



Photosynthetic activity buffers ocean acidification in seagrass meadows

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Abstract. Macrophytes growing in shallow coastal zones characterised by intense metabolic activity have the capacity to modify pH within their canopy and beyond. We observed diel pH changes in shallow (5–12 m) seagrass (*Posidonia oceanica*) meadows spanning 0.06 pH units in September to 0.24 units in June. The carbonate system (pH, DIC, and aragonite saturation state (Ω_{Ar})) and O₂ within the meadows displayed strong diel variability driven by primary productivity, and changes in chemistry were related to structural parameters of the meadow, in particular, the leaf surface area available for photosynthesis (LAI). LAI was positively correlated to mean, max and range pH_{NBS} and max and range Ω_{Ar} . In June, vertical mixing (as Turbulent Kinetic Energy) influenced max and min Ω_{Ar} , while in September there was no effect of hydrodynamics on the carbonate system within the canopy. Max and range Ω_{Ar} within the meadow showed a positive trend with the calcium carbonate load of the leaves, pointing to a possible link between structural parameters, Ω_{Ar} and carbonate deposition.

Calcifying organisms, e.g. epiphytes with carbonate skeletons, may benefit from the modification of the carbonate system by the meadow. There is, however, concern for the ability of seagrasses to provide modifications of similar importance in the future. The predicted decline of seagrass meadows may alter the scope for alteration of pH within a seagrass meadow and in the water column above the meadow, particularly if shoot density and biomass decline, on which LAI is based.

Organisms associated with seagrass communities may therefore suffer from the loss of pH buffering capacity in degraded meadows.

1 Introduction

Forecasts predict that ocean acidification will become a significant threat to calcifying organisms in the near future (Orr et al., 2005; Gazeau et al., 2007; Talmage and Gobler, 2010; Waldbusser et al., 2011), many of which live in coastal habitats. However, coastal ecosystems are characterised by large temporal and spatial variability in carbonate chemistry and pH (Hofmann et al., 2011; Mercado and Gordillo 2011; Duarte et al., 2013), many of which regularly exceed predicted decreases in pH. In highly productive ecosystems this variability follows daily and seasonal cycles as O₂ and DIC concentrations in the water column are modulated through metabolic activity, with a signal that often prevails over physical forcing (Delille et al., 1997; Duarte et al., 2013). Whereas watershed effects can be a significant source of pH regulation and variability in coastal, estuarine waters, these are restricted in islands, where vulnerability to ocean acidification can only be offset by metabolic-intense ecosystems able to remove CO₂ (Duarte et al., 2013). This is the case of Mediterranean islands, which have small watersheds and little or no runoff to the coast, but where seagrass, *Posidonia*

oceanica, meadows support intense metabolism (Duarte and Chiscano, 1999; Duarte et al., 2010), possibly contributing to alleviate the expected impacts of ocean acidification.

Mediterranean *Posidonia oceanica* meadows are able to modify pH in the water column by as much as 0.2–0.7 pH units diurnally through photosynthetic activity and community metabolism (Frankignoulle and Distèche, 1984; Frankignoulle and Bouqueneau, 1990; Invers et al., 1997). The diurnal range in pH is greatest in shallow sites and the influence on the water column is diluted with increasing distance from the meadow (Invers et al., 1997), although the influence of the meadow stretches far beyond the canopy itself (Frankignoulle and Distèche, 1984; Gazeau et al., 2005). The magnitude of diurnal variations is largest in summer, coinciding with the peak in productivity, and decreases during the winter (Frankignoulle and Distèche, 1984). Whereas the capacity of Mediterranean *P. oceanica* meadows to affect pH is well characterised, and the relationship between pH variability, metabolic activity and water residence times in seagrass meadows have been described, not always a strong relationship is found. For instance Duarte et al. (2010) only found a weak relationship between biomass and metabolic rates; therefore detailed and simultaneous evaluation of several structural traits believed to drive these changes to assess which of those is the most important is still lacking. Focussing on the effect of structural traits on pH instead of direct measurements of metabolism has an advantage as approaches involving chambers, the most common approach in the literature to determine metabolism (Duarte et al., 2010), interferes with the effect of hydrodynamics and turbulent mixing; especially in systems with unidirectional flow, in buffering effects on pH and Ω_{Ar} and therefore might inflate the fluctuations in saturation states relative to those actually occurring in the meadow. Open water determinations of metabolism work best when there is a unidirectional flow, such as in tidal dominated systems, and a set-up with upstream and downstream sensors to properly resolve advection processes is used. However, this approach requires detailed knowledge of the origin of measured water bodies and therefore can be problematic in wave-dominated systems. Another advantage is that LAI is a non destructive method that can be easily assessed and can be resolved at large scales, thereby providing options to map where conditions may be most suitable for calcifiers, while metabolic rates over large scales would be cumbersome to derive.

Metabolic activity in highly productive seagrass meadows exposes marine organisms to pH environments that can differ greatly from those of the surrounding bulk water. Seagrasses may therefore provide chemical “refugia” for vulnerable organisms where photosynthetic activity may raise pH above the thresholds for impacts on calcification and/or limit the time spent below some critical pH threshold. There is evidence that organisms associated with seagrass meadows might benefit from this function. High pH values modified due to seagrass photosynthesis enhanced calcification

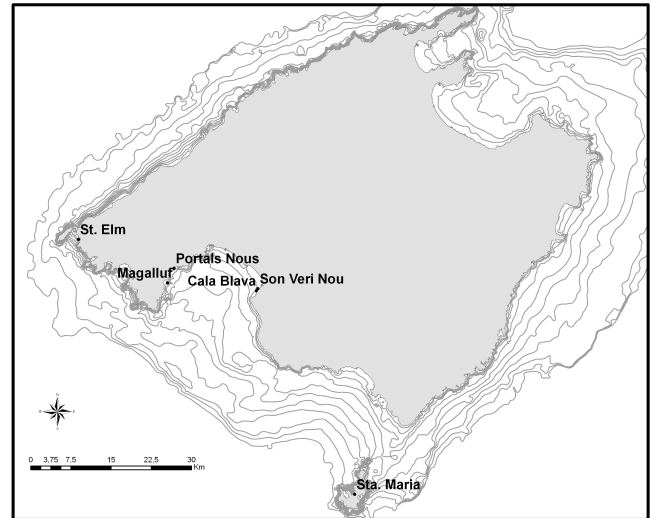


Fig. 1. Geographical location and sample sites of the study area in the Balearic Islands (western Mediterranean). Continuous lines show isobaths.

rates of calcareous red macroalgae (*Hydrolithon* sp. and *Mesophyllum* sp.) and the green macroalga *Halimeda renschii* growing within a tropical seagrass bed (Semese et al., 2009). A recent model based on records of seagrass metabolism in the Indo-Pacific suggested that pH increases with hypothetical maxima of up to 0.38 units, and theoretical Ω_{Ar} increases of up to 2.9 in seagrass meadows could potentially enhance calcification of scleratinian corals downstream of seagrasses by 18 % (Unsworth et al., 2012). The drawdown of dissolved inorganic carbon (DIC) due to photosynthesis of algae can result in a local net increase of pH and Ω_{Ar} , while the spatial patterns of the benthic community structure (i.e. percent cover of algal and coral communities) affects the upstream – downstream patterns of carbonate chemistry and impacts overall calcification rates on reef flats (Kleypas et al., 2011). However, field investigations linking the mitigating capacity of metabolically intense macrophyte ecosystems to their structural parameters like LAI are lacking.

Here, we evaluate the effect of structural parameters (shoot density, leaf area index, biomass) of the meadow and the interaction with physical forcing (hydrodynamics) on the resulting carbonate system in the meadow during the period where these effects are likely to be more important, i.e. between June and September. We demonstrate that the metabolic effects of *P. oceanica* meadows on pH along the coast of Mallorca (Balearic islands, Spain) are closely related to structural parameters of the meadow. These effects are large enough as to possibly help mitigate the impacts of future ocean acidification for calcifying organisms associated with these meadows.

Table 1. Mean (\pm SD) environmental parameters (temperature in $^{\circ}\text{C}$, light intensity in lux), hydrodynamics (\pm SE) and characteristics of the seagrass meadows (shoot density (\pm SE), biomass, LAI) at the sites sampled in this study.

Station	Plot	Mean Temp. ($^{\circ}\text{C}$)	Light intensity (lux)	Shoot density (m^{-2})	Biomass (g dry wt m^{-2})	LAI	U (m s^{-1})	TKE ($10^{-6} \text{ m}^2 \text{ s}^{-2}$)	Re Stress (Pa)
September									
Sta Maria	1	26.6 (± 0.16)	6644 (± 841)	582 (± 68)	515.48	1.23	0.012 ($\pm 3 \cdot 10^{-4}$)	2129 (± 20)	-285 (± 7)
Sta Maria	2	26.5 (± 0.16)	6644 (± 841)	778 (± 87)	419.57	1.22			
St Elm	1	26.8 (± 0.07)	5442 (± 414)	368 (± 90)	465.75	0.69	0.013 ($\pm 5 \cdot 10^{-4}$)	1883 (± 11)	158 (± 2)
St Elm	2	26.8 (± 0.08)	5442 (± 414)	456 (± 56)	647.37	1.39	0.012 ($\pm 5 \cdot 10^{-4}$)	1930 (± 13)	-91 (± 2)
Magalluf	1	26.4 (± 0.20)	6711 (± 1097)	580 (± 51)	606.02	1.35	0.018 ($\pm 6 \cdot 10^{-4}$)	2084 (± 23)	-50 (± 2)
Magalluf	2	26.3 (± 0.20)	6711 (± 1097)	582 (± 60)	793.42	2.1	0.019 ($\pm 6 \cdot 10^{-4}$)	2055 (± 23)	-77 (± 2)
June									
Son Veri Nou	1	23.4 (± 0.33)	8230 (± 1525)	607 (± 107)	714.85	1.9	0.007 ($\pm 3 \cdot 10^{-4}$)	279 (± 8)	-0.46 (± 2)
Son Veri Nou	2	23.4 (± 0.30)	8230 (± 1525)	577 (± 102)	417.34	1.1			
Cala Blava	1	23.2 (± 0.35)	7056 (± 842)	624 (± 104)	1012.86	2.9	0.006 ($\pm 2 \cdot 10^{-4}$)	238 (± 10)	-14 (± 1)
Cala Blava	2	23.2 (± 0.35)	7056 (± 842)	537 (± 157)	648.51	2.47	0.007 ($\pm 3 \cdot 10^{-4}$)	254 (± 11)	10 (± 1)
Magalluf	3	23.4 (± 0.24)	8752 (± 2348)	467 (± 144)	712.99	2.76	0.004 ($\pm 2 \cdot 10^{-4}$)	748 (± 10)	-17 (± 1)
Magalluf	4	23.7 (± 0.40)	8752 (± 2348)	587 (± 156)	623.02	2.41	0.003 ($\pm 1 \cdot 10^{-4}$)	741 (± 9)	-31 (± 1)
Portals	1	23.6 (± 0.25)	8646 (± 2894)	440 (± 177)	636.78	2.42	0.002 ($\pm 1 \cdot 10^{-4}$)	768 (± 8)	4 (± 1)
Portals	2	23.6 (± 0.24)	8646 (± 2894)	610 (± 184)	807.46	3.48	0.002 ($\pm 1 \cdot 10^{-4}$)	821 (± 4)	-8 (± 0.3)

2 Methods

We examined pH and O_2 fluctuations in six *P. oceanica* meadows off the coast of Mallorca (W. Mediterranean, Spain; Fig. 1). Measurements were made in September (7–23 September 2011), just before leaf shedding and removal by autumn storms and in June (5–15 June 2012), at the peak of *P. oceanica* production (Frankignoulle and Disteché, 1984). Three meadows were visited in September and four in June with one meadow (Magalluf) sampled in both seasons (Fig. 1). We chose shallow (5–12 m depth) meadows with a wide range of shoot densities (Table 1) to evaluate the influence of structural parameters. At each meadow we carried out measurements in two stands of relatively dense *P. oceanica* separated by at least 20 m of meadow and sandy patches. Additionally, in September we took measurements in the centre of one bare sandy patch (2–20 m diameter) per station.

2.1 Carbonate system and oxygen measurements

A multiparametric sensor (Hydrolab DS5X) was deployed within the seagrass canopy 0.1 m above the bottom at each site and recorded local pH_{NBS} , O_2 , salinity and temperature every 15 min. A central cleaning system was attached to avoid fouling of the sensors. The oxygen sensors (Hach LDO[®] Sensor) were calibrated with the water-saturated air method and the pH sensors (with Integrated Reference) with a two-point calibration (before and after each deployment) using NBS standard buffers of 7.00 and 10.00 pH_{NBS} . During the September campaign we were unable to obtain oxygen data from one vegetated and one bare site due to instrument malfunction. During the June deployments, one instrument was flooded, leading to the loss of those data. Total

alkalinity samples were taken at the bottom and surface before and after each deployment, fixed with 20 μL HgCl_2 and measured within 3 months (using the Metrohm Titrando 808 after SOP3b of Dickson et al., 2007). Light conditions were registered with a HOBO data logger (Pendant[®], Onset Computer Corporation) attached to the Hydrolab. Additionally, we obtained irradiance data (W m^{-2}) from the meteorological station at Ses Salines (located at the Southeastern point of Mallorca) as an additional measure of the light conditions on the surface during our campaigns. The maximum, minimum, and average pH_{NBS} were extracted for each 24 h period from data obtained during the full deployment. Since not all measurements covered 72 h, we calculated mean pH_{NBS} over 24 h from 2.15 pm to the same time the next day for the first two deployment days, while from 11:15 to the same time for the third deployment day. Consequently, there is a 3 h overlap for the average pH_{NBS} on day two and three. The range of the pH fluctuation was calculated as the difference from the lowest or highest pH_{NBS} to the maximum or minimum pH_{NBS} during the next day. Additional parameters of the carbonate system were calculated from the in situ pH_{NBS} , temperature, and salinity data, and the discrete total alkalinity samples, which were linearly interpolated across the deployment time. DIC and the saturation state of aragonite (Ω_{Ar}) were calculated using CO2SYS excel programme (Pierrot et al., 2006) with the K1 and K2 constants from Mehrbach et al. (1973), as modified by Dickson and Millero (1987), and the K_{HSO_4} constant from Dickson (1990).

2.2 Hydrodynamic regime

At every site, water velocity in 3 dimensions was measured during bursts programmed in time (every 15 min; in

sync with the Hydrolab measurements) at 32 Hz, with a total of 5000 samples using Acoustic Doppler Velocimeters (Nortek, Vector). Measurements were taken just above the canopy level, at 1.2 m above the bottom. Absolute water velocity (u in m s^{-1}) was calculated for each site (Table 1) from the measurements in the x and y direction (horizontal plane); as well as Turbulent Kinetic Energy (TKE, as $0.5 * (\overline{u'^2} + \overline{v'^2} + \overline{w'^2})$ in $\text{m}^2 \text{s}^{-2}$), and Reynolds Stress (as $\rho (\overline{u'w'})$ in Pa or N m^{-2}).

2.3 Meadow characterisation

At each sampling location we characterised the structural parameters of the meadow. Shoot density was estimated in eight replicate 0.0625 m^2 quadrats in September and six replicate 0.05 m^2 quadrats in June. To determine biomass and Leaf Area Index (LAI), twelve shoots were randomly collected at each sampling site. The length and width of all leaves were measured, and the mean total leaf area per shoot multiplied by the shoot density to obtain the LAI ($\text{m}^2 \text{ leaves m}^{-2}$). All leaves were dried at 60°C for 48 h and the aboveground dry weight (g m^{-2}) was determined as the product of the average shoot weight and density.

To obtain the total leaf carbonate load, dried shoots were burned at 550°C for 4 h and weighed to determine organic matter (OM) content. Shoots were then combusted at 1000°C for 2 h and weighed again. The weight lost between 550 and 1000°C represents the carbonate load (Smith and Atkinson 1984). We assume that the bulk of the carbonate can be attributed to the associated epiphytes on the leaf surface. Internally precipitated inorganic carbonate is also included with this method, although internal content of carbonates in the leaves should be negligible (Gacia et al., 2003).

2.4 Statistical analyses

We tested the effect of structural parameters of the meadow on oxygen concentrations (mg L^{-1}) and the carbonate system (pH_{NBS} and Ω_{Ar}) with a Generalized Linear Mixed Model (GLMM) in R (lme4 package; R Development Core Team 2011) using site (variation of daily mean, max, min and range per day) as a random factor. We tested the effects of hydrodynamics on Ω_{Ar} using Generalized Linear Models (GLM) in R since the distinction between seasons meant we were left with too few data points to evaluate a random effect. We used the same approach (GLM) for the analysis of the effect of Ω_{Ar} (max, min, mean, range) on the carbonate load of the leaves. We evaluated which set of parameters (structural, hydrodynamic, metabolism) was the best predictor for Ω_{Ar} in the meadow by model selection using Akaike's Information Criterion (AIC). As our several structural and hydrodynamic parameters are auto-correlated, we performed a Principal Component Analysis (PCA) in R to obtain 1 principal component for the structural and 1 for the hydrodynamic

set explaining most of the variation which we used as input, together with the range of oxygen concentrations for our GLMM (prediction Ω_{Ar}) or GLM (prediction CaCO_3).

In figures portraying correlations with mean, max, min, and range pH and Ω_{Ar} , linear regressions are based on repetitive measurements and significance should be inferred from the GLMM models.

3 Results

Cumulative light ($\text{W m}^{-2} \text{ day}^{-1}$) was $54\,622 \pm 2691$ (SE) in September and $74\,000 \pm 1615$ (SE) in June. Like the average daily light intensity, 402 ± 21 (SE) and 477 ± 10 (SE) W m^{-2} respectively this represents a significant difference (Students t test, $p < 0.01$) between seasons. Salinity was on average 40 ± 0.10 SD ppt in September and 39 ± 0.92 ppt in June. See Table 1 for specification of the environmental parameters of the sites.

Oxygen concentrations in the water column followed the diurnal cycle of daylight and photosynthetic activity of the plants with highest concentrations observed in the afternoon and the lowest around sunrise (Fig. 2). In September, oxygen concentrations were overall lower and typically ranged from 6.04 to $7.23 \text{ mg O}_2 \text{ L}^{-1}$ compared to those in June (Table 2, S1). The highest value measured in September was $8.02 \text{ mg O}_2 \text{ L}^{-1}$ and the lowest $4.18 \text{ mg O}_2 \text{ L}^{-1}$ (111 % and 66 % saturation, respectively, mean water temperature 26.5 ± 0.23 SD $^\circ\text{C}$). In June, the range was larger and the overall values higher with a mean range from 7.62 to $9.94 \text{ mg O}_2 \text{ L}^{-1}$. The highest value measured in June was $11.7 \text{ mg O}_2 \text{ L}^{-1}$ and the lowest $5.29 \text{ mg O}_2 \text{ L}^{-1}$ (161 % and 77 % saturation, respectively, mean water temperature 23.4 ± 0.18 SD $^\circ\text{C}$).

We observed clear diurnal patterns in pH_{NBS} , following those of oxygen (Fig. 2a and b, Table 2). Oxygen production by photosynthesis, or metabolic activity of the plants during the day directly influenced the carbonate system in the meadow, as there was a strong correlation between O_2 (in $\mu\text{mol kg}^{-1}$) and DIC (in $\mu\text{mol kg}^{-1}$) in the canopy with an average daytime relationship for all the experimental sites of $-0.97 \mu\text{mol DIC}/\mu\text{mol O}_2$ in September and $-0.96 \mu\text{mol DIC}/\mu\text{mol O}_2$ in June (average mean r^2 of 0.90). During the nighttime, when respiration is dominant, this relationship was $-1.13 \mu\text{mol DIC}/\mu\text{mol O}_2$ in September and $-0.92 \mu\text{mol DIC}/\mu\text{mol O}_2$ in June (average mean r^2 of 0.88). The mean pH_{NBS} for all sites was similar in September (8.03 ± 0.02) and June (8.06 ± 0.22 ; $t = -0.95$, $p = 0.36$). However, the maximum observed pH_{NBS} during the daily cycles was lower in September (8.09 ± 0.02) than in June (8.19 ± 0.09 ; $t = -3.44$, $p < 0.01$), driven by the higher productivity of the plants, while the minimum pH_{NBS} was the same in both seasons (7.97 ± 0.03 and 7.97 ± 0.03 in September and June, respectively, $t = 0.08$, $p = 0.93$). See Table S1 for an overview of all maximum and minimum values. Consequently, the

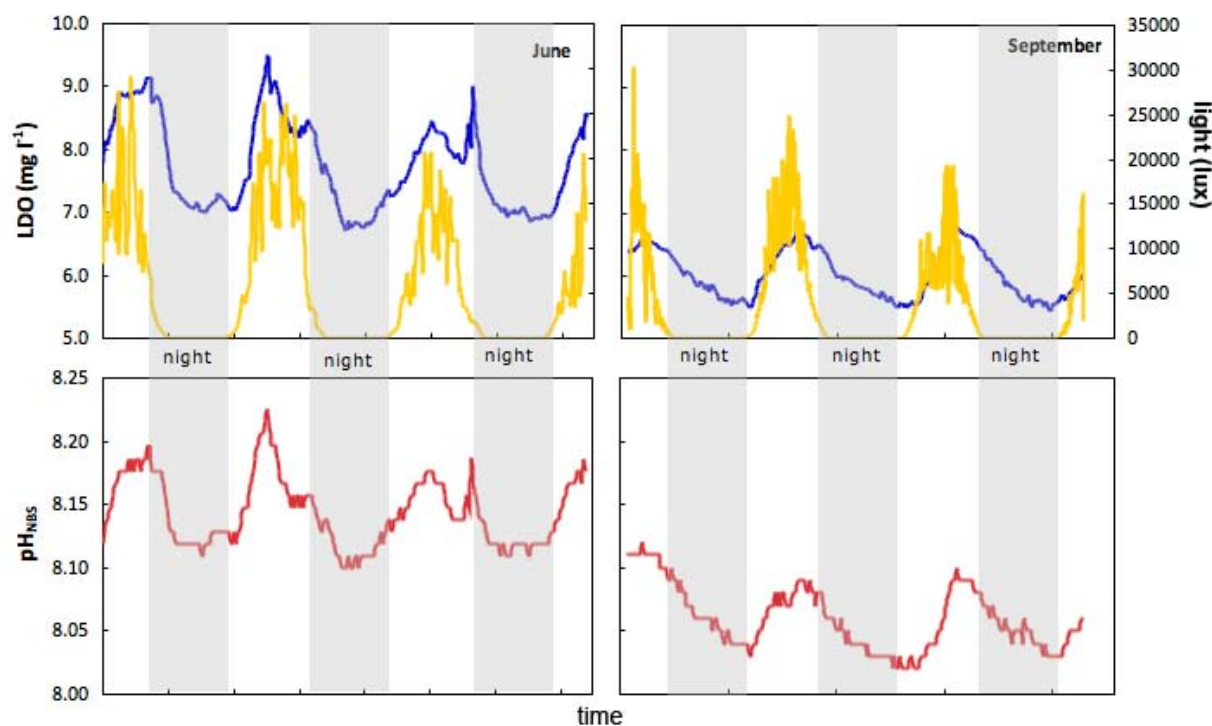


Fig. 2. Diurnal profiles of light levels (lux) and of oxygen concentration (mg L^{-1} ; upper panels) and pH (lower panels) in the canopy during the June (left panels) and September campaigns (right panels) in Magalluf.

mean range in pH was smaller in September (0.08 ± 0.01) than in June (0.16 ± 0.01 ; $t = -4.41$, $p = 0.001$). The smallest diel ranges of 0.05 pH units were observed in the meadows of St. Maria and St. Elm in September and maximum diel ranges of 0.24 pH units were observed in the Bay of Palma (Cala Blava) in June (Table 2).

Measurements of pH_{NBS} and oxygen in bare areas adjacent (max. 10 m from the nearest edge) to the seagrass meadows ($n = 3$; September campaign only) demonstrated clear diurnal patterns (data not shown) similar to those found in the seagrass canopy, indicating a large spatial footprint for seagrass metabolic effects on O_2 and pH. Oxygen ranged from 5.72 to 6.95 $\text{mg O}_2 \text{L}^{-1}$, which is comparable to the values measured inside the meadow during September. Mean pH_{NBS} was 8.02 ± 0.04 SD, ranging diurnally between 0.06 to 0.21 units, significantly lower than the mean pH_{NBS} in the vegetated sites (8.03 ± 0.02 , $t = 13.98$, $p < 0.001$).

The biomass of seagrass at the sites affected the mean, maximum and minimum oxygen concentrations within the canopy (GLMM; $p < 0.05$) while the leaf surface available for photosynthesis (LAI) affected all measured oxygen concentrations (mean, max, min and range, Table S3, Fig. S2; $p < 0.01$). We found strong relationships between oxygen within the canopy and pH suggesting photosynthetic rates and metabolism are important drivers of the carbonate system within the meadow (Fig. S4). Oxygen concentration (max and mean) was correlated to the maximum pH_{NBS}

measured during the deployments ($r^2 = 0.54$, $F = 10.68$, $p < 0.01$ with slope $a = 0.03$ and $r^2 = 0.72$, $F = 23.28$, $p < 0.001$ with slope $a = 0.08$ for max and mean, respectively). The range of pH measurements was correlated to oxygen concentrations (in mg L^{-1}) through production of oxygen and carbon consumption during photosynthesis by the metabolic activity of the plants (max and mean; $r^2 = 0.87$, $F = 61.86$, $p < 0.0001$ and $r^2 = 0.67$, $F = 18.29$, $p < 0.01$, respectively), probably as a direct result of the higher maximum pH_{NBS} . The range of Ω_{Ar} was correlated to oxygen concentrations (maximum and mean O_2 ; $r^2 = 0.70$, $F = 20.61$, $p < 0.01$ and $r^2 = 0.65$, $F = 16.44$, $p < 0.05$, respectively), but the maximum saturation state in the meadow was not significantly correlated ($F = 4.71$, $p = 0.06$) to the mean oxygen concentration.

LAI emerged as the most consistent driver of pH variability (Table 3; Fig. 3). The observed differences in mean pH_{NBS} (Table 2) and pH fluctuations (max and range) within seagrass canopies could be attributed to differences in LAI between meadows, while they could not be linked to density or biomass (Table 3), while the minimum pH_{NBS} was independent of structural meadow parameters (Table 3). We used the intercept of the linear regression between LAI and mean pH ($\text{pH} = 0.04 \text{ LAI} + 7.97$, $r^2 = 0.31$; Fig. 3) as a hypothetical value for a scenario without vegetation present in the area ($\text{LAI} = 0$). Compared to this hypothetical value, the assessed sites elevated the pH between 53 and 100 % of the time, with

Table 2. Biogeochemical parameters of the carbonate system (mean and range pH_{NBS} measured as well as the estimated % of time the pH was maintained above the hypothetical threshold where no vegetation would be present ($\text{LAI} = 0$); $p\text{CO}_2$, DIC and Ω_{Ar} calculated with the excel version of CO2SYS), oxygen concentration in the canopy (mg L^{-1}) and CaCO_3 (m^{-2}) content of seagrass leaves in the meadows.

Station	Plot	CaCO_3 (m^{-2})	Mean O_2 (mg L^{-1})	Range O_2 (mg L^{-1})	Mean pH	% time over unvegetated pH	pH Range
Sta Maria	1	51.72	5.81	3.45	7.99	66	0.11
Sta Maria	2	45.41	5.84	2.78	8.00	84	0.11
St Elm	1	35.70	6.12	1.51	8.02	100	0.06
St Elm	2	54.17			8.06	100	0.10
Magalluf	1	88.05	6.02	1.34	8.06	100	0.06
Magalluf	2	94.44	6.41	2.30	8.06	100	0.09
Son Veri Nou	1	113.46	7.44	2.75	8.03	89	0.17
Son Veri Nou	2	83.48	7.19	2.99	7.99	67	0.15
Cala Blava	1		7.70	6.41	7.98	53	0.23
Cala Blava	2	123.97	7.68	5.53	8.02	89	0.24
Magalluf	3	75.15	7.70	2.74	8.14	100	0.13
Magalluf	4	68.09					
Portals	1	73.68	7.87	4.72	8.14	100	0.17
Portals	2	58.26	7.77	4.33	8.14	100	0.17

station	Plot	$p\text{CO}_2$ mean	$p\text{CO}_2$ range	mean DIC	range DIC	mean Ω_{Ar}	range Ω_{Ar}
Sta Maria	1	714.01	381.32	2237.40	120.40	2.84	1.07
Sta Maria	2	685.26	257.01	2227.95	78.19	2.93	0.68
St Elm	1	655.27	119.20	2204.51	63.16	2.99	0.45
St Elm	2	586.76	202.39	2180.18	79.32	3.23	0.84
Magalluf	1	582.69	105.46	2194.53	45.66	3.22	0.45
Magalluf	2	583.60	155.81	2194.66	62.51	3.23	0.65
Son Veri Nou	1	628.62	452.32	2247.03	154.70	2.81	1.57
Son Veri Nou	2	704.35	286.02	2272.93	78.13	2.58	0.75
Cala Blava	1	714.48	507.65	2266.70	147.30	2.54	1.38
Cala Blava	2	645.85	490.79	2247.51	170.96	2.73	1.67
Magalluf	3	462.70	155.98	2183.75	86.28	3.43	0.81
Magalluf	4	463.08	281.34	2174.50	136.76		
Portals	1	471.85	265.46	2182.80	130.77	3.45	1.35
Portals	2	714.01	381.32	2237.40	120.40	3.41	1.29

an average of 88 ± 16 (SD) % of the time above this value (Table 2). For Ω_{Ar} the maximum and range were correlated with LAI, while biomass did influence the range significantly as well (Table 3, Fig. 4).

3.1 Hydrodynamics

Biomass and density did not have significant effects on measured hydrodynamics (water flow, TKE and Reynolds stress) while LAI affected the flow of water through the meadow as well as the TKE ($t = -3.089$, $p < 0.05$ and $t = -3.25$, $p < 0.01$, respectively). Since water velocity was different between June and September ($t = -5.61$, $p < 0.001$), we separated the analyses of the effect of hydrodynamics on the carbonate system by season (Fig. 5, Table 4). In September, no significant effect of water velocity or mixing on the carbonate system was found. Vertical mixing (as TKE) affected the mean ($t = 9.733$, $p < 0.001$) and minimum ($t = 4.255$,

$p < 0.05$) Ω_{Ar} positively, raising the saturation state with higher mixing intensities. A higher absolute water velocity lowered the mean Ω_{Ar} in June ($t = -3.772$, $p < 0.05$).

Ω_{Ar} (mean, max, min and range) does not significantly correlate with the harvested CaCO_3 on the leaf surfaces (Table 5) even though there is a positive trend discernable with the maximum and range of Ω_{Ar} within the canopy and CaCO_3 .

3.2 Model selection

The best models predicting minimum Ω_{Ar} included meadow metabolic activity (as range O_2 concentration, Table 6), however the mean, max and min Ω_{Ar} were best determined by models with only hydrodynamic components (Table 6). The best model to predict CaCO_3 content per m^2 of the leaves included all factors; structural parameters, hydrodynamics and the range of oxygen concentration within the canopy

Table 3. Results from Generalized Linear Mixed Models (lme4 package in R) with Gaussian distribution, and link identity with site as a random effect (repeated measures) testing the effect of structural parameters on the mean, max, min and range of pH and Ω_{Ar} . Where no results are given the no-slope model explained more variation.

		Shoot density		Biomass		LAI	
		χ^2	<i>p</i>	χ^2	<i>p</i>	χ^2	<i>p</i>
pH	Mean	1.826	0.18	1.0069	0.32	5.293	< 0.05*
	Max	0.9655	0.33	3.6949	0.05	15.831	< 0.001***
	Min	2.453	0.12	0.1176	0.73	1.456	0.23
	range	0.0214	0.88	3.5856	0.06	9.2126	< 0.01**
Ω_{Ar}	Mean	7.441	0.23	7.723	0.73	12.287	0.33
	Max	1.0926	0.30	2.2928	0.13	8.7876	< 0.01**
	Min	1.8925	0.17	–	–	–	–
	range	–	–	1.0926	0.04	14.2	< 0.001***

Significance levels: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

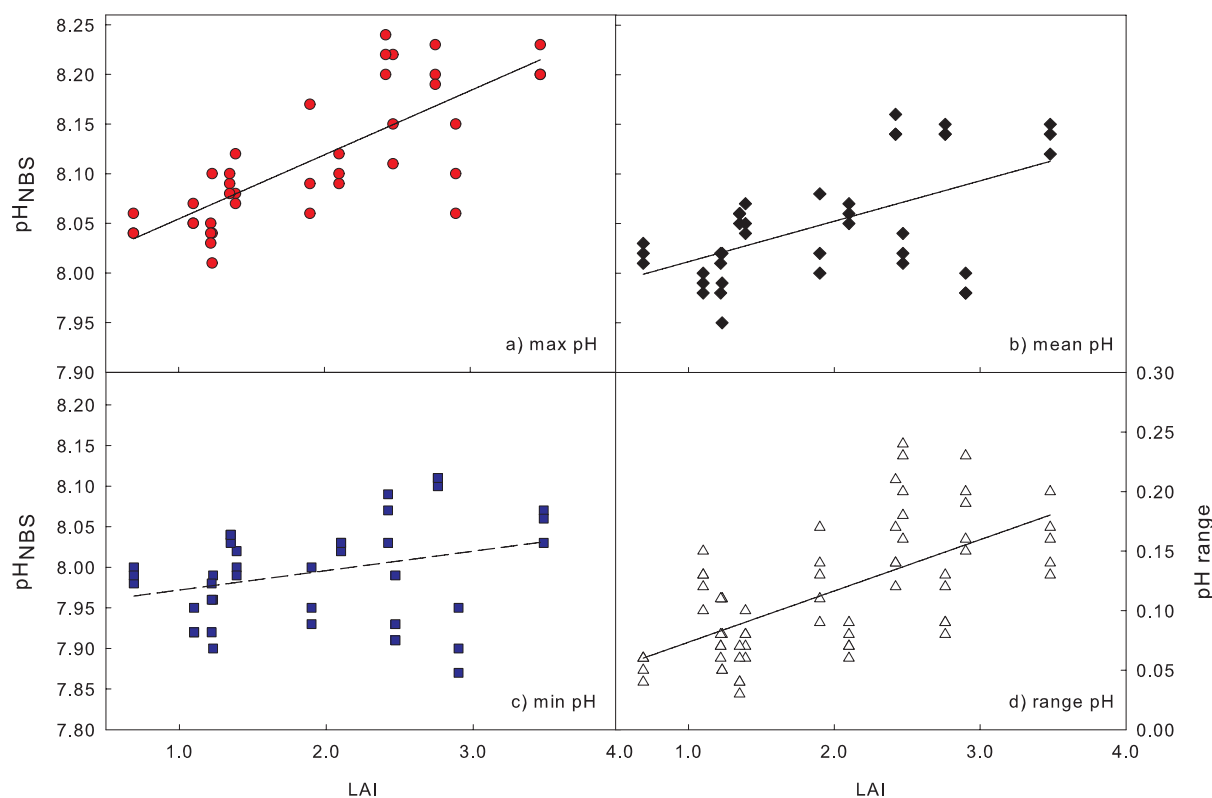


Fig. 3. The relationships between leaf area index (LAI) and (a) max, (b) mean, (c) min pH and (d) pH range. Non-significant relationships are dotted lines. Linear regressions are described for maximum pH (red circles) as $0.06 \text{ LAI} + 7.99$ ($r^2 = 0.60$), Mean pH (black diamonds) by $0.04 \text{ LAI} + 7.97$, ($r^2 = 0.31$), Minimum pH are blue squares while the range of pH (right y axis) are white triangles with linear regression $0.04 \text{ LAI} + 0.03$ ($r^2 = 0.42$).

(Table 7). The second best model with only a slightly higher score, explains CaCO_3 content through metabolic activity only.

4 Discussion

The island of Mallorca lacks rivers and surface runoff, although CO_2 from soil respiration can be delivered to coastal waters through groundwater inputs (Basterretxea et al., 2010). However, salinity maintains open-sea Mediterranean water properties, thereby pointing to a clear dominance

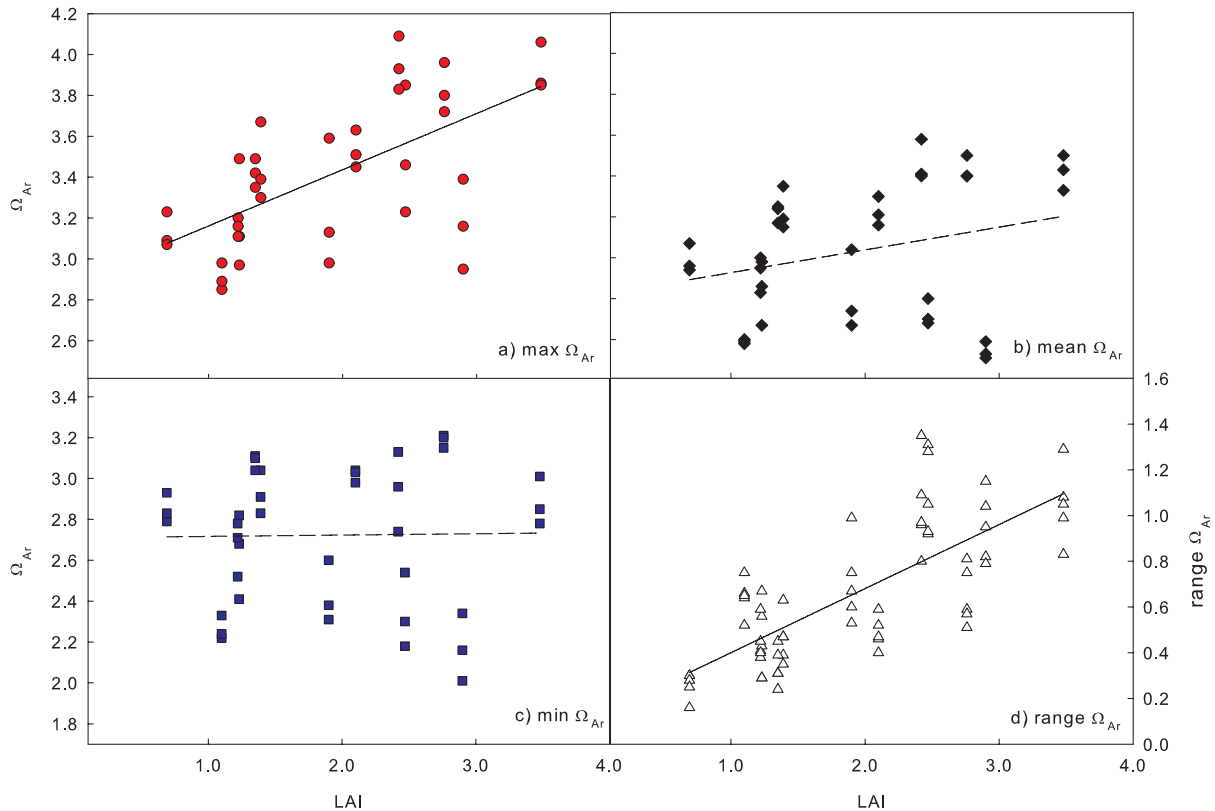


Fig. 4. The relationships between leaf area index (LAI) and (a) max, (b) mean, (c) min Ω_{Ar} and the (d) range of Ω_{Ar} . Non-significant relationships are dotted lines. The linear regression for maximum Ω_{Ar} (red circles) is $0.28 \text{ LAI} + 2.87$ ($r^2 = 0.40$). Mean Ω_{Ar} are black diamonds, Minimum Ω_{Ar} are blue squares while the range of Ω_{Ar} (right y axis) are white triangles with linear regression $0.28 \text{ LAI} + 0.12$ ($r^2 = 0.56$).

Table 4. Results from Generalized Linear Models (glm package in R) with gaussian distribution testing the effect of hydrodynamics on the Ω_{Ar} .

		TKE		<i>U</i> velocity		Re stress	
		<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>	<i>t</i>	<i>p</i>
September	Mean	−0.303	0.78	1.333	0.27	0.475	0.67
	Max	0.618	0.58	0.417	0.70	−1.261	0.30
	Min	−0.380	0.73	2.005	0.14	1.128	0.34
	Range	0.742	0.51	−1.128	0.34	−2.909	0.06
June	Mean	9.733	< 0.001***	−3.772	< 0.05*	−0.289	0.79
	Max	2.162	0.10	−1.511	0.21	0.721	0.51
	Min	4.255	< 0.05*	−2.110	0.10	−0.723	0.51
	Range	−1.804	0.15	1.220	0.289	2.452	0.07

Significance levels: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$

of oceanic forcing on biogeochemical properties, including pH. Island environments with small watersheds have been suggested to be particularly vulnerable to ocean acidification, unless they contain metabolically intense ecosystems (Duarte et al., 2013), such as *Posidonia oceanica* meadows in Mediterranean islands. We show that the metabolism of *P. oceanica* meadows, which are autotrophic ecosystems, can

affect pH even imposing a range of pH daily comparable to the predicted range due to ocean acidification over the 21st Century (Doney et al., 2009). We found highly temporally variable pH environments in seagrass ecosystems with the magnitude of diurnal pH variation strongly related to seagrass productivity, with the largest ranges coinciding with the peak in seagrass productivity and directly related to the leaf

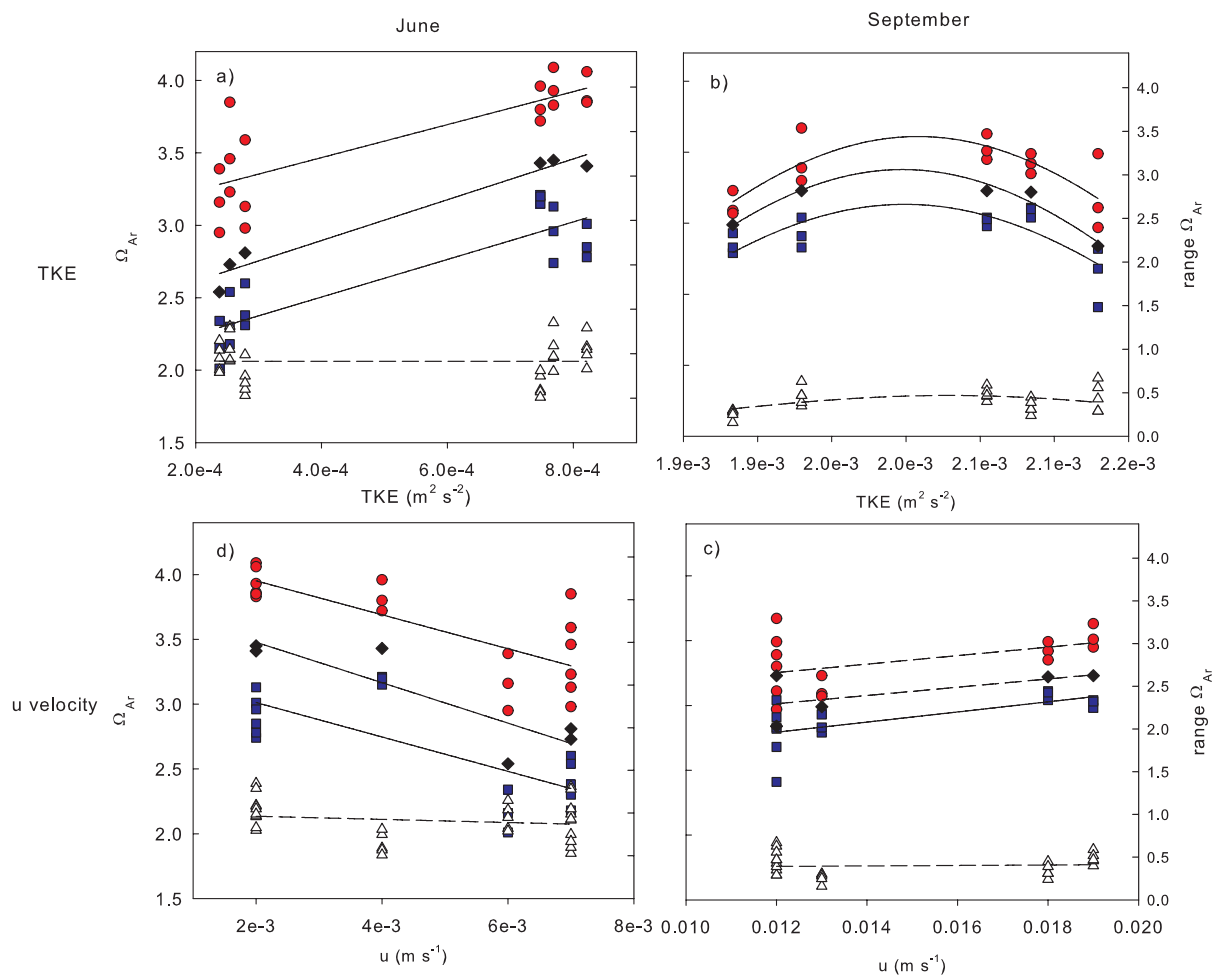


Fig. 5. The relationship between (a), (b) TKE (m^2s^{-2}) and (c), (d) u (m s^{-1}) and max, mean, min and the range of Ω_{Ar} . Non-significant relationships are dotted lines. Regressions are linear ($y = ax + b$), except for TKE in September, where they are peak models ($y = a - \sqrt{((x-x_0)/b)^2}$). Maximum Ω_{Ar} is represented with red circles, Mean Ω_{Ar} are black diamonds, Minimum Ω_{Ar} are blue squares while the range of Ω_{Ar} (right y-axis) are white triangles.

Table 5. Results from Generalized Linear Models (glm package in R) with gaussian distribution testing the effect of saturation of omega aragonite (Ω_{Ar} , predictor) on the CaCO_3 load (m^{-2}) on the leaves.

Ω_{Ar}	t	p
Mean	-0.830	0.43
Max	1.775	0.11
Min	-1.028	0.33
Range	2.064	0.07

area index of the plants, which reflects the density of photosynthetic tissues. Leaf area index is not routinely measured, but could be a parameter of interest when evaluating the importance of seagrass meadows on water chemistry.

4.1 Potential for buffering of the carbonate system in seagrass-dominated coastal ecosystems

The correlation between oxygen and pH with an increase in max pH and the range of Ω_{Ar} with increasing oxygen concentrations suggests that seagrass metabolic activity controls the carbonate system in seagrass canopies. The metabolic signal varies seasonally and the influence on carbonate chemistry is likely to be most pronounced at the peak of seagrass production, in June. Our results highlight the role of hydrodynamic processes in modulating the carbonate system within the canopy. Hydrodynamics control fluxes in and out of the meadow and may modify or dampen the metabolic signal. High community metabolism in seagrass meadows is common, with higher primary productivity rates in tropical meadows as compared to temperate ones (Duarte et al., 2010). The capacity to modify coastal pH in shallow near-shore water with submerged vegetation is wide-spread, in

Table 6. Model selection for Generalized Linear Mixed Models (lme4 package in R) predicting Ω_{Ar} with Gaussian distribution and site as random effect (repeated measures). Structural and hydrodynamic components are summarized in the principal component from a PCA analysis (in R), explaining 73 and 99 %, respectively of the original parameters. For Metabolism we used the range of oxygen concentration (mg L^{-1}) as a proxy. Aikake's information criterion (AIC) is as less-is-better, the best model value is highlighted in bold.

Model	range Ω_{Ar}	min Ω_{Ar}	max Ω_{Ar}	mean Ω_{Ar}^{\dagger}
structural	<i>17.74</i>	<i>31.51</i>	<i>28.93</i>	<i>26.95</i>
structural * season	<i>-26.06</i>	<i>26.49</i>	<i>30.78</i>	<i>27.85</i>
structural + season	<i>-27.98</i>	<i>26.73</i>	<i>30.08</i>	<i>27.87</i>
structural (site random)	-13.85	13.30	28.53	-3.26
structural + hydrodynamics (site random)	-16.12	8.41	22.61	-3.86
structural + hydrodynamics + metabolism (site random)	-49.11	13.01	27.93	3.28
structural + metabolism (site random)	-68.13	20.26	33.60	4.60
metabolism (site random)	-85.22	5.80	19.44	-10.34
metabolism + hydrodynamics (site random)	-65.53	0.02	13.36	-10.51
Hydrodynamics (site random)	-29.43	-5.38	7.68	-18.04

[†] Values in italics are evaluated using a GLM without random factor.

Table 7. Model selection for GLM models predicting $\text{CaCO}_3 \text{ m}^{-2}$ with gaussian distribution and link identity. Structural and hydrodynamic components are summarized in the principal component from a PCA analysis (in R), explaining 73 and 99 %, respectively of the original parameters. For Metabolism we used the range of oxygen concentration (mg L^{-1}) as a proxy. Aikake's information criterion (AIC) is as less-is-better, the best model value is highlighted in bold.

Model	AIC
structural	115.88
structural * season	116.11
structural + season	118.23
structural + hydrodynamics	99.79
structural + hydrodynamics + metabolism	92.29
structural + metabolism	108.62
metabolism	92.88
metabolism + hydrodynamics	100.14

areas with seagrass (Buapet et al., 2013; Hofmann et al., 2011; Invers et al., 1997; Semesi 2009; Schmalz and Swanson, 1969) and as well as in macrophyte habitats in general, such as kelps (Delille et al., 2000; Frieder et al., 2012; Hofmann et al., 2011; Menendez et al., 2001; Middelboe and Hansen, 2007), but the magnitude of buffering will depend on both structural and metabolic parameters and hydrodynamic processes of each system while the properties of the emerging canopy of the meadow (e.g. LAI) simultaneously control photosynthetic rates and affect hydrodynamic processes (Gutierrez et al., 2012).

4.2 Future potential for calcifiers living in the meadow

The changes in pH and Ω_{Ar} associated with *Posidonia oceanica* meadows are sufficiently large to be able to facilitate calcification processes. This effect is driven by struc-

tural parameters of the meadow, with LAI being the best predictor, as this affects both metabolic activity and hydrodynamic regimes. LAI is a relative measure including both shoot length and density and therefore takes both seasonality (leaf length) and meadow health (shoot density) into account. LAI is therefore a key parameter that should be measured during experiments. Vertical mixing, related to LAI by its influence on leaf movement in flow, enhances the mean and minimum Ω_{Ar} by mixing water from the top of the canopy, where irradiation is at its peak and high productivity is expected, with water from within the canopy. The near-bottom water has a longer residence time, and heterotrophic sediment processes influence the final measured pH as well as the autotrophic meadow. Therefore enhanced vertical mixing positively influences the carbonate system, measured by the multiparametric sensor in the lower canopy region. The leaf-inhabiting calcifying epiphytes might directly benefit from the modification of the carbonate system by the meadow as the positive trend (Table 5) between Ω_{Ar} and the carbonate load of the leaves found in this study point to possible beneficial effects. However, the growth of leaf epiphytes is on larger time scales than daily fluctuations and therefore a response in CaCO_3 mass might be only visible at the level of seasonal changes in saturation states rather than daily maximum and minimum. The second best model predicting explains CaCO_3 load on the leaves included metabolic activity only, with only decimals of difference with the best model including all components (Table 7). Epiphytes living on the leaf surface will experience modifications of pH and Ω_{Ar} much more pronounced than we measured within the meadow, as the diffusive boundary layer limits exchange processes and a gradient between the leaf surface and the water column is developed (Hurd et al., 2011). The present-day meadow might provide refugia for calcifiers by providing a daily window of maximum Ω_{Ar} where calcification is more cost efficient.

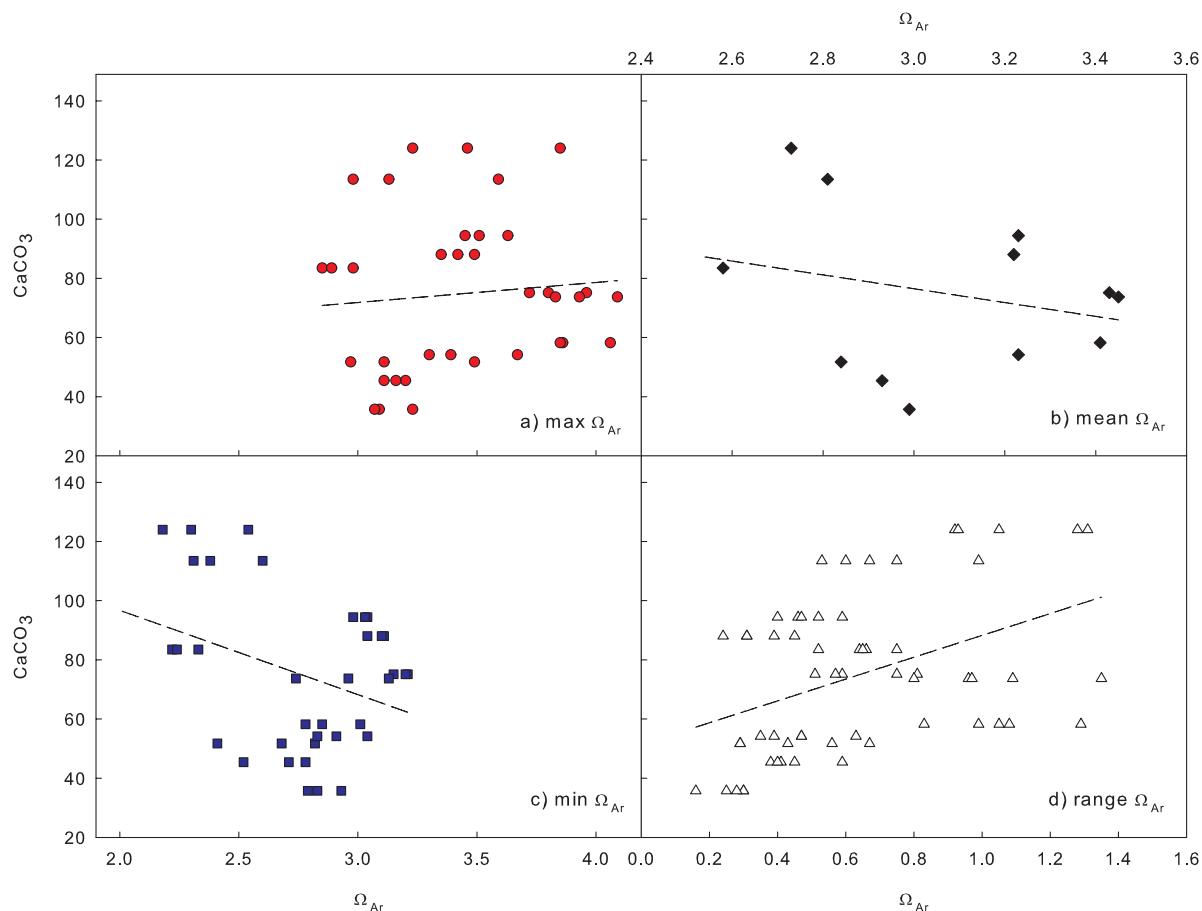


Fig. 6. Calcium carbonate content of the leaves vs. the saturation state of Aragonite (Ω_{Ar}) in the meadow. The linear regression is described as $\text{CaCO}_3 = 20.12 \Omega_{Ar} - 16.48$.

There is, however, concern for the ability of seagrasses to continue to provide this function in the future. Seagrass meadows are declining worldwide (Waycott et al., 2009) and, in the Mediterranean, shoot densities are diminishing at an alarming rate (Marbà and Duarte, 2010). Since the pH modification is directly linked to the structural parameters of the meadow the ability of seagrass meadows to provide beneficial conditions for calcifiers in the Mediterranean and globally is threatened.

Future increased levels of CO_2 in the atmosphere and a subsequent increase in dissolved CO_2 are predicted to have significant direct effects on aquatic plant communities (Wetzel and Grace, 1983; Edwards, 1995; Short and Neckles, 1999). At present seagrass photosynthesis is frequently limited by DIC availability under natural conditions (Beer 1989; Durako 1993; Madsen et al., 1993; Koch, 1994; Beer and Koch, 1996). Photosynthetic rates (Durako, 1993; Zimmerman et al., 1997) and growth and biomass (Zimmerman et al., 1997) might increase with increasing CO_2 concentrations, although long-term evidence for this is lacking (Short and Neckles, 1999). Acclimation following prolonged exposure

to elevated CO_2 may lead to down-regulation (Durako, 1993; Madsen et al., 1996) or up-regulation (Zimmerman et al., 1997) of photosynthesis. Long-term responses are therefore likely to depend on the degree of physiological and morphological adaptation to increased CO_2 (Drake, 1992; Dahlman, 1993; Amthor, 1995). It is therefore difficult to predict how this may affect the ability of seagrass meadows to buffer the pH environment within their canopies.

Measurements of diurnal pH cycles in volcanic vent systems of the Mediterranean Sea indicate that the ability of the meadows to modulate pH will be significant. The maximum diurnal range in a *P. oceanica* meadow in the Ischia CO_2 vent system was very large, at 1.0–1.6 of pH units at high $p\text{CO}_2$ sites (Duarte et al., 2013). These large diurnal fluctuations are probably the result of a combination of high productivity and photosynthesis in shallow DIC-rich meadows and variability produced by stochastic changes in CO_2 venting rates and hydrodynamic conditions, but, in any case, the capacity of seagrasses to modulate pH through their metabolic activity does not appear to be diminished, and is possibly enhanced, under conditions of increased $p\text{CO}_2$.

Even though seagrass productivity might be enhanced in a high- $p\text{CO}_2$ world, other stresses associated with global change might play a negative role. Like other seagrasses, *P. oceanica* meadows are highly vulnerable to coastal deterioration and are currently threatened by eutrophication, invasive species, coastal erosion and mechanical impacts (Williams, 2007; Diaz-Almela et al., 2008; Boudouresque et al., 2009). Declines of *P. oceanica* have been reported across the entire Mediterranean basin and it has been estimated that 13–50 % of *P. oceanica* area may have been lost, and that shoot density has declined in the remaining areas, with little scope for recovery, provided the very slow growth of this species (Marbà and Duarte, 1998). Rapid warming of the Mediterranean is enhancing seagrass decline further (Marbà and Duarte, 2010) and will enhance shoot mortality and trigger population decline as critical temperature thresholds are exceeded (Marbà and Duarte, 2010; Jordà et al., 2012).

The predicted global decline of seagrass meadows (Orth et al., 2006; Waycott et al., 2009) may alter the ability of the meadows to modify pH in the water column, in particular if meadows suffer declines in shoot density and biomass. The mean dry weight of the meadows at the height of their production (in June) is very close, even below, the predicted threshold for autotrophy of *P. oceanica* meadows (694.1 vs. 735.3 g DW m⁻² in Duarte et al., 2010). The ongoing shoot density decrease of seagrass meadows could bring the meadows around Mallorca closer to the threshold for the functional role of *P. oceanica* meadows as a refuge for calcifying. Organisms associated with seagrass communities will therefore be exposed to lower pH regimes in the future as pH decreases through ocean acidification and pH-buffering capacity is lost in declining meadows. Effective conservation of seagrass meadows is not only required to preserve these habitats under threat, but also the role they can play in the future in providing pH modification at local scales for calcifying organisms.

Supplementary material related to this article is available online at <http://www.biogeosciences.net/11/333/2014/bg-11-333-2014-supplement.pdf>.

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