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Characterization of the CO₂ system in a coral reef, a seagrass meadow and a mangrove forest in the central Red Sea

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Key points

- Dominance of heterotrophy and dissolution in winter – spring and autotrophy and calcification in summer – autumn in the coral reef.
- Negative anomaly of TA and DIC in the seagrass meadow relative to open water.
- The mangrove station exhibited the widest variations but no systematic anomaly of TA and DIC relative to open water.

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Abstract

The Red Sea is characterized by its high seawater temperature and salinity, and the resilience of its coastal ecosystems to global warming is of growing interest. This high salinity and temperature might also render the Red Sea a very favorable ecosystem for calcification, and therefore resistant to ocean acidification. However, there is a lack of survey data on the CO₂ system of Red Sea coastal ecosystems. A one-year survey of the CO₂ system was performed in a seagrass lagoon, a mangrove and a coral reef in the central Red Sea, including fortnight seawater sampling and high-frequency pH_T monitoring. In the coral reef, the CO₂ system means and variability over the measurement period are within the range of other world's reefs with pH_T, DIC, TA, *p*CO₂, and Ω_{arag} of 8.016±0.077, 2061±58 μmol kg⁻¹, 2415±34 μmol kg⁻¹, 461±39 μatm and 3.9±0.4. Comparisons with offshore site highlights dominance of calcification and photosynthesis in summer-autumn, and dissolution and heterotrophy in winter-spring. In the seagrass meadow, the pH_T, DIC, TA, *p*CO₂ and Ω_{arag} were 8.00±0.09, 1986±68 μmol kg⁻¹, 2352±49 μmol kg⁻¹, 411±66 μatm and 4.0±0.3. The meadow TA and DIC were consistently lower than offshore water. The mangrove showed the highest amplitudes of variation, with pH_T, DIC, TA, *p*CO₂, and Ω_{arag} were 7.95±0.26, 2069±132 μmol kg⁻¹, 2438±91 μmol kg⁻¹, 493±178 μatm and 4.1±0.6. We highlight the need for more research on sources and sinks of DIC and TA in coastal ecosystems.

Plain Language Summary

The consequences of the human emissions of CO₂ to the atmosphere, global warming, and ocean acidification are major threats to marine ecosystems. The Red Sea waters are naturally warm and saline. The resilience of its coral reefs, mangroves and seagrass meadows is of growing interest for the scientific community in the context of global warming. The high temperature and salinity might render the Red Sea quite resistant to Ocean acidification as well as an environment chemically very favorable for calcification, notably by corals. Calcification is a process dampened by the acidity (pH) of water, which depends on the chemistry of CO₂ in seawater. Warm and saline water naturally tend to have a more basic pH and then be less corrosive to calcareous skeletons. However, the chemistry of the CO₂ and acidity baselines and variability in the Red Sea are poorly documented. We conducted a year-round survey of the CO₂ chemistry of seawater in a seagrass, mangrove and coral reef ecosystem, involving discrete water sampling and high-frequency measurements.

Introduction

Increasing anthropogenic carbon dioxide (CO₂) emissions have led to a global increase in atmospheric CO₂ concentration over the past two decades, causing global warming and a decrease of seawater pH known as Ocean Acidification (OA) (e.g. Orr, 2011). Separately or in combination, warming and acidification are considered major threats to marine systems (e.g. Harvey et al., 2013), particularly to coral reefs, suffering recurrent wide-scale bleaching in recent years due to major heatwave events (Hughes et al., 2017).

Hence, understanding the resilience of organisms and ecosystems naturally exposed to permanent or periodical extreme conditions of temperature and partial pressure of CO₂ ($p\text{CO}_2$) is of particular interest (Camp et al., 2018). The Red Sea is the hottest sea on the planet, with mean annual maximum sea surface temperatures above 30 °C in the central and southern part (Chaidez et al., 2017), and provides an extreme temperature environment for coral reefs. Nevertheless, Red Sea corals are vulnerable to thermal stress, with the 2015 global coral bleaching event leading to mass mortality south of 20°N (Hughes et al., 2018; Monroe et al., 2018).

Besides homing extensive coral reefs, the Red Sea is also a global hotspot of seagrass diversity (Kenworthy et al., 2006). Moreover, the sea surface temperature above 20 °C in winter allows the presence of mangrove forests along most of its coastline (Almahasheer et al., 2016a). However, mangroves face adverse conditions for growth, due to lack of freshwater run-off, salinity over 40, and nutrient limitation (Almahasheer et al., 2016b).

The Red Sea is unlikely to be vulnerable to OA due to its high water temperature, salinity and total alkalinity (TA) favoring high saturation states for carbonate minerals (e.g. Takahashi et al., 2014). On the other hand, the high temperature of the seawater leads to low pH (all other parameters constants) due to the increased activity of hydrogen ions (Hunter, 1998). Thus, the coastal ecosystems of the Red Sea, particularly coral reefs, might be exposed to a unique CO₂ system in terms of both the baseline and variability. The CO₂ system of the Red Sea coastal ecosystems have been so far poorly studied. The only available data on the carbonate system of Red Sea in coral reefs derive from the Gulf of Aqaba, the coldest area of the Sea (Silverman et al., 2007).

Recently, Hughes et al. (2017) advocated for the need to test for “realistic” OA future scenarios using $p\text{CO}_2$ around 450 μatm , corresponding to pH in the range of 7.9 - 8.1. However, these projections apply to the open ocean and do not consider coastal ocean conditions, where vulnerable organisms reside, and subject to strong fluctuations in $p\text{CO}_2$. These highly dynamic

CO₂ systems are observed due to the ecosystems metabolism and inputs of freshwater and alkalinity from the watershed (Duarte et al., 2013; Wahl et al., 2015). As such, there is a need to characterize the CO₂ system and natural variability of coastal ecosystems to inform realistic ecosystem-specific high *p*CO₂ experiments (e.g. Andersson and Mackenzie, 2012; Fassbender et al., 2016; Rivest et al., 2017). Different coastal ecosystems (coral reefs, seagrass and seaweed meadows, mangroves) have complex CO₂ system baseline and variability, due to their different community and sediment structure (Challener et al., 2016; Cyronak et al., 2018a; Cyronak et al., 2018b; Rosentreter et al., 2018).

The present study is a baseline study aiming at characterizing the CO₂ system in three key benthic ecosystems of the central Red Sea over one year; a mangrove forest, a seagrass meadow, a coral reef and an additional pelagic station as a reference site for comparison. We aimed at characterizing 1) the seasonal and diel variations of the CO₂ system and 2) the potential drivers of TA and DIC at each ecosystem. The pH was surveyed at high resolution using SeaFET sensors and water samples were taken every second week for the full characterization of the CO₂ system.

2. Material and Methods

2.1 Sites, sampling and measurements

The three study sites were located at a coral reef, a mangrove forest and a seagrass meadow in the central Red Sea (Fig. 1). The sensor packages for the benthic moorings were composed of a SeaFET pH sensor (Sea Bird Scientific, Halifax, Canada; Martz et al., 2010) and a salinity - temperature - depth multiparametric sensor (CTD) equipped with a central wiping device (EXO2, YSI Inc., Yellow Springs, USA). The pH on the total scale (pH_T) was recorded at a frequency of 5 to 10 min and CTD with a frequency of 10 min. The coral reef site was located on the inner slope of the backreef of Al-Fahal reef (22°14'59"N, 38°57'45"E), a 14 km long barrier-type reef about 12 km offshore and marking the transition with open sea. The sensors were attached to a frame vertically on a reef spur, their sensing head approximately 120 cm above the sandy bottom. The seagrass site was located in an extensive *Enhalus acoroides* meadow in the Khor Almesena'a coastal lagoon (22°23'50"N, 39°08'06"E). The sensors were moored within the meadows canopy on a metallic pole anchored to the sediment, their sensing head approximately 55 cm above the sediment. The mangrove site was located at the fringe of a dwarf mangrove stand (*Avicennia marina*; 22°20'21 "N, 39°05'19"E). Transparent sections of

polycarbonate pipes were buried vertically to create casings in the sediment. The CTD and SeaFET sensors were positioned vertically in the pipes sensing heads up. To protect the SeaFET sensing head from desiccation at low tide, a transparent cylindrical cut was glued to the top of the SeaFET head (as a sleeve), protruding approx. 15 cm from sediment. We considered that the SeaFET was not capable of measuring pH when the CTD was not able to measure salinity (water level < 20 cm).

The time-series sampling took place from summer 2016 to summer 2017. The SeaFET moorings were from the 06.09.2016 to the 23.08.2017 in the seagrass meadow and, in the mangrove, from the 16.08.2016 to 19.08.2017 with an interruption between the 23 and 31.10.2016. At the coral reef site, the SeaFET mooring started the 16.06.2016 and was interrupted the 09.05.2017 because of sensor malfunction, with three interruptions for maintenance, between the 31.08.2016 and the 30.09.2016, the 11 and the 18.11.2016 and the 27 and the 30.03.2017. The CTD moorings were conducted in parallel to the SeaFET moorings. At the seagrass site, a malfunction of the CTD caused a gap of data between the 12.11.2016 and the 20.01.2017, two more interruptions for maintenance occurred between the 03 and the 09.03.2017 and between the 11 and the 20.06.2017. At the coral reef site, two interruptions for maintenance occurred between the 05 and the 17.11.2017 and between the 03 and the 09.06.2017.

Discrete seawater samples for TA, DIC, and pH measurements, as well as samples for total phosphate and silicate, were taken approx. every second week at the head of the SeaFET in the coral reef (29.06.2016 – 23.08.2017) and seagrass (20.09.2016 – 23.08.2017) stations and at the peak of high tide at noon at the mangrove station (07.09.2016 – 14.08.2017). Sampling and storage of the samples for determination of the CO₂ system was performed according to the standard operating procedures described in Dickson et al., 2007. Additionally, water samples were taken every 15 days at a pelagic reference station (22°18'33 "N, 38°59'50 "E) at 1-meter depth using a Niskin bottle. The salinity and temperature were recorded at the time of sampling using a calibrated Ocean Seven 305 Plus multiparameter sonde (Idronaut S.r.l, Brughiero, Italy). The pelagic station did not have a SeaFET sensor.

2.2 Sample analysis

Samples for total phosphate and total silicate were measured according to Grasshoff et al. (1999), using a Skalar San Plus auto-analyzer (Skalar Analytical B.V., Breda, the Netherlands). The TA was measured by open-cell titration (Dickson et al., 2007) using an AS-ALK2 titrator

(Apollo SciTech, Newark, USA). DIC was measured using an AS-C3 analyzer (Apollo SciTech, Newark, USA), based on the infrared determination of the CO₂ in air resulting of the complete outgassing of the DIC after acidification of seawater with phosphoric acid. Both TA and DIC instruments were calibrated every measurement day with Certified Reference Material (CRM) (A. Dickson, Scripps Institution of Oceanography, La Jolla, USA). Based on recent inter-calibration effort by Andrew Dickson and Emily Bockmon (Scripps Institution of Oceanography, La Jolla), the accuracy (mean $\pm$ SD) of our TA and DIC measurements are 0.21 ± 1.93 and -3.34 ± 2.2 $\mu\text{mol kg}^{-1}$ respectively.

The CO₂ system was overdetermined (i.e. measurement of TA, DIC, and pH_T) in 36 discrete samples. The pH_T in this subset of discrete samples was measured by spectrophotometry in 10 cm pathlength quartz cuvettes following Dickson et al. (2007), using a custom-made Ocean Optics (Largo, USA) spectrometer system (Flame-S spectrometer, DH-mini light source) and m-Cresol purple purified dye obtained from Robert H. Byrne and Nora K. Douglas at the University of South Florida in St Petersburg. The samples and dye were maintained at 25 °C before measurement via the use of a thermostatic bath. Based on measurement on CRM, we estimate the mean accuracy of the pH_T estimates at 0.004 units.

2.3 Data analysis

The CO₂ system parameters were derived from the TA and DIC of the discrete samples, using the function “carb” of the R package Seacarb (Gattuso et al., 2018) with the first and second dissociation constants of the CO₂ system by Millero (2010) and the dissociation constants for HF and HSO₄⁻ of Dickson and Riley (1979) and Dickson (1990), respectively. The combined standard uncertainties in computed carbonate system variables were estimated by propagating instrumental error according to Orr et al., 2018 using the function “errors” of the R package Seacarb (Gattuso et al., 2018). The DIC and TA were normalized for salinity according to Friis et al. (2003), using the mean from all discrete samples and, as non-zero TA endmember, the intercept of the regression between TA and salinity for each ecosystem. The SeaFET pH data was converted to total scale using the temperature and salinity from the CTD. When not available (due to CTD malfunction), the temperature of the SeaFET thermistor was used, and the salinity was linearly interpolated over time. The pH was corrected using spectrophotometric pH_T measurements of a discrete sample collected after 15 days of initial deployments (Bresnahan et al., 2014; Kapsenberg et al., 2016; Rivest et al., 2016) using the Saltlantic Software SeaFETCom.

The mean $\pm$ SD difference between the spectrophotometric pH_T in samples and the SeaFET measures are -0.001 ± 0.012 , 0.003 ± 0.050 and 0.02 ± 0.20 in the coral reef, seagrass lagoon and mangrove intertidal, respectively (Supplementary Fig. 1.). The precision and accuracy of the pH measurement in the coral reef and seagrass was comparable to other studies in coastal ecosystems (McLaughlin et al., 2017). The precision and accuracy were, however, one order of magnitude lower in the mangrove waters, probably due to the extreme deployment conditions (high temperature and salinity, low water level with periods of emersions, exposure to sediment) and the high potential for large differences of the CO_2 system within a few cm between sampling point and sensor. In samples in which the CO_2 system was overdetermined ($n = 12, 11$ and 6 in the coral reef, seagrass meadow and mangrove, respectively), the mean ($\pm$ SD) difference between calculated pH_T from DIC and TA and pH_T spectrophotometric was 0.001 ± 0.015 , -0.001 ± 0.014 and 0.028 ± 0.064 in the coral reef, seagrass meadow and mangrove respectively. These differences include instrumental error and a marginal contribution from organic alkalinity (Kuliński, 2014).

To compare between periods and ecosystems, we reduced the data by averaging the pH per hour of the day (1 to 24) over 15-day periods, based on the moon phases, to normalize for the influence of the semi-diurnal constituent of the tide and the neap to spring tide cycle. This allowed us to extract the influence of day-night cycles over tidal (and other non-light mediated parameters) influence. Thus, the spread of the value around the hourly means, expressed as the mean absolute deviation (the average of the absolute deviations from mean; MAD), is indicative of the influence of tide and other fluctuations on pH.

$$\text{MAD} = \frac{1}{n} \times \sum_{h=1}^n |\text{pHh} - \overline{\text{pHh}}|$$

With n the number of days, pHh the pH at hour h and $\overline{\text{pHh}}$ the mean pH for hour h for the n days.

3. Results and Discussion

3.1. Coral Reef

The mean ($\pm$ SD) temperature during the sampling period in the coral reef was 28.9 ± 3.6 °C with a mean diel variation ($\pm$ SD) of 1.5 ± 0.4 °C (Fig. 2. A.). The mean salinity in the coral reef was 39.3 ± 0.5 with 24h variations of 0.1 ± 0.9 (Fig. 2. B.). The mean ($\pm$ SD) pH_T during

the complete recording period in the coral reef was 8.016 ± 0.077 (Fig. 2. C.). The period with the minimum daily mean pH_T occurred between the 27.06.2016 and the 12.07.2016 with 7.949 increasing from summer to winter and peaking at 8.074 on the period from the 18.02.2017 to the 05.03.2017 (Fig. 3. A.).

By comparison, the mean ($\pm\text{SD}$) pH_T (calculated from TA and DIC) in the pelagic reference station during the whole measurement period was 8.006 ± 0.043 (95% CI of 0.016) (Fig. 2. C.). The pH_T in the reef exceeded the 95% CI range of the pelagic reference for durations of 4.4 ± 2.5 and 4.9 ± 2.7 hours per day (mean $\pm$ SD) in summer and autumn (dataset Saderne et al., 2019). Reciprocally, the pH_T in the coral reef was lower than the pelagic 95% CI range during 15.8 ± 1.4 and $12.7 \pm 7.14 \text{ h d}^{-1}$ in summer and autumn (Saderne et al., 2019). The situation reverses in winter, with a coral reef pH_T higher than the pelagic station 95% CI range $18.8 \pm 6.3 \text{ h d}^{-1}$, while lower for only $1.8 \pm 3.5 \text{ h d}^{-1}$ (Saderne et al., 2019).

The pH_T daily maxima were around 14:00 MST (mean solar time) and the minima around 5:00 MST (Fig. 4. A.). The maximum daily range of pH_T occurred in summer, during the first 15 days of measurement with 0.202. It narrowed through autumn - winter to a minimum value of 0.046 during the first half of December, increasing thereafter (Fig. 3. B.). A similar decrease in pH_T variations between summer and winter has been observed at Heron Island reef (Great Barrier Reef; Kline et al., 2015). However, the amplitudes of the diel variations in winter are lower than generally observed in other Indo-Pacific reef systems (Hofmann et al., 2011; Kline et al., 2015; Ohde and Van Woesik, 1999). Over the complete measurement period, the mean daily range of pH_T variation was 0.124 ± 0.04 . As a comparison, mean diurnal changes of pH 0.12 ± 0.02 and 0.21 ± 0.02 were observed during a one-year survey in two coral reefs sites in Waimanalo (Oahu Island, Hawaii; Lantz et al., 2014). The mean absolute deviation, representative of the influence of non-light mediated forcings on pH_T (i.e. principally tide), is $< 50\%$ than the pH_T variations due to light (Fig. 3. C.), following the same seasonal pattern as the daily range of pH_T variations. This seasonal dynamic of the MAD may be due to the seasonal variations of the water level in the Red Sea (Pugh and Abualnaja, 2015). Water level in the coral reef was lower by 0.23 cm on average in July – August 2016 compared to December – January (Fig. 2. F.). The reduction of water depth over the coral reef may increase the influence of the diurnal tidal variations on seawater temperature and tend to amplify concentration of the TA and DIC, and therefore the pH variations, produced or released by the corals and other organisms.

A 24h survey of the complete CO_2 system was conducted on the 23-24th of November (Fig. 5.

A.-D.). The DIC_n and TAn were lower during day than during night of 94 $\mu\text{mol DIC kg}^{-1}$ and 35 TA $\mu\text{mol kg}^{-1}$ respectively. The calculated diel $p\text{CO}_2$ and Ω_{arag} decreased during that particular day by 121 μatm and 0.67 units respectively. If considering all TA variation due to calcification, and a stoichiometric uptake of 2 $\mu\text{mol TA kg}^{-1}$ per $\mu\text{mol DIC kg}^{-1}$, we estimate that approximatively 18% of the diurnal DIC variation is due to calcification on that day. The diel variations of TA and DIC observed during the 24h sampling event in November 2016 compare with variations observed in Eilat in December (15 $\mu\text{mol TA kg}^{-1}$; Silverman et al., 2007). This 24h survey was conducted during a period of seasonally low diel variations, as revealed by the SeaFET mooring, and is therefore likely not representative of the diel variations in that location.

The mean ($\pm\text{SD}$) $p\text{CO}_2$, Ω_{arag} , DIC_n and TAn for the whole measurement period in the coral reef were $461 \pm 39 \mu\text{atm}$, 3.88 ± 0.43 , $2061 \pm 58 \mu\text{mol DIC kg}^{-1}$ and $2415 \pm 34 \mu\text{mol TA kg}^{-1}$, respectively (Fig. 6. A.–D.). We observed a decrease of DIC_n and TAn during the summer months compared to winter months. That reveals higher photosynthetic and calcification rates in summer, with $2032 \pm 14 \mu\text{mol DIC kg}^{-1}$ and $2399 \pm 10 \mu\text{mol TA kg}^{-1}$, compared to $2086 \pm 17 \mu\text{mol DIC kg}^{-1}$ and $2441 \pm 20 \mu\text{mol TA kg}^{-1}$ in winter (mean $\pm 95\%\text{CI}$). We observed a similar trend for Ω_{arag} with 4.03 ± 0.14 in summer compared to 3.89 ± 0.34 (mean $\pm 95\%\text{CI}$) in winter (Fig. 4. D.). The mean and variability of the seasonal pH_T , Ω_{arag} , and $p\text{CO}_2$ in our study coral reef are comparable to those reported for Media Luna Reef in Puerto Rico (Gray et al., 2012), The Florida Reef Tract (Manzello et al., 2012), Kaneohe Bay and Waimanalo in Hawaii (Drupp et al., 2013; CRIMP2 sampling site), the Bahamas (Yeakel et al., 2015) and Palmyra Island, Kingman Reef and Jarvis Island in the Line Islands (Price et al., 2012) i.e. pH_T between 7.9 and 8.1, Ω_{arag} between 3.5 and 4.5 and $p\text{CO}_2$ between 300 and 500 μatm (See Kline et al., 2015 for review).

The slope of the regression between TAn and DIC_n is informative of the dominant metabolic processes in coral reefs ecosystems (Andersson and Gledhill, 2013; Cyronak et al., 2018b; Lantz et al., 2014; Sippo et al., 2016). In Al-Fahal reef, the regression between TAn and DIC_n over the complete measurement period is statistically significant (F-statistic = 30.4, $p < 0.001$, $R^2 = 0.51$, $n = 25$), with a slope of 0.42 ($p < 0.001$) (Fig. 7. A.). This slope closely corresponds to the average ($\pm \text{SD}$) of the world coral reefs reported by Cyronak et al. (2018b) of 0.41 ± 0.18 . The ratio between the TAn and DIC_n differences between the coral reef and the pelagic reference station (Fig. 6. E.-F. and 7. D.) points at a dominance of heterotrophy and carbonate dissolution in winter – spring (November to May) and a prevalence of autotrophy and

calcification in summer – autumn (June to November). This dynamic corroborates the findings of Roik et al. (2018) on the same coral reef during the period 2012 – 2015 using the ReefBudget approach (Perry et al., 2012). During the complete survey period, the coral reef was a sink of TA compared to open water with a mean difference of $15 \mu\text{mol TA kg}^{-1}$, highlighting a minor dominance of calcification over dissolution.

In summary, our study reef site does not display the high Ω_{arag} and low pH_T and pCO_2 that we could expect considering the high temperatures, salinities, and TA when compared to available data for other coral reefs around the world. This could be explained by low DIC values relative to the TA in our study coral reef. The seasonal covariations of TA and DIC relative to open water tend to show higher autotrophy and calcification with increasing temperature from June to November. The current mean and variability of pCO_2 and pH recorded encompasses the OA projections for 2100 in coral reefs by Hughes et al., 2017. This highlight the need to consider local means and variability of the CO_2 system in OA scenario and experiments.

3.2. Seagrass meadow

The mean ($\pm\text{SD}$) temperature during the sampling period in the seagrass was $29.1 \pm 2.6 \text{ }^\circ\text{C}$ (Fig. 2. A.), with a mean diel variation ($\pm\text{SD}$) of $1.6 \pm 0.9 \text{ }^\circ\text{C}$. The mean salinity for the whole period was 41.2 ± 1.3 , with 24 h variations 0.8 ± 0.4 (Fig. 2. B.). The mean salinity and temperature, as well as their diel variations, were higher in the seagrass meadow compared to the coral reef.

The mean ($\pm\text{SD}$) pH_T during the whole recording period in the seagrass meadow was 8.00 ± 0.09 (Fig. 2. D.), with a relatively narrow diel variability from maximum values (mean $\pm \text{SD}$ of 8.06 ± 0.04) at 16:00 to minimum values (7.96 ± 0.10) at 07:00 (Fig. 4. B.). The minimum pH_T recorded occurred in late summer (7.84) and increased during autumn and winter to reach a maximum of 8.09 in February (Fig. 3. A.). The diel variations followed the same seasonal trend, decreasing from 0.28 in September to 0.02 in February (Fig. 3. B.). Over the measurement period, the MAD was 0.05 ± 0.04 , compared to a mean diel variation of 0.10 ± 0.08 (mean $\pm \text{SD}$) (Fig. 3. C.). So as in the coral reef, the influence of light-mediated processes directly or indirectly caused by photosynthesis on the pH_T is approx. twice the influence of the tide and other physicochemical forcings.

The pH_T in the meadow during the summers 2016 and 2017 was below the 95% CI range in the pelagic reference station (8.006 ± 0.016) 16.8 ± 5.1 and 15.1 ± 3.7 hours per day (mean $\pm \text{SD}$), while higher only 2.9 ± 2.5 and $4.8 \pm 4.7 \text{ h d}^{-1}$ (Saderne et al., 2019). The situation

reversed in winter and spring, with a pH_T in the meadow above the pH_T in the reference station for 21.5 ± 4.3 and 11.0 ± 5.8 h d⁻¹, respectively, while 0.3 ± 0.8 and 4.6 ± 4.5 h d⁻¹ below (Saderne et al., 2019). In autumn, the duration periods during which the pH_T in the meadow is above and below the reference station pH_T 95% CI range are equivalent, 9.2 ± 9.7 and 10.9 ± 8.8 h d⁻¹, respectively (Saderne et al., 2019).

There are only a few studies that document seasonal variations of the CO₂ systems of seagrass meadows. Kapsenberg et al. (2016) recorded pH_T (using SeaFET sensors) from 2012 to 2015 in a *Zostera pacifica* meadow in the California Channel Islands. They found a mean $pH_T \pm SD$ of 8.00 ± 0.06 over the whole measurement period, close to our value of 8.00 ± 0.09 . However, seasonal patterns were very different. Kapsenberg et al. (2016) found a maximum of mean pH_T occurring in June and declining through to October (from 8.06 ± 0.02 to 7.98 ± 0.02). Such seasonal trend was also observed in a *Thalassia testudinum* meadow in Florida (Eagle Harbor, St Joseph Bay; Challener et al., 2016). We found an opposite pattern in the Central Red Sea, with a pH_T minimum occurring in September and a maximum in February. However, this pattern is largely explained by the effect of the variation of temperature on pH. Normalized for 30 °C, the pH_T maximum is reached in June and the winter maximum disappears (Supplementary Fig. 2.), highlighting an increased primary production. Kapsenberg et al., 2016 observed a seasonal reduction of the diel variations from spring to autumn, with a minimum variation of 0.07 in November – December and a maximum variation of 0.2 in April, comparable to our observations.

We conducted a 24h survey on the 11-12th of January (Fig. 5. E.-H.). We observed a modest diel variation of DIC_n and TAN on that day, $30 \mu\text{mol DIC kg}^{-1}$ and $25 \mu\text{mol TA kg}^{-1}$. The minimum DIC_n occurred in the early evening while the minimum TAN occurred at mid-day. Both maximum values were reached at night (approx. 2:00 MST). The Ω_{arag} and $p\text{CO}_2$ variations mirrored each other, with values between Ω_{arag} between 3.7 and 4.1 and 385 and 326 μatm . These variations are quite modest compared to documented diel variations in seagrass meadows, often exceeding 100 μatm (e.g. Smith 1981: Western Australia; Yates et al., 2007: Tampa and Florida Bay, Jiang et al., 2011: Taiwan, Challener et al., 2016: St Joseph Bay). However, the sampling was made during the period of the year when the amplitudes of variations are the minimum, as revealed by the pH_T series.

Over the whole measurement period, the means ($\pm SD$) DIC_n, TAN, $p\text{CO}_2$ and Ω_{arag} were $1986 \pm 68 \mu\text{mol DIC kg}^{-1}$, $2352 \pm 49 \mu\text{mol TA kg}^{-1}$, $411 \pm 66 \mu\text{atm}$ and 4.0 ± 0.3 , respectively (Fig. 6. A.-D.). The difference of DIC_n and TAN between the pelagic reference station and the seagrass

station were of $-67 \pm 70 \mu\text{mol kg}^{-1}$ and $-63 \pm 65 \mu\text{mol kg}^{-1}$ (mean $\pm$ SD) (Fig. 6. E.-F.; Fig. 7. B.-E.), suggesting that the meadow is a sink for DIC and TA. We observed higher DIC_N and TA_N in winter than summer, with means ($\pm$ 95%CI) of $2038 \pm 43 \mu\text{mol DIC kg}^{-1}$ and $2401 \pm 39 \mu\text{mol TA kg}^{-1}$ in winter compared to $1925 \pm 37 \mu\text{mol DIC kg}^{-1}$ and $2311 \pm 15 \mu\text{mol TA kg}^{-1}$ in summer. The mean $p\text{CO}_2$ was close to global atmospheric values (406 ppm in May 2017, NOAA – ESRL), varying from a seasonal minimum of $362 \pm 37 \mu\text{atm}$ (mean $\pm$ 95%CI) in winter to a maximum of $427 \pm 50 \mu\text{atm}$ in autumn. This seasonal difference is mainly due to the seasonal variation of temperature. Normalized for temperature ($T = 30^\circ\text{C}$), the calculated mean ($\pm$ 95%CI) $p\text{CO}_2$ are lower in summer than in winter, with $379 \pm 48 \mu\text{atm}$ and $452 \pm 26 \mu\text{atm}$. These seasonal variations are of lesser amplitudes than observations made in *Thalassia testudinum* meadows in Florida (Eagle Harbor, St Joseph Bay; DIC_N: $330 \mu\text{mol kg}^{-1}$, TA_N: $220 \mu\text{mol kg}^{-1}$, $p\text{CO}_2$: $430 \mu\text{atm}$; Challener et al., 2016), but comparable to observations made in Mediterranean *Posidonia oceanica* meadows (Calvi, Corsica; DIC: $100 \mu\text{mol kg}^{-1}$, TA: $50 \mu\text{mol kg}^{-1}$; Frankignoulle and Bouquegneau, 1990).

3.3. Mangrove forest

The mangrove station experienced comparable mean temperature and salinity as the coral reef station, but with more pronounced diel variations. The mean ($\pm$ SD) temperature during the sampling period in the mangrove was $28.5 \pm 3.5^\circ\text{C}$ (Fig. 2. A.), with a mean diel variation ($\pm$ SD) of $5.2 \pm 1.6^\circ\text{C}$. The mean salinity in the mangrove was 39.6 ± 0.9 , with a mean diel variation of 3.8 ± 1.7 (Fig. 2. B.).

The mean ($\pm$ SD) pH_T during the entire study period in the mangrove was 7.95 ± 0.26 (Fig. 2. E.), with a steady decrease of pH_T from the 21.11.2016 (8.30) to the 30.07.2017 (7.63, Fig. 3. A.). The mean diel variations for the entire measurement period was 0.14 ± 0.08 with maximum pH at 16:00 (8.00 ± 0.27) and minimum pH at 7:00 (7.91 ± 0.25) (Fig. 4. C.). The diel variations increased from winter to summer months, with means ($\pm$ 95% CI) of 0.110 ± 0.001 compared to 0.226 ± 0.002 (Fig. 3. B.). The mean $\pm$ SD MAD over the whole measurement period was 0.11 ± 0.09 , comparable to the mean diel variations (0.14 ± 0.08) (Fig. 3. C.), indicating that non-light mediated forcing, principally tides, have comparable influence on the CO_2 system than autotrophy.

The pH_T in the mangrove was higher than the pelagic reference station 95% CI range for 7.6 ± 3.7 , 14.8 ± 9.5 and 14.7 ± 8.4 hours per day in summer 2016, autumn and winter, respectively, while lesser for 2.8 ± 3.6 , $4.1 \pm 6.2 \text{ h d}^{-1}$ and $6.6 \pm 7.7 \text{ h d}^{-1}$ during those same seasons (Saderne

et al., 2019). It reverses in spring and summer 2017, with lower pH_T than the reference station 95% CI range most of the days, 17.4 ± 8.2 and 13.3 ± 5.9 h d⁻¹ (mean $\pm$ SD), respectively (Saderne et al., 2019). The pH_T in the mangrove was higher than the reference station only 3.1 ± 6.6 h d⁻¹ and 0.2 ± 0.8 h d⁻¹ on average ($\pm$ SD) in spring and summer 2017 (Saderne et al., 2019).

Part or all parameters of the CO₂ system of mangrove swamp waters have been characterized in several studies (e.g. Borges et al., 2003; Bouillon et al., 2007; Call et al., 2015; Camp et al., 2016; Ray et al., 2018; Sippo et al., 2016; Rosentreter et al., 2018; Yates et al. 2014), but, to our knowledge, this is the first study to report a year-round survey of the CO₂ system of mangrove waters. All studies are pointing at large day-night and tidal variations of the CO₂ system, with pCO_2 variations of several thousand μ atm and pH variations of more than one unit (e.g. Bouillon et al., 2007; Rosentreter et al., 2018; Sippo et al., 2016). As an example, daily mean pH of 6.30 to 6.91 with diel variations up to 1.12 were found in Queensland (Australia) mangrove systems with salinities above 30 (Rosentreter et al., 2018). Our survey shows a similar pattern, with diel and tidal variations of the pH of similar amplitude. Similarly, the decrease of the mean pH from winter to summer could be linked to the low water stage during summer months in the Red Sea due to seasonal variations in wind regimes and water mass exchanges with the Indian Ocean (Pugh and Abualnaja, 2015).

The mean ($\pm$ SD) yearly DIC_n and TAn in mangrove were 2069 ± 132 μ mol DIC kg⁻¹ and 2438 ± 91 μ mol TA kg⁻¹ (Fig. 6. A.-B), representing differences with the pelagic reference station of 17 ± 96 μ mol DIC kg⁻¹ and 14 ± 123 μ mol TA kg⁻¹ (Fig. 6. E.-F., 7. C.-D.). Thus, we did not find systematic differences between mangrove and open water DIC and TA. The mean $\pm$ SD pCO_2 and Ω_{arag} in the mangrove were 493 ± 178 μ atm and 4.1 ± 0.6 (Fig. 6. C.-D).

To isolate the influence of light from the influence of tidal stage on the CO₂ system variations and therefore obtain a better picture of the processes driving TA and DIC, we performed extra samplings at high tide at different hours of the day- night cycle throughout 10 days (Fig. 5. I.-K.). We observed a day - night cycle of DIC and TA, centered on noon. The DIC_n amplitude was 100 μ mol DIC kg⁻¹ and TAn 48 μ mol TA kg⁻¹. It resulted in maximum amplitude of Ω_{arag} and pCO_2 of 0.38 and 191 μ atm (ranging from 3.4 to 3.8 and 380 μ atm to 573 μ atm). We found a relative increase of TAn and decrease of DIC_n at daytime (compared to nighttime), causing an increase of Ω_{arag} . This sampling effort highlights the circadiancy of TA and DIC and call for more in-depth studies on the short time scale variability of the CO₂ system in mangroves.

3.4. Drivers of the CO₂ system in the mangrove and seagrass ecosystems

The variations of the CO₂ systems in mangrove and seagrass ecosystems are the result of numerous and complex metabolic processes of the plant themselves, as well as of the associated flora, fauna, and the sediment. These metabolic processes are driven by physical and chemical variables, such as light, tides, temperature or salinity. Partitioning between the causes of the observed CO₂ system variations is highly difficult. Generally, the most important processes at play are primary production (new and recycled), respiration, calcification and red-ox reactions in the sediment involving various aerobic and anaerobic processes. The plants indirectly drive these reactions through the injection of O₂ and organic matter into the sediment.

Mangroves and seagrass meadows (and saltmarshes) are often highlighted for their high burial rates and sequestration of organic matter in their sediments and have therefore been coined “blue carbon” ecosystem. In those sediments, the labile part of the buried organic matter follows a sequence of degradation and remineralization from surface to depth. In surface oxic sediments, the organic matter is degraded through aerobic respiration, generating CO₂ (DIC). Below O₂ penetration depth in the sediment, the degradation of organic matter occurs by hydrolysis and fermentation though a cascade of reductive processes, the final reduced metabolite produced at depth being methane (Middelburg and Levin, 2009). These reduced metabolites are however being re-oxidized in surface sediments, consuming therefore O₂. In that regards, the sulfate reduction - sulfide oxidation cycle is predominant, due to the high amount of sulfate in seawater. Sulfide is phytotoxic and marine angiosperms actively supply O₂ to the sediment through their roots and rhizome system to prevent the accumulation of this reduced compound (Lamers et al., 2013). Doing so, marine angiosperms strongly influence the redox status of their sediment, and therefore the emissions of TA and DIC to the water column, causing variations of the CO₂ system. Thus, mangrove and seagrass sediments have specific metabolic activities, different from non-vegetated sediment, and are therefore an active component of the ecosystem.

The stoichiometry of the relationship between DIC and TA informs of the dominant processes driving the CO₂ system (Krumins et al., 2013; Sippo et al., 2016). In both seagrass and mangrove ecosystems, the TAN - DIC_n regression were highly significant (F-statistic = 145, $n =$, $p < 0.001$, $R^2 = 0.86$, $n = 21$ and $F = 79$, $p < 0.001$, $R^2 = 0.76$, $n = 20$, respectively) with a similar value for the slopes of 0.65 ± 0.05 and 0.65 ± 0.07 respectively (both $p < 0.001$) (Fig. 7. B. and C.). These slopes are close to the stoichiometry of the anaerobic processes of denitrification and sulfate reduction. The TAN - DIC_n relationship in our mangrove and

seagrass meadow corresponds to previous observations in seagrass and mangroves (Challener et al., 2016; Sippo et al., 2016).

Corroborating the slopes, Garcias-Bonet et al., 2018 demonstrated very high rates of net denitrification in our study meadow, 1 to 6-fold higher than in seagrass meadows elsewhere. We do not have information regarding the balance between sulfate reduction – sulfite oxidation at our mangrove and seagrass sites. However, there are arguments in the literature against net sulfate reduction in carbonate sediments containing low iron (Burdige et al., 2010; Holmer et al., 2005; Hu and Burdige, 2006; Krumins et al. 2013), such as in our seagrass and mangrove sites (Almahasheer et al., 2016b; Anton et al., 2018; Saderne et al., 2018).

We observed a negative anomaly of DIC and TA in the seagrass meadow relative to the pelagic station (Fig. 7. E.). This seems to be in contradiction with net denitrification as a driver of the CO₂ system, as this process is source of TA. Rather, that comparison seems to point at the dominance of photosynthesis, calcification and oxidative reactions. Photosynthesis seems to be an obvious driver of the DIC depletion observed in the meadow. Primary production has a slight effect on TA, which depends on the source of nitrogen used. New primary production, based on nitrate, produces 0.16 unit of TA per DIC produced while recycled primary production, based on Ammonium, consumes about 0.14 unit of TA per DIC produced (Goldman and Brewer, 1976; Brewer and Goldman, 1980). Biologically mediated calcification (biomineralization) in the meadow as a driver of the negative anomaly of DIC and TA does not appear obvious. Leaves of *E. acoroides* at our survey site are free of calcifying epibionts and we could only observe the presence in the meadow of sparse corals of the genus *Porites* as major benthic calcifiers. Chemogenic precipitation of CaCO₃ can occur in low iron, carbonate sediments of tropical seagrass beds (Burdige and Zimmerman, 2002; Hu and Burdige, 2007; Ku et al., 1999). Besides calcification, the two other main TA sinks in sediments are sulfide and reduced iron burial (Krumins et al., 2013). However, the lack of iron in the Red Sea sediment preclude reduced iron burial as an important sink of TA in our ecosystems.

In the mangrove site, we did not find systematic differences between the pelagic reference station and the mangrove station throughout the year (Fig. 7. F.). A strong variability of export rates of TA and DIC from Australian mangroves have been found by Sippo et al., 2016, ranging from -1 to 116 mmol TA m⁻² d⁻¹ and -97 to 85 mmol DIC m⁻² d⁻¹. To have comparable samples all along the year, we only sampled at high tide and around noon, corresponding to an alignment of the two astronomic cycles only occurring for a few days every two weeks. Noon corresponds to the lowest DIC of the day and intermediate TA value and the high tide corresponds to the

maximum dilution potential (Cyronak et al., 2018a). As shown by the pH variability, there is a large variation of the CO₂ system due to the tide and the time of the day. A very different time series of TA and DIC could have resulted from sampling along a different time and tidal stage.

Our survey sites - the barrier reef, seagrass coastal lagoon, mangrove stand, and the pelagic reference station - are not isolated from each other but are on a continuum from open sea to nearshore. Depending on the direction and strength of the currents and residency time of water, the CO₂ system measured in one ecosystem will partially depend on the processes that affected the water masses upstream. Thus, for example, the CO₂ system anomaly relative to open water observed at the seagrass site in a coastal lagoon could be partially due to calcification by reefs upstream. Quantifying the exports of TA and DIC by benthic ecosystems requires hydrological and bathymetrical data and models we do not have available now. Quantifying those TA and DIC exchanges between coastal ecosystems could inform of how blue carbon ecosystems could contribute to the growth of downstream reefs (Sippo et al., 2016).

Conclusions

In the coral reef, we observed a summer decrease of TA and DIC, possibly attributable to an increase of calcification and photosynthesis rates. The CO₂ system levels and variability in the coral reef are comparable to other reefs around the world, as revealed by the TA to DIC relationship and despite the higher salinity and warmer temperature. Our site already experiences pH and *p*CO₂ within the probable acidification scenario in coral reefs for the century described in Hughes et al., 2017. This survey proves the relevance of taking into account the local conditions of the CO₂ system to design acidification scenarios.

We observed a negative anomaly of TA and DIC in the seagrass *E. acoroides* meadow relative to open water. The mangrove ecosystem showed the largest variation in pH, due to day-night and tidal cycles. Higher-frequency studies at different spatial scales, made possible by emerging new technologies (e.g. TA sensor in Briggs et al., 2017), are needed to fully characterize the ecosystems CO₂ system and determine their role as a source or sink of TA and DIC. Hydrological data and models, absent in our study, are needed to quantify the actual contribution of nearshore vegetated ecosystems to the CO₂ system in reefs and therefore answer the question of the benefits of vegetated ecosystems to coral reef calcification in a context of ocean acidification.

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Figure 1. Deployment maps.

Figure 2. Time series of temperature (A.) and salinity (B.) in the coral reef (blue), seagrass meadow (green) and mangrove stand (brown). pH_T (SeaFET) in the coral reef (C.), seagrass meadow (D.), mangrove stand (E.); Plain dots are the pH_T calculated from discrete samples at the reference pelagic site; open dots are discrete measures of pH_T (spectrophotometric). F. Water level in the reef station.

Figure 3. Diel pH_T mean (A.), amplitude (B.) and mean absolute deviation (MAD) (C.) per 15 days periods in the reef (blue), seagrass meadow (green), mangrove (brown); plain dots are the pH_T calculated from discrete samples at the reference pelagic site.

Figure 4. Hourly means $\pm$ SD of pH_T for the entire measuring periods in: A. coral reef, B. seagrass meadow, D. mangrove forest.

Figure 5. Diel cycle (24h sampling) of the CO₂ system in: A. – D. Reef (Nov. 2016); E. – H. *Enhalus acoroides* meadow (Jan. 2017); I. – K. artificial 24:00 series of pHT and TA in the mangrove at high tide (Oct. 2016), samples were taken at high tide during a period of 10 days to determine light-mediated diel variation. A., E., I.: pHT continuous readings from SeaFET sensors, open dots are spectrophotometric pHT. Error bars are the propagated instrumental error on the CO₂ system parameters derived from TA and DIC.

Figure 6. A. - B. Time series of measured TAN and DICn in the reef (light blue), seagrass meadow (green), mangrove (brown) and reference pelagic station (black). C. - D. calculated $p\text{CO}_2$ and Ω_{arag} in the three benthic ecosystems. E. – F., TAN and DICn difference between benthic ecosystems and pelagic reference station. Error bars are the propagated instrumental error on the CO_2 system parameters derived from TA and DIC.

Figure 7. A. – C., TAn - DICn relationship in reef (blue), seagrass meadow (green) and mangrove (brown). Dotted lines represent the stoichiometric ratios of the major biogeochemical processes. Red solid line: linear regression; D. – E., TAn and DICn anomaly due to benthic ecosystems estimated as the difference with the pelagic reference station and the reef, seagrass and mangrove. D. Open dots are Winter-Spring data and plain dots are summer - autumn data in the Reef.