel rate of change in DIC and the rate of change in DO. All rates are corrected for atmospheric exchange and expressed in mmol L^{-1} d^{-1}. The least-squares fitted regression line (black line) and the 1:1 line (dotted) are also shown. *Relación entre las tasas de cambio nictemeral de DIC y de DO (ambas corregidas por el intercambio atmosférico). Las líneas corresponden a la regresión lineal de la relación (línea continua) y a la relación 1:1 (línea discontinua).*

and horizontal variability is in accordance with the physicochemical variability expected within dense macrophyte beds (Frodge *et al.*, 1990; Jeppesen *et al.* 1998; Barker *et al.*, 2010).

Spatial variations in metabolism

Metabolic estimates based on the FWDM are affected by the equations used to estimate the air-water exchange. In this study, the air-water exchange accounted for a minor fraction of the diel change in concentration for both DIC and DO. We tested the effect of alternative K-wind parameterisations (Crusius & Wanninkhof, 2003; Liss & Merlivat, 1986) on our metabolic estimates, and the resulting GPP and R rates were within 9 % of the rates presented here for both DIC and DO (data not shown). Apart from this source of error, the discrete approach to the FWDM used here was subject to inaccuracy due to the assumption that dusk and dawn coincide with the inflexion of the diel gas curves, which is not always necessarily true (Hanson *et al.*, 2003). For this reason, the FWDM should ideally be based on continuous measurements, and sampling frequencies of 5-30 minutes are common (Staehr *et al.*, 2010). Nonetheless, approaches based on small numbers of data points are common in the literature (Bachmann *et al.*, 2000; Carmouze *et al.*, 1991; Kemp & Boynton, 1980; Swaney *et al.*, 1999). McKellar (1977) compared the abbreviated dusk-dawn measurements to complete diel cycles in a Florida estuary and found no significant differences, except under rainy or cloudy conditions. Cronk & Mitsch (1994) also found the same results with the dusk-dawn approach as with a complete diel cycle. Our aim here was to assess the spatial variability in the estimates and to explore the discrepancy between the DO and DIC derived rates. In this sense, we favoured precision over accuracy in our sampling design. The precision of our estimates was affected by errors associated with the analytical measurements, the lag of 45 minutes between samplings at the different sites, and, in the case of DIC, the assumption of surface alkalinity in bottom-water samples. The overall combined uncertainty in our estimates of R and GPP was 11 % for DIC-derived rates and 7 % for DO-derived rates. We believe that this error is acceptable and supports the validity of the results discussed here. Overall, the GPP and R rates found in the Albufera des Grau are similar to those reported in other macrophyte-dominated lagoons (Ziegler & Benner, 1998) and are within the range for coastal ecosystems (Kemp & Testa, 2011).

In accordance with expectations, surface littoral waters with high macrophyte densities had the highest GPP and R rates (Fig. 4) and were net autotrophic throughout the summer, when macrophyte meadows grow at maximum rates (Obrador & Pretus, 2010). In comparison, lower GPP and R rates and negative NEP were found in bottom littoral waters (Fig. 4) dominated by the canopy-forming species *R. cirrhosa*, which is mostly distributed at the top of the water column and which is thus intensely self-shaded (Duarte *et al.*, 2002).

The lower GPP and R rates at the pelagic site are expected from the occasional and short macrophyte stands in that area, as discussed previously. The rates of pelagic metabolism calculated from the generic relationships given in del Giorgio & Peters (1994) at the observed chlorophyll-*a* and DOC concentrations (Table 1) were 0.004-0.008 mmol L^{-1} d^{-1} for GPP and 0.009-0.013 mmol L^{-1} d^{-1} for R. According to these values, the planktonic metabolism was one order of magnitude lower than the measured water-column rates at the pelagic site (Fig. 4). Planktonic metabolism thus likely does not contribute substantially to the diel signals in DO and DIC waters in the centre of the lagoon. At the pelagic site, diel changes in DO and DIC most likely resulted from local benthic metabolism and exchange of gases with littoral sites.

Overall high variability in metabolism was observed in the lagoon. The coefficient of variation (CV) at all sampling sites was 48 % for DO-derived rates and above 50 % for DIC-derived rates (Fig. 7). The variability was even higher for NEP. Such high variability is in accordance with the variability in GPP and R rates observed between different habitats (pelagic, macrophytes and bare sediment) in north-temperate lakes

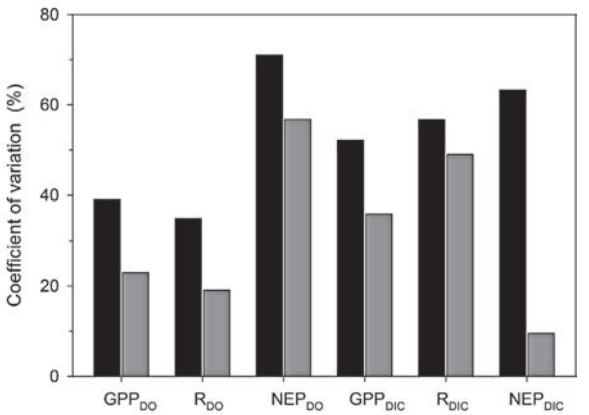

Figure 7. Spatial variability in metabolism between all sampling stations (dark bars) and between the three littoral stations (light bars). The coefficient of variation is shown for the DO and DIC-derived metabolic rates (mmol L^{-1} d^{-1}). *Variabilidad espacial en metabolismo entre todas las estaciones (barras negras) y entre las estaciones litorales (barras grises). Se muestra el coeficiente de variación para las tasas basadas en DO y en DIC (mmol L^{-1} d^{-1}).*

(Lauster *et al*., 2006). Our results also agree with previous findings of spatial variability in a lake with low presence of submerged vegetation (Van de Bogert *et al*., 2007) and in a high-altitude lake without macrophytes (Sadro *et al*., 2011). Interestingly, however, most of the variability observed in the Albufera des Grau occurred within the littoral zone, as observed by the high CV at the littoral sites (higher than 20 % for the DO-derived GPP and R rates and approximately 40 % for the DIC-derived rates; see light bars in Fig. 7). This high variability in the littoral metabolism can be ascribed to chemical microheterogeneity within high-density macrophyte meadows (Lee & McNaughton, 2004), which are frequently characterised by high spatial heterogeneity and patchiness.

To the best of our knowledge, no previous studies have documented spatial heterogeneity in open-water estimates of metabolism in macrophyte meadows. Consequently, high spatial heterogeneity in metabolic rates should be expected in densely vegetated systems. In such systems, the accurate determination of littoral metabolic rates requires multiple sampling stations; this accuracy is especially important to partition whole-system metabolism into benthic and pelagic sources (e.g., Lauster *et al*., 2006, van de Bogert *et al*., 2007 Sadro *et al*., 2011, Kemp & Testa 2012). Although the Albufera des Grau is characterised by very high macrophyte biomass (Obrador *et al*., 2010), the range of *R. cirrhosa* biomass during the studied period was within the range for other coastal systems, indicating that our conclusions can be extrapolated to other shallow systems dominated by submerged vegetation.

Carbon and oxygen metabolism

The estimated metabolic rates derived from DO changes were much smaller than those derived from DIC changes. The metabolic quotient ($\Delta DIC / \Delta DO$) averaged 1.99, which falls outside the range described by Williams & del Giorgio (2005) for different types of organic matter (respiratory quotient (RQ) between 0.67 and 1.24). Deviations from this range may be expected if the organic matter being processed has extremely different stoichiometric C:N:P ratios compared to typical aquatic (106:16:1) or terrestrial (790:7.6:1) organic matter (Torgersen & Branco, 2007). In the Albufera des Grau, however, the respiratory quotients of macrophyte biomass (236C:8N:1P, authors' unpublished data) and sedimentary organic matter (1000C:102N:1P, López, 2004) were 0.94 and 0.83, respectively. The higher metabolic quotient observed here must thus be related to factors other than organic-matter composition. Ziegler & Benner (1998) found similar results in a seagrass-dominated lagoon (much higher GPP and R values with DIC than with DO). The authors attributed that discrepancy largely to errors in the estimates of atmospheric exchange and to a differential effect of water advection on DIC and DO.

In the Albufera des Grau, the relationship between the rates of change of DIC and DO (corrected for atmospheric exchange) showed a strong relationship, with a slope approaching 2 (Fig. 6). Interestingly, the same relationship was observed for both littoral and pelagic sites and for both surface and bottom waters. When the relationship was analysed in each of these subsets independently, the slopes were not

significantly different from 2 (data not shown). Thus, common biogeochemical processes drive the robust 2:1 relationship between DIC and DO diel changes observed in this study.

The only process yielding a net 2:1 relationship is related to calcite precipitation and redissolution along the diel cycle. The precipitation of 1 mol of $CaCO_3$ yields a net decrease of 1 mol of DIC and no change in DO ($Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O$). The coexistence of photosynthesis ($CO_2 + H_2O \rightarrow$ "CH_2O" $+ O_2$) and calcite precipitation results in the net reaction $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 +$ "CH_2O" $+ O_2$, yielding a 2:1 negative relationship between changes in DIC and DO (−2 mol of DIC; +1 mol of DO) such as that observed here. Thus, calcite supersaturation would promote calcite precipitation during the strong increase in pH that results from the intense photosynthetic activity during the day. The maintenance of the 2:1 relationship during the night (Fig. 6, left) would be explained by the redissolution of carbonates during the nocturnal decline in pH. Unfortunately, we do not have the detailed calcium-concentration data that would allow us to calculate the mass balances of calcium along the diel surveys. The few available concentration data (one measure for each survey) show strong calcite supersaturation at all the sites (n = 37; Table 1). In the summer of 2002, the invasive reef-forming polychaete *Ficopomatus aenigmaticus* was observed at high density in the lagoon. This organism builds large carbonate reefs in brackish waters and is especially productive in the Albufera des Grau (annual production of up to 21.3 kg $CaCO_3$ m^{-2} y^{-1} in the 1990s; Fornós *et al*., 1997). Although independent estimates of tube growth rates in the period 2002-2003 suggest lower annual carbonate-production rates during the studied period (~4.5 kg $CaCO_3$ m^{-2} y^{-1}; authors' unpublished data), the presence of such a significant carbonate-forming organism would support our hypothesis of high fluxes of calcium carbonate in summer.

It is possible that either anaerobic processes in the sediments or chemical oxidations of released reduced compounds contributed to the DIC/DO relationship that was observed in this study. Sulphate reduction can account for up to 90 % of organic-matter remineralisation in coastal systems (Jørgensen, 1982), and the literature is rich in studies dealing with the biogeochemistry of nitrogen, sulphur, phosphorus and iron in coastal vegetated sediments (Bartoli *et al*., 2008; Azzoni *et al*., 2001). Nonetheless, despite the huge biomass accumulation in littoral areas, we did not observe frequent anoxic conditions in bottom waters, even at dawn (only 15 % of the surveys showed bottom hypoxia, DO < 2 mg L^{-1}; Rabalais & Turner, 2001). Potentially, the transport of oxygen from leaves to roots and its release into the rhizosphere increases oxygen availability, making anaerobic processes unlikely in the water column; such a process has been described for several macrophytes and specifically for *Ruppia* (Thursby, 1984; Azzoni *et al*., 2001). The systematic relationship between the DIC and DO diel changes observed in this study is explained by the coupling between the metabolic activity of the meadows and the fluxes of calcium carbonate. Thus, metabolism should be better estimated from DO variations than from DIC variations. Our results stress the need for simultaneous DIC and DO estimates of metabolism in this type of ecosystem.

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