“High-resolution ocean pH dynamics in four subtropical North Atlantic coastal habitats

~~High-resolution ocean pH dynamics in four subtropical Atlantic benthic habitats~~

C. A. Hernández, S. Clemente, C. Sangil and J. C. Hernández*

[1]{Departamento de Biología Animal, Edafología y Geología, Facultad de Ciencias (Sección Biología), Universidad de La Laguna, Tenerife, Canary Islands, Spain}

Correspondence to: J. C. Hernández (jocarher@ull.es)

Abstract

Oscillations of ocean pH have not been well studied in shallow coastal waters, and such variability remains not available for certain world regions. However, these dataset are of great importance for ocean acidification studies, yet they have been relatively neglected~~Oscillations of ocean pH are largely unknown in coastal environments and ocean acidification studies often do not account for natural variability yet most of what is known about marine species and populations is found out via studies conducted in near shore environments. Most experiments designed to make predictions about future climate change scenarios are carried out in coastal environments with no research that takes into account the natural pH variability~~. In order to fill this knowledge gap and to provide reliable measures of pH oscillation, seawater pH was measured over time using moored pH sensors in four contrasting ~~phytocenoses~~ sites typical of the north Atlantic subtropical region. Each ~~phytocenosis~~ site was characterized by its predominant engineer species: 1) *Cystoseira abies-marina*, 2) a mix of gelidiales and geniculate corallines, 3) *Lobophora variegata*, and 4) encrusting corallines. The autonomous pH measuring systems consisted of a pH sensor; a data logger and a battery encased in a waterproof container and allowed the acquisition of high-resolution continuous pH data at each of the study sites. A diurnal pH and temperature cycle was detected at all sites: pH ranged at the different studied sites ~~The pH variation observed~~ ~~ranged~~ by between 0.09 and 0.24 pH_{NBS} units. A clear daily variation in seawater pH, driven by the

photosynthesis – respiration cycle, was detected at all the studied sites, with minimum values in the morning and high values in the afternoon (mean daily variation range of 0.04 - 0.12 pH_{NBS} units). Also, seawater pH at these coastal sites was higher in winter – spring when compared to autumn. Significant differences in daily pH oscillations were also observed between ~~phytocenoses~~sites, which show~~s~~ that macroalgal communities influence the seawater pH in benthic habitats. Natural oscillations in pH must be taken into account in future ocean acidification studies to put findings in perspective and for any ecological recommendations to be realistic.

1 Introduction

Over the past 250 years, anthropogenic CO_2 emissions have caused an increase of atmospheric CO_2 concentration from 280 ppmv (parts per million volume) to 397.15 ± 0.10 ppm averaged over 2014~~387 ppmv~~ (Le Querè et al., ~~2009~~2015). It has been stated that ~~-~~this concentration can be over 500 ppm for the most optimistic scenario at the end of the current century and exceed 800 ppm for the most pessimistic ones ~~will double by the end of the current century~~ (~~Houghton et al., 2001~~IPCC, 2014). Oceans act as an important carbon sink: from ~~2000 -~~1750 to ~~2006~~2014, the oceans absorbed approximately ~~24~~29% of total anthropogenic CO_2 emissions (~~Canadell et al., 2007~~Le Quéré et al., 2015) reducing CO_2 ~~levels present~~increase in the atmosphere (~~IPCC, 2007;~~ Sabine and Feely, 2007, IPCC, 2014). However, when CO_2 dissolves in seawater the gas reacts and forms carbonic acid (H_2CO_3) which then can dissociate and ~~lose~~ release hydrogen ions resulting ~~in~~ in an increase in bicarbonate ions and a decrease in carbonate ions~~the formation of bicarbonate and carbonate ions~~. It is the increase in concentrations of bicarbonate and hydrogen ions that lower the pH of seawater and causes ocean acidification. Over the last 200 years surface ocean pH has ~~ocean pH is thought to have~~ decreased by approximately 0.1 units, from 8.21 to 8.10 (Royal Society, 2005; Kleypas, 2006). Based on specific scenarios, ~~I~~it is predicted that pH ~~will~~ can decrease by a further 0.3 - 0.4 units by the end of the century (Orr et al., 2005; Doney et al., 2009; IPCC, 2014).

Recently, the effects of ocean acidification on marine ecosystems have been an important research area. Numerous laboratory studies have been published showing evidence that ocean acidification influences development, growth, physiology and survival of marine organisms, especially calcifying species (Orr et al., 2005; Fine and Tchernov, 2007; Ries et al., 2009; Dupont et al., 2013). Studies have demonstrated a wide range of responses to seawater

Con formato: Fuente: Sin Cursiva

acidification by different taxonomic groups (Doney et al., 2009; Kroeker et al., 2013). However, most studies designed to identify the effects of ocean acidification use as 'control' conditions ~~already available~~ global average values of surface water carbon chemistry parameters~~use already available average values of carbon chemistry parameters~~ (pH ~~oscillation~~, total alkalinity, pCO_2 and dissolved inorganic carbon) instead of measuring them in situ (McElhany and Busch, 2012). Separate studies specifically measuring pH and carbonate levels in the same habitats often result in values that are inconsistent with pCO_2 averages used in laboratory ~~studies~~studies, because these averages do not take into consideration the natural spatial and temporal variability of these parameters. Experiments designed to assess the impact of ocean acidification should therefore also measure carbon chemistry within the studied habitats of the model species used. Laboratory experiments also tend to focus on testing responses to values of pH and pCO_2, and saturation states for calcite and aragonite, ~~.~~anticipated in the near future based on atmospheric CO2 values~~anticipated in the near future~~ (Kroeker et al., 2013; CBD, 2014;~~see review by~~ Dupont and Thorndyke, 2013). Yet it has also been reported that pH in the oceans is not constant; temporal and spatial variations do exist (Hoffman et al., 2011). Experimental studies often neglect local environmental pH variability as well as other important environmental parameters and stressors that have adaptive impacts on populations (Joint et al., 2011). The combined impacts of ocean acidification and multiple stressors and their natural variability are largely unknown but may have a large influence on our predictions of future climate change scenarios (Breitburg et al., 2015). In coastal environments in particular, variability may be amplified due to the ambient heterogeneity and biological activity (Middelboe and Hansen, 2007). For instance, little is known about the influence of different macroalgae stands on seawater pH.

~~Little is known about the influence of different phytocenoses on pH. However, a~~ In oligotrophic open ocean areas pH variation tends to be lower, for example daily variations in pH were between 0.02 to 0.10 units over a 30 days period (Hoffman et al., 2011). A pronounced 24 hour cycle of pH has been documented in Pacific coastal environments around America, with pH values varying by ± 0.24 units in a single day (Wooton et al., 2008). In the open ocean, diurnal variation is not as pronounced: an average pH range of 0.024 units is more typical (Hoffman et al., 2011). In shallow water coastal environments surface water pCO_2 ~~is also~~may be significantly higher and pH levels lower than the values expected based on equilibrium with current atmospheric levels (Fagan and Mackenzie, 2007; Bates et al.,

2010; Thomsen et al., 2010; Shamberger et al., 2011; Yu et al., 2011; Hofmann et al., 2011). ~~However, little is known about the influence of different phytocenoses on seawater pH.~~

In this ~~paper~~paper, we studied temporal pH variation in four different shallow water phytocenoses common in the North Atlantic subtropical region. Our main objective was to assess natural in situ pH values and daily cycles in contrasting coastal habitats, in order to provide information of this geographic area that will inform future ocean acidification studies.

2 Material and Methods

Four study sites, each with a contrasting dominant engineer species, were selected in shallow water coastal sites around the Canary Islands. The sites (four different phytocenoses) represent the most common rocky bottom ecosystems occurring in the Atlantic archipelagos (Azores, Madeira, Salvages and the Canary Islands): (1) *Cystoseira abies-marina* canopy-forming systems (2) a mixed turf of Gelidiales and geniculate corallines (*Gelidium canariense*, *G. arbuscula*, *Pterocladiella capilacea*) and geniculate corallines (*Haliptilon virgatum*, *Ellisolandia elongata*, *Jania adhaerens*) (3) *Lobophora variegata* stands (Sangil et al., 2011) and (4) sea urchin barren grounds dominated by crustose algae due to the grazing activity of the sea urchin *Diadema africanum* (Hernández et al., 2008). The characteristics of each phytocenosis are summarized in Supplement 1A.

A moored pH measuring system was deployed at each of the study sites (Supplement 1B). Each system consisted of a Seabird SBE 18 pH sensor attached to a data logger combined with a temperature sensor and a lead battery protected inside a waterproof container. Each system was placed inside a plastic box with several openings to allow water circulation and this box was firmly attached to the rocky bottom using a pneumatic drill at ~~about~~ the range of 6 to 8 meters depth~~5 to 10 meters depth~~ in each site (Fig. 1). Changes of depth due to local tydes were of near 1.5 meters.

The pH sensors were previously calibrated against NIST buffer solutions (4, 7 and 10 pH ±0.02) using the software SEASOFT and its module pHfit. The loggers were programmed to take pH and temperature measurements once every 30 minutes and the systems were deployed for 15 days during two time periods at each site (see details in Table 1). One of the time periods took place during autumn, when sea surface temperature reaches the annual maximum and a seasonal thermocline, causing the stratification of the water column, is

formed. The other deployment time period was in winter – spring, after that seasonal thermocline has disappeared, causing the mixing of the water column and the input of new nutrients from deep waters (De León & Braun 1973; Barton et al., 1998). We found that with a deployment time of 15 days problems associated with biofouling did not occur and the calibration parameters had not significantly changed. The timing of deployment and retrieval of the pH systems was dependent on sea state and measurements could therefore not be made simultaneously at all four sites due to logistic restrictions. The study was also disrupted because the pH sensor located in the encrusting coralline algae site was subject to vandalism during the second sampling period - no data could be gathered for this particular time in this phytocenosis. The location and study periods for each different site are summarized in Table 1.

Carbonate system parameters

At each site, samples were taken during each deployment for the measurement of carbonate system parameters. Triplicate water samples were taken during three different days of each sensor deployment. The samples were stored in borosilicate bottles and hermetically sealed with a plastic cap. Seawater total alkalinity (TA) was measured using an open cell potentiometric titration with a Metrohm Dosimat 665 titrator using 0.01 N HCl with a salinity of about 35 and following the Standard Operation Procedure 3b (Dickson et al., 2007). Alkalinity measurements took place two to three hours after sampling, so there was no need of poisoning the samples. Salinity was measured in situ using a handheld conductivity meter (WTW COND 315i). The rest of the carbonate chemistry parameters were calculated using salinity, temperature, TA and pH using the package seacarb 3.08 for R (https://cran.r-project.org/web/packages/seacarb/). Calculations were based on a set of constants, K1 and K2, taken from Lueker et al. (2000).

3 Results.

3 Diurnal variability

All four sites displayed a clear 24 hour pH cycle. The lowest pH values were recorded in the morning between 8:00 and 10:00 am, and values were highest between 15:00 and 19:00 pm, though there were differences between phytocenoses (Fig. 2, Table 1a). Mean site-specific pH_{NBS} ~~Overall pH_{NBS}~~ values measured in this study ranged between 8.04 (*Cystoseira abies-*

Con formato: Subrayado, Inglés (Estados Unidos)
Con formato: Normal
Con formato: Subrayado
Con formato: Subíndice

marina community, autumn) and 8.10 (gelidiales-genicullate corallines and *C. abies-marina*, spring). The greatest pH_{NBS} per sampling period variation occurred in the *C. abies-marina* community during autumn 2011 (0.24, ranging from 8.04 to 8.28). The lowest pH_{NBS} variation was 0.09 recorded in the gelidiales-genicullate coralline community in autumn 2011. In the remaining sites and time periods pH_{NBS} varied by 0.12 - 0.16. The highest mean pH_{NBS} per time period was measured in the gelidiales-genicullate corallines and *Cystoseira* communities in spring 2012 (pH_{NBS} 8.23) and the lowest mean value was recorded in the gelidiales-genicullate corallines in autumn 2011 (pH_{NBS} 8.10).

The exact timing of daily pH_{NBS} maxima and minima was different in each phytocenoses (Fig. 2 and 3). The highest daily values were generally recorded in the afternoon, between 15:00 and 16:00 pm hrs. but at the *C. abies-marina* site these maxima occurred later in the day, between 18:00 and 19:00 pm hrs.

~~In the gelidiales-genicullate coralline site, daily variation and daily means differed between the two studied periods. In the gelidiales-genicullate phytocenosis, pH_{NBS} varied by 0.08 units over a 24 hour cycle in March 2012 compared to 0.04 units variation in autumn 2011 (Fig. 2). At the same site mean pH_{NBS} was higher in the spring period (pH_{NBS} 8.23) compared to autumn (pH_{NBS} 8.10) (Table 1).~~Based on mean pH_{NBS} per hour, the diurnal cycle was more noticeable in the *C. abies-marina* site in autumn 2011, where daily pH_{NBS} values varied by; 0.12 units (Figs. 2 and 4). The same site in May 2012 still showed a clear daily pattern (Fig. 4) but the variation in values was smaller, just 0.08. Mean daily variation was lowest (0.04 pH_{NBS} units/day) in the gelidiales-genicullate coralline site in November 2011 and *Lobophora variegata* site in 2011(Fig. 2 and 4). The crustose algae phytocenosis could only be examined in Oct 2011, due to vandalism of experimental equipment, and daily pH_{NBS} varied by 0.05 units at this site (Figs. 2 and 4).

Seawater temperature at each site showed the expected daily variations. The daily distribution of temperature followed a pattern similar to that of pH, with minimum values in the morning (between 8:00 and 10:00) and daily peaks in the afternoon (between 15:30 and 18:00) (Fig. 3). The afternoon temperature peak occurred later, at 18:00, in the *Cystoseira abies-marina* site in autumn and earlier, at 15:30, in the *Lobophora variegata* site in autumn.

Seawater temperature variation range during the studied time periods ranged from 0.8ºC recorded at the *L. variegata* site in winter (from 17.9ºC to 18.6ºC) to 3.1 ºC at the *C. abies-marina* site in autumn (from 19.ºC to 22.1ºC) (Table 1b). The *C. abies-marina* temperature

data in autumn oscillated 2.4ºC (from 22.4 ºCto 24.8ºC)., Gelidiales variation range in autumn was 2.3ºC (20.7ºC-23ºC) and 1.1ºC (17.7ºC – 18.8ºC) in spring. *L. variegata* in autumn showed a temeperature range of 1.2 ºC (22.7ºC-23.9ºC) and at the crustose coralline site, which only could be studied during an autumn time period, seawater temperature ranged from 23.0ºC to 24.2ºC, a 1.2ºC variation range.

Seasonal variability

Seasonal variations in pH_{NBS} existed along with the daily cycle, with a similar variation range. Mean seawater pH during the sampling periods was generally lower in autumn at all sites. In the *Cystoseira abies-marina* site, mean pH during the autumn sampling period was 8.15+-0.05 (Table 1), while at the same site during the spring period it was 8.23+-0.03. In the Gelidiales and geniculate corallines site, mean pH was 8.10+-0.02 in autumn and 8.23+-0.03 in spring. The *Lobophora variegata* site showed less differences in pH between periods, with a mean pH of 8.15+-0.02 in autumn and 8.17+-0.03 during the winter data collection.

In the gelidiales-genicullate coralline site, daily variation and daily means differed between the two studied periods. In the gelidiales-genicullate phytocenosis, pH_{NBS} varied by 0.08 units over a 24 hour cycle in March 2012 compared to 0.04 units variation in autumn 2011 (Fig. 2). At the same site mean pH_{NBS} was higher in the spring period (pH_{NBS} 8.23) compared to autumn (pH_{NBS} 8.10) (Table 1a).

Mean seawater temperature during the autumn data collection periods ranged from 22.2+-0.4 ºC at the Gelidiales site to 23.6+-0.3ºC at the Crustose Corallines site. At —*Lobophora variegata* it was 23.3+-0.2ºC and at *Cystoseira abies-marina*, 23.4+-0.5ºC (Table 1b). During –the winter – spring periods, seawater temperature was lower. The sensors were deployed during February – March at the Gelidiales and *L. variegata* sites (Table1b) and temperature at these locations was 18.3+-0.3ºC and 18.2+-0.1ºC respectively. Data from *Cystoseira abies-marina* -wereas collected later, in May, and seawater temperature was higher (20.2+-0.7ºC, Table 1b).

Carbonate System parameters.

Contrary to pH, total alkalinity did not show a noticeable pattern between measurements performed in the morning and in the evening at the studied sites. (Table XX2). The daily pH oscillation was related to a daily oscillation of pCO2, DIC and calcite and aragonite saturation states. pCO2 at the *C. abies-marina* site, where pH variation was more noticeable, reached

Con formato: Subrayado

Con formato: Subíndice

Con formato: Fuente: Cursiva

Con formato: Fuente: Cursiva

Con formato: Fuente: Cursiva

Con formato: Resaltar

minimum values of 195.77 µatm in the spring period and a maximum pCO2 of 425.42 µatm in autumn, in the morning, when pH was lower. Aragonite saturation states were always higher than 3, with a maximum value of 5.13 at *C. abies-marina*, being always the water oversaturated respect to this CaCO3 polymorph. ~~Despite seasonal variations in pH_{NBS}, a daily pattern was still apparent though its range was relatively small in comparison. Based on mean pH_{NBS} per hour the diurnal cycle was clearest in the *C. abies-marina* site in autumn 2011, where daily pH_{NBS} values varied by; 0.12 units (Fig. 2 and 3). The same site in May 2012 still showed a clear daily pattern (Fig. 3) but the variation in values was smaller, just 0.08. Mean daily variation was lowest (0.04 pH_{NBS} units/day) in the gelidiales-genicullate coralline site in November 2011 and *Lobophora variegata* site in 2011(Fig. 2 and 3). The crustose algae phytocenosis could only be examined in Oct 2011, due to vandalism of experimental equipment, and daily pH_{NBS} varied by 0.05 units at this site (Fig. 3).~~

~~The exact timing of daily pH_{NBS} maxima and minima was different in each phytocenoses (Fig. 2 and 3). The highest daily values were generally recorded in the afternoon, between 15:00 and 16:00 pm hrs. but at the *C. abies marina* site these maxima occurred later in the day, between 18:00 and 19:00 pm hrs.~~

~~In the gelidiales-genicullate coralline site, daily variation and daily means differed between the two studied periods. In the gelidiales-genicullate phytocenosis, pH_{NBS} varied by 0.08 units over a 24 hour cycle in March 2012 compared to 0.04 units variation in autumn 2011 (Fig. 2). At the same site mean pH_{NBS} was higher in the spring period (pH_{NBS} 8.23) compared to autumn (pH_{NBS} 8.10) (Table 1).~~

4 Discussion

The data showed that daily pH variation differed between phytocenoses, and that the observed differences seem to be related to algae productivity. This suggests that in coastal environments the type of phytocenosis present influences the pH gradient inhabited by all organisms within that ecosystem. Continuous monitoring of pH in four contrasting habitats has revealed that the largest variation in pH throughout the sampling period and the highest daily variation in pH values occurred in the *Cystoseira abies-marina* phytocenesis in autumn 2011. Daily fluctuations in pH were clear at this site, where algal cover was higher compared to the three other studied phytocenoses (Table 1). *Cystoseira abies-marina* is a perennial species present throughout the whole year and tends to form large accumulations of drift algae

along the edge of the seashore. The high algal biomass of *Cystoseira abies-marina* and associated high levels of primary production could be key to the large daily fluctuations in pH at this site; since high levels of CO_2 uptake during periods of photosynthesis and CO_2 release during non-photosynthetic periods could cause pH to vary more widely.

The diel patterns exhibited in the coastal ecosystems studied are similar to diel patterns observed in coral reef ecosystems in Hofmann et al. (2011). Daily variation was characterized by consistent and moderate fluctuations ranging from 0.1 to 0.25 pH units/day. Other comparable diurnal pH fluctuations measured elsewhere were 0.1 units/day in spring in the Bay of Calvi in the Mediterranean (Frankignoulle and Bouquegneau, 1990) and 0.15/day in autumn in the Bay of Bengal in the Indian Ocean (Subramanian and Mahadevan, 1999). ~~In oligotrophic open ocean areas pH variation tends to be lower, for example daily variations in pH were between 0.02 to 0.10 units over a 30 days period (Hoffman et al., 2011).~~ In comparison, diurnal variations up to 0.5 units/day were observed in a productive Kelp forest close to the Kerguelen Archipelago in the Southern Ocean in austral summer (Delille et al., 2009). In coastal areas influenced by nutrient-laden rivers, eutrophication has shown to enhance acidification, with bacterial respiration causing hypoxia and lowering seawater pH after a period of high algae production (Cai et al., 2011).

Seawater pH can be modulated by different sources of variation, including temperature, currents or tides and biological activity (Dai et al., 2009). In open ocean oligotrophic areas, temperature is the main source of pH variability, affecting the CO2 solubility in seawater, while in nearshore areas tidal effects that cause the mixing of water masses and biological activity have a bigger role in the carbonate system dynamics, as seen in Jiang et al. (2011).

The daily pH cycle detected at all four sites in the present study can be explained mainly by daily variations in photosynthesis and~~,~~ respiration, though ~~and~~ seawater temperature can have some minor influence. The daily SST variation follows a daily pattern similar to that of pH daily variation (Fig. 3), following the diurnal cycle of solar radiation, which affects the diurnal cycle of photosynthetic activity, but the pH variation range is too large (especially in the *C. abies-marina* site) to be explained solely by the effect of temperature. Another pH controlling factor may be the water masses mixing driven by tidal activity, currents or upwelling processes. However, and although ~~,~~we did not obtain data to assess the importance of these sources of pH variation (ie. tidal height), reduced tidal range in the Islands (1.5m) would have little effect on pH. In the studied sites there are not nearby sources of fresh water,

Con formato: Resaltar

Con formato: Fuente: Sin Cursiva

Con formato: Fuente: Sin Cursiva

Con formato: Fuente: Sin Cursiva

as there are not permanent streams of water in the Canary Islands, so possible effects of fresh water input are discarded. All the studied sites showed a pH increase during the day, reaching a maximum during the afternoon and a decrease during the night with a minimum early in the morning. This cycle can be mainly explained by the ~~Seawater pH increase~~of seawater pH~~s~~the biological activity of the sites. PH increases throughout the daytime ~~when~~when ~~–~~CO2 is captured by photosynthetic organisms (macroalgae and phytoplankton)~~ throughout the daytime~~, and then decrease~~s~~ at night when CO2 is respired and diffuses from the ocean to the atmosphere (Bensoussan and Gattuso, 2007).

Our data also shows that some seasonal variation in pH exists; mean pH values were higher in the winter-spring period compared to the autumn. The late winter-spring season is when the highest growth rates of engineer species occur in these phytocenosis ~~in~~ off the Canary Islands (Medina and Haroun, 1994; Montañés et al., 2006). The spring growth of these engineer species is triggered by the breakdown of the seasonal thermocline, at late winter or early spring, when cold nutrient-rich deep waters mix with the upper, nutrient-depleted waters (De León & Braun 1973; Barton et al., 1998), and by the availability of more daylight hours.

The highest seasonal pH variability, as much as 0.13 pHNBS units, was recorded in the gelidiales-genicullate coralline phytocenosis. The variation in pH recorded here was double that previously observed in the Canary Islands region; a value of 0.055 pH units from the European Station for Time Series in the Ocean (González-Dávila and Santana-Casiano, 2011). At this oceanic station, pH variability is closely coupled to temperature variability, with lowest values during winter and an increase during summer (Santana-Casiano et al., 2007), which contrasts with our data ~~,~~ ~~–~~where the lower pH values were recorded in autumn and higher pH occurred in winter-spring. ~~–~~However, seawater samples from the European Station for Time Series in the Ocean were collected in an open ocean area, not in shallow coastal water sites such as we used in our study, where the main pH modulating factor is the biological activity (photosynthesis – community respiration).~~.~~

The shallow coastal areas studied here, as well as others around the world, are subject to greater variation in a number of environmental parameters that influence spatial and temporal pH; both biotic factors (photosynthesis, respiration) and abiotic (freshwater input, nutrient concentration, tides, local upwelling or volcanic activity). The influence of these factors on seawater pH can surpass the effect of temperature. The organisms living in coastal areas are therefore continuously coping with relatively large oscillations in pH and these oscillations

Con formato: Fuente: Sin Cursiva

may increase in the future due to rising seawater CO_2 concentrations that will decrease the ocean's natural buffering capacity (Schulz and Riebsell, 2012).

Coastal regions have complex spatial and temporal variation in carbon chemistry. The results of our study suggest that local carbon chemistry should be measured and taken into consideration when designing ocean acidification experiments in preference to the use of regional averages. The existence of diurnal, seasonal and spatial variation in pH should also be incorporated into models of ocean pH and allowed for in studies with benthic species and populations that aim to assess the effect of ocean acidification.

Author contribution

CAH and JCH design the study and JCH, CS and SC carried them out. CAH and JCH prepared the manuscript with contributions from all co-authors.

Acknowledgements

This manuscript was written within the framework of the project Plan Nacional de Investigación of the Spanish Ministerio de Economía y Competitividad, BLUEROCK, CGL 2013_43908_R. Thanks to J. Manning (from 'Science Correct') who improved earlier versions of the manuscript.

References

Barton, E. D., Arístegui, J., Tett, P., Cantón, M., García-Braun, J., Hernández-León, S., Nykjaer, L., Almeida, C., Almunia, J., Ballesteros, S., Basterretxea, G., Escánez, J., García-Weill, L., Hernández-Guerra, A., López-Laatzen, F., Molina, R., Montero, M. F., Navarro-Pérez, E., Rodríguez, J. M., van Lenning, K., Vélez. H. and Wild, K.: The transition zone of the Canary Current upwelling region, Progr. Oceanogr., 41, 455-504, 1998.

Bates, N. R., Amat, A. and Andersson, A. J.: Feedbacks and responses of coral calcification on the Bermuda reef system to seasonal changes in biological processes and ocean acidification. Biogeosciences, 7, 2509-2530, 2010.

Bensoussan, N. and Gattuso, J. P.: Community primary production and calcification in a NW Mediterranean ecosystem dominated by calcareous macroalgae. Mar. Ecol. Prog. Ser., 334: 37-45, 2007.

Breitburg, D.L., J. Salisbury, J.M. Bernhard, W.-J. Cai, S. Dupont, S.C. Doney, K.J. Kroeker, L.A. Levin, W.C. Long, L.M. Milke, S.H. Miller, B. Phelan, U. Passow, B.A. Seibel, A.E. Todgham, and A.M. Tarrant. And on top of all that… Coping with ocean acidification in the midst of many stressors. Oceanography 28(2):48–61, 2015. http://dx.doi.org/10.5670/oceanog.2015.31.

Cai, W. J., Hu, X., Huang, W., Murrell, M. C., Lehrter, J.C., Lohrenz, S.E:, Chou, W-, Zhai, W., Hollibaugh, J.T., Wang, Y. Zhao, P. Guo, X., Gundersen, K., Dai, M. And Gong, G: Acidification of subsurface coastal waters enhanced by eutrophication, Nat Geosci, 4(11), 766-770, 2011.

Canadell, J.G., Le Quere, C., Raupach, M. R., Field, C. B., Buitenhuis, E. T., Ciais, P., Conway, T. J., Gillett, N. P., Houghton, R. A. and Marland, G.: Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks. Proc. Natl. Acad. Sci. USA, 104, 18866-18870, 2007.

Dai, M. H., Lu, Z. M., Zhai, W. D., Chen B. S., Cao Z. M., Zhou K. B., Cai W. J., and. Chen, C. T. A: Diurnal variations of surface seawater pCO2 in contrasting coastal environments, Limnol. Oceanogr., 54(3), 735-745, 2009.

De León, A. R. and Braun, A. G.: Ciclo anual de la producción primaria y su relación con los nutrientes en aguas canarias. Bol. Inst. Esp. Oceanogr., 167, 1-24. 1973.

Con formato: Español (España)

Con formato: Español (España)

Delille, B., Borges, A. V. and Delille, D.: Influence of giant kelp beds (*Macrocystis pyrifera*) on diel cycles of pCO2 and DIC in the Sub-Antarctic coastal area. Estuar. Coast. Shelf. Sci., 81, 114-122. 2009.

Dickson, A. G., Sabine, C. L. and Christian, J. R. Guide to best practices for ocean CO2 measurements. PICES Special Publication. 3, 191, 2007.

Doney, S. C., Fabry, V. J., Feely, R.A. and Kleypas, J. A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Ann. Rev. Mar. Sci.~~Annual Review of Marine Science~~, 1, 169-192, 2009.

Dupont, S., Dorey, N., Stumpp, M., Melzner, F. and Thorndyke, M.: Long-term and trans-life-cycle effects of exposure to ocean acidification in the green sea urchin *Strongylocentrotus droebachiensis*, Mar. Biol., 160, 1835-1843, 2013.

Dupont, S. and Thorndyke, M. C.: Direct impacts of near-future ocean acidification on sea urchins, in: J. M. Palacios, L. De Nascimiento, J. P. Díaz-González, S. Clemente and J.C. Hernández (eds) Climate Change Perspectives from the Atlantic: Past, Present and Future. Servicio de Publicaciones de la Universidad de La Laguna, 2013.

Fagan, K. E. and Mackenzie, F. T.: Air-sea CO_2 exchange in a subtropical estuarine-coral reef system, Kaneohe, Bay, Oahu, Hawaii. Mar. Chem., 106, 174-191, 2007.

Fine, M., and Tchernov, D.: Scleractinian coral species survive and recover from decalcification. Science, 315, 1811, 2007.

Frankignoulle, M. and Bouquegneau, J. M.: Daily and yearly variations of total inorganic carbon in a productive coastal area. Estuar. Coast. Shelf. Sci., 30, 79-89, 1990.

González-Dávila, M. and Santana-Casiano, J. M.: Sea surface and atmospheric fCO_2 data measured during the ESTOC time series cruises from 1995-2009. data/ Carbon dioxide information analysis center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee Greenhouse Gas Sinks, CABI Publishing, Oxfordshire, UK, 1990.

Hofmann, G. E., Smith, J. E., Johnson, K. S., Send, U., Levin, L. A., Micheli, F., Paytan, A., Price, N. N., Peterson, B., Takeshita, Y., Matson, P. G., Crook, E. D., Kroeker, K. J., Gambi, M. C., Rivest, E. B., Frieder, C. A., Yu, P. C. and Martz, T. R.: High-frequency dynamics of ocean pH: a multi-ecosystem comparison. PloS one 6, 12, 2011.

Con formato: Español (España)

Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., Van der Lin- den, P. J., Dai, X., Maskell, K. and Johnson, C. A.: Climate Change 2001: The Scientific Basis. Cambridge University Press, Cambridge, UK, 2001.

IPCC Climate Change 2014: Impacts, Adaptation, and Vulnerability. Part A: Global and Sectoral Aspects. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Field, C.B., V.R. Barros, D.J. Dokken, K.J. Mach, M.D. Mastrandrea, T.E. Bilir, M. Chatterjee, K.L. Ebi, Y.O. Estrada, R.C. Genova, B. Girma, E.S. Kissel, A.N. Levy, S. MacCracken, P.R. Mastrandrea, and L.L. White (eds)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1132 pp., 2014.~~IPCC: Climate Change 2007: The Physical Science Basis. IPCC, Geneva, 2007.~~

Jiang, Z.-P., J. C. Huang, M. H. Dai, S. J. Kao, D. J. Hydes, W. C. Chou, and S. Jan: Short-term dynamics of oxygen and carbon in productive near shore shallow seawater systems off Taiwan: Observations and modeling, Limnol. Oceanogr., 56(5), 1832-1849, 2011.

Joint I, Doney SC, Karl DM Will ocean acidification affect marine microbes? The ISME Journal 5: 1–7., 2011.~~,~~

Kleypas, J. A., Feely, R. A., Fabry, V. J., Langdon, C., Sabine, C. L. and Robbins, L. L.: Report of a workshop sponsored by NSF, NOAA, and the U.S. Geological Survey. St. Petersburg, Florida, in: Impacts of ocean acidification on coral reefs and other marine calcifiers: a guide for future research, 2006.

Kroeker, K. J., Kordas, R. L., Crim, R. N. and Singh, G.: Meta-analysis reveals negative yet variable effects of ocean acidification on marine organisms. Ecol. Lett. 13, 1419-1434, 2013.

Le Quéré, C., Moriarty, R., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Friedlingstein, P., Peters, G. P., Andres, R. J., Boden, T. A., Houghton, R. A., House, J. I., Keeling, R. F., Tans, P., Arneth, A., Bakker, D. C. E., Barbero, L., Bopp, L., Chang, J., Chevallier, F., Chini, L. P., Ciais, P., Fader, M., Feely, R. A., Gkritzalis, T., Harris, I., Hauck, J., Ilyina, T., Jain, A. K., Kato, E., Kitidis, V., Klein Goldewijk, K., Koven, C., Landschützer, P., Lauvset, S. K., Lefèvre, N., Lenton, A., Lima, I. D., Metzl, N., Millero, F., Munro, D. R., Murata, A., Nabel, J. E. M. S., Nakaoka, S., Nojiri, Y., O'Brien, K., Olsen, A., Ono, T., Pérez, F. F., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Rödenbeck, C., Saito, S., Schuster, U., Schwinger, J., Séférian, R., Steinhoff, T., Stocker, B. D., Sutton, A. J., Takahashi, T., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., van Heuven, S., Vandemark, D.,

Viovy, N., Wiltshire, A., Zaehle, S., and Zeng, N.: Global Carbon Budget 2015, Earth Syst. Sci. Data, 7, 349-396, 2015. doi:10.5194/essd-7-349-2015, 2015.

~~Le Quéré, C., Moriarty, R., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Friedlingstein, P., Peters, G. P., Andres, R. J., Boden, T. A., Houghton, R. A., House, J. I., Keeling, R. F., Tans, P., Arneth, A., Bakker, D. C. E., Barbero, L., Bopp, L., Chang, J., Chevallier, F., Chini, L. P., Ciais, P., Fader, M., Feely, R. A., Gkritzalis, T., Harris, I., Hauck, J., Ilyina, T., Jain, A. K., Kato, E., Kitidis, V., Klein Goldewijk, K., Koven, C., Landschützer, P., Lauvset, S. K., Lefèvre, N., Lenton, A., Lima, I. D., Metzl, N., Millero, F., Munro, D. R., Murata, A., Nabel, J. E. M. S., Nakaoka, S., Nojiri, Y., O'Brien, K., Olsen, A., Ono, T., Pérez, F. F., Pfeil, B., Pierrot, D., Poulter, B., Rehder, G., Rödenbeck, C., Saito, S., Schuster, U., Schwinger, J., Séférian, R., Steinhoff, T., Stocker, B. D., Sutton, A. J., Takahashi, T., Tilbrook, B., van der Laan-Luijkx, I. T., van der Werf, G. R., van Heuven, S., Vandemark, D., Viovy, N., Wiltshire, A., Zaehle, S., and Zeng, N.: Global Carbon Budget 2015, Earth Syst. Sci. Data, 7, 349-396, 2015. doi:10.5194/essd-7-349-2015, 2015.~~

Lueker, T. J., Dickson, A.G. and Keeling, C. D. Ocean pCO2 calculated from dissolved inorganic carbon, alkalinity, and equations for K1 and K2: validation based on laboratory measurements of CO2 in gas and seawater at equilibrium. ~~Marine Chemistry~~Mar. Chem.~~,~~ 70, 105-119, 2000.

McElhany, P. and Busch, D. S.: Appropriate pCO2 treatments in ocean acidification experiments. Mar. Biol. 160, 1807-1812, 2013.

Medina, M., and Haroun, R.: Dinámica regresiva de una pradera submareal de *Cystoseira abies-marina* (Cystoseiraceae, Phaeophyta) en la isla de Tenerife. Vieraea, 23, 65-71, 1994.

~~Montañés, M. A., Sansón, M. and Reyes, J.: Vegetative and reproductive phenology of *Zonaria tournefortii* (Dictyotales, Phaeophyceae) in sublittoral populations off the Canary Islands. Bot. Mar. 49, 406-416, 2006.~~

Middelboe, A. L. and Hansen, P. J.: High pH in shallow-water macroalgal habitats. Mar. Ecol. Progr. Ser., 338, 107-117, 2007.

Montañés, M. A., Sansón, M. and Reyes, J.: Vegetative and reproductive phenology of *Zonaria tournefortii* (Dictyotales, Phaeophyceae) in sublittoral populations off the Canary Islands. Bot. Mar., 49, 406-416, 2006.

Con formato: Inglés (Estados Unidos)

Orr, J. C., Fabry, V. J., Aumont, O., Bopp, L., Doney, S. C., Feely, R. A., Gnanadesikan, A., Gruber, N., Ishida, A., Joos, F., Key, R. M., Lindsay, K., Maier-Reimer, E., Matear, R., Monfray, P., Mouchet, A., Najjar, R. J., Plattner, G. K., Rodgers, K. B., Sabine, C. L., Sarmiento, J. L., Schlitzer, R., Slater, R. D., Totterdell, I. J., Weirig, M. F., Yamanaka, Y. and Yool, A.: Anthropogenic ocean acidification over the twenty-first century and its impact on calcifying organisms. Nature, 437, 681-686, 2005.

Ries, J. B., Cohen, A. L. and McCorkle, D. C.: Marine calcifiers exhibit mixed responses to CO_2-induced ocean acidification., Geol. 37, 1131-1134, 2009.

Royal Society: Ocean acidification due to increasing atmospheric carbon dioxide. London: The Royal Society, 2005.

Sabine, C. L. and Feely, R. A.: Greenhouse Gas Sinks, in D. Reay, N. Hewitt, J. Grace, and K. Smith (eds), CABI Publishing, Oxfordshire, UK, 31-49, 2007.

Santana-Casiano, J. M.,M. González-Dávila,M.-J. Rueda, O. Llinás, and E.-F. González-Dávila: The interannual variability of oceanic CO_2 parameters in the northeast Atlantic subtropical gyre at the ESTOC site. Global Biogeochem. Cycles, 21, GB1015, 2007. doi:10.1029/2006GB002788.

Schulz, K. G. and Riebesell, U.: Diurnal changes in seawater carbonate chemistry speciation at increasing atmospheric carbon dioxide. Mar. Biol., 160, 1889-1899, 2013.

Secretariat of the Convention on Biological Diversity (SCBD). An Updated Synthesis of the Impacts of Ocean Acidification on Marine Biodiversity (Eds: S. Hennige, J.M. Roberts & P. Williamson). Montreal, Technical Series No. 75, 99 pages, 2014.g

Shamberger, K. E. F., Feely, R. A., Sabine, C., Atkinson, M. J., DeCarlo, E. H., Mackenzie, F. T., Drupp, P. S. and Butterfield, D. A. Calcification and organic production on a Hawaiian coral reef, Mar. Chem., 127, 64-75, 2011.

Subramanian, B. and Mahadevan, A.: Seasonal and diurnal variation of hydrobiological characters of coastal water of Chennai (Madras), Bay of Bengal. Ind. J. Mar. Sci., 28, 429-433, 1999.

Thomsen, J., Gutowska, M. A., Saphorster, J., Heinemann, A., Trubenbach, K., Fietzke, J., Hiebenthal, C., Eisenhauer, A., Kortzinger, A., Wahl, M. and Melzner, F.: Calcifying

Con formato: Fuente: (Predeterminada) Times New Roman, 12 pto

Con formato: Fuente: (Predeterminada) Times New Roman, 12 pto

Con formato: Fuente: (Predeterminada) Times New Roman, 12 pto

invertebrates succeed in a naturally CO_2-rich coastal habitat but are threatened by high levels of future acidification. Biogeosciences, 7, 3879-3891, 2010.

Yu, P. C., Matson, P. G., Martz, T. R. and Hofmann, G. E.: The ocean acidification seascape and its relationship to the performance of calcifying marine invertebrates: Laboratory experiments on the development of urchin larvae framed by environmentally-relevant pCO_2/pH, J. Exp. Mar. Biol. Ecol., 400, 288-295, 2011.

Supplement 1:

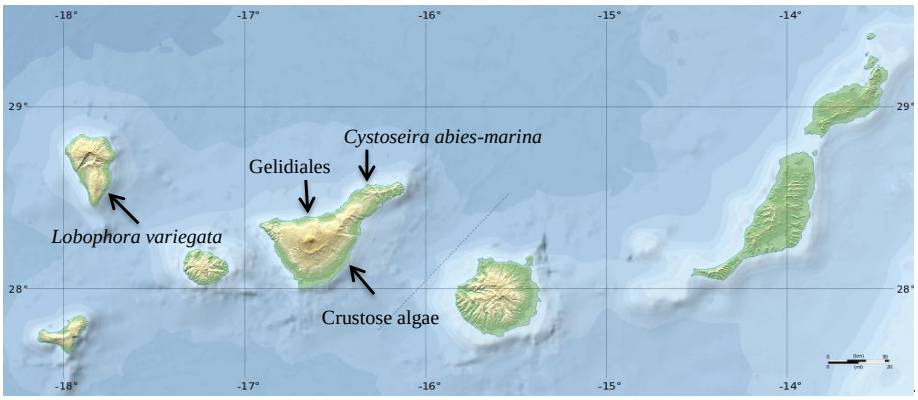
A. Characteristics of the four studied phytocenoses.

Phytocenosis	*Growth form*	*Cover*	*Thalli lengh*
Cystoseira abies-marina	Perennial	200-400%	300-600 mm
Gelidiales and geniculate corallines	Perennial	40-80%	100 mm
Lobophora variegata	Perennial	150-250%	50-100 mm
Crustose algae	Perennial and annual	40-60%	5 mm

B. Locations of study sites where pH sensors were deployed.

Phytocenosis	*Site*	*Island*	*Latitude*	*Longitude*
Cystoseira abies marina	Punta del Hidalgo	Tenerife	28º34'07.23''N	16º20'00.12''W
Gelidiales and geniculate corallines	Puerto de la Cruz	Tenerife	28º25'05.03''N	10º32'44.71''W
Lobophora variegata	Las Cabras	La Palma	28º27'54.02''N	17º49'51.72''W
Crustose coralline	Abades	Tenerife	28º08'27.73''N	16º26'09.81''W

C. Location of each site and their associated phytocenoses.



Con formato: Inglés (Reino Unido)

Table 1.

a) Descriptive statistics for pH profiles at each site.

Phytocenosis	Time period	Range	Min	Max	Mean	*SD*
Cystoseira abies-marina	Autumn 28/9/11-13/10/11	0.24	8.04	8.28	8.15	0.05
	Spring 4/5/12-18/5/12	0.15	8.16	8.31	8.23	0.03
Gelidiales and geniculate corallines	Autumn 25/10/11-9/11/11	0.09	8.07	8.16	8.10	0.02
	Spring 14/3/12-29/3/12	0.14	8.17	8.31	8.23	0.03
Lobophora variegata	Autumn 19/10/11-3/11/11	0.12	8.08	8.20	8.15	0.02
	Winter 17/2/12-3/3/12	0.15	8.09	8.24	8.17	0.03
Crustose coralline	Autumn 7/10/11-22/10/11	0.16	8.08	8.24	8.14	0.03

b) Descriptive statistics for Temperature profiles at each site.

Phytocenosis	Time period	Range	Min	Max	Mean	*SD*
Cystoseira abies-marina	Autumn 28/9/11-13/10/11	2.4ºC	22.4ºC	24.8ºC	23.4ºC	0.5ºC
	Spring 4/5/12-18/5/12	3.1ºC	19.01C	22.1ºC	20.2ºC	0.7ºC
Gelidiales and geniculate corallines	Autumn 25/10/11-9/11/11	2.3ºC	20.7ºC	23.0ºC	22.2ºC	0.4ºC
	Spring 14/3/12-29/3/12	1.1ºC	17.7ºC	18.8ºC	18.3ºC	0.3ºC
Lobophora variegata	Autumn 19/10/11-3/11/11	1.2ºC	22.7ºC	23.9ºC	23.3ºC	0.2ºC
	Winter 17/2/12-3/3/12	0.8ºC	17.9ºC	18.6ºC	18.2ºC	0.1ºC
Crustose coralline	Autumn 7/10/11-22/10/11	1.2ºC	23.0ºC	24.2ºC	23.6ºC	0.3ºC

Tabla con formato

		Ta (µmoles kg-1)		pH		pCO2 (µatm)		DIC (µmoles kg-1)		Ωaragonite	
Phytocoenosis	**Time period**	**Morning**	**Evening**	**Morning**	**Evening**	**Morning**	**Evening**	**Morning**	**Evening**	**Morning**	**Evening**
Cystoseira abie-marina	Autumn	2435.353	2426.542	8.04	8.28	425.42	209.00	2135.47	1954.86	3.36	5.13
	Spring	2443.968	2449.023	8.16	8.31	305.43	195.77	2095.13	1986.03	3.79	4.97
Gelidiales - gen. corallines	Autumn	2479.797	2466.544	8.09	8.12	377.93	344.66	2155.90	2120.73	3.62	3.85
	Spring	2437.573	2431.570	8.19	8.27	280.25	220.99	2088.53	2024.71	3.77	4.36
Lobophora variegata	Autumn	2605.231	2592.200	8.13	8.17	350.22	309.77	2223.38	2180.78	4.28	4.58
	Winter	2715.180	2717.560	8.15	8.21	350.41	295.21	2361.30	2318.85	3.96	4.43
Crustose coralline	Autumn	2430.051	2438.120	8.12	8.17	335.14	290.05	2073.55	2041.33	3.91	4.34

Table 2. Mean carbon system parameters at each site.

Tabla con formato

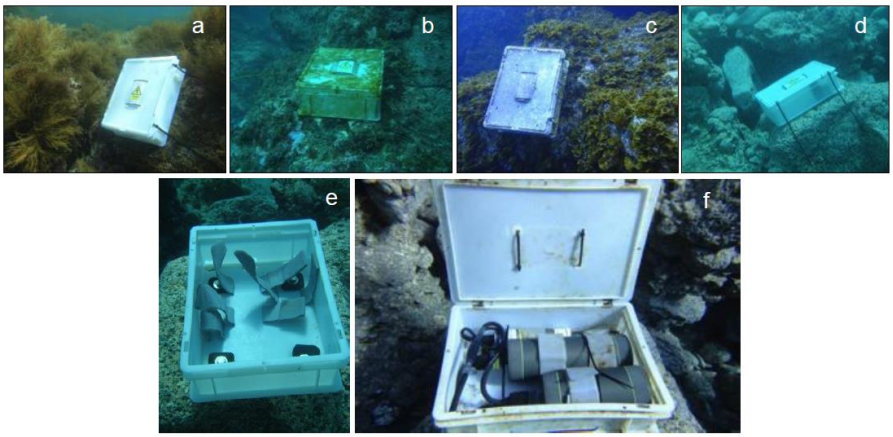


Figure 1. pH sensor cases deployed at each of the sites studied: a) *Cystoseira abies-marina;* b) Gelidiales and geniculate corallines; c) *Lobophora variegata;* d) Crustose algae. e) Internal set up of the underwater case; and f) pH *sensor*, data logger and lead battery.

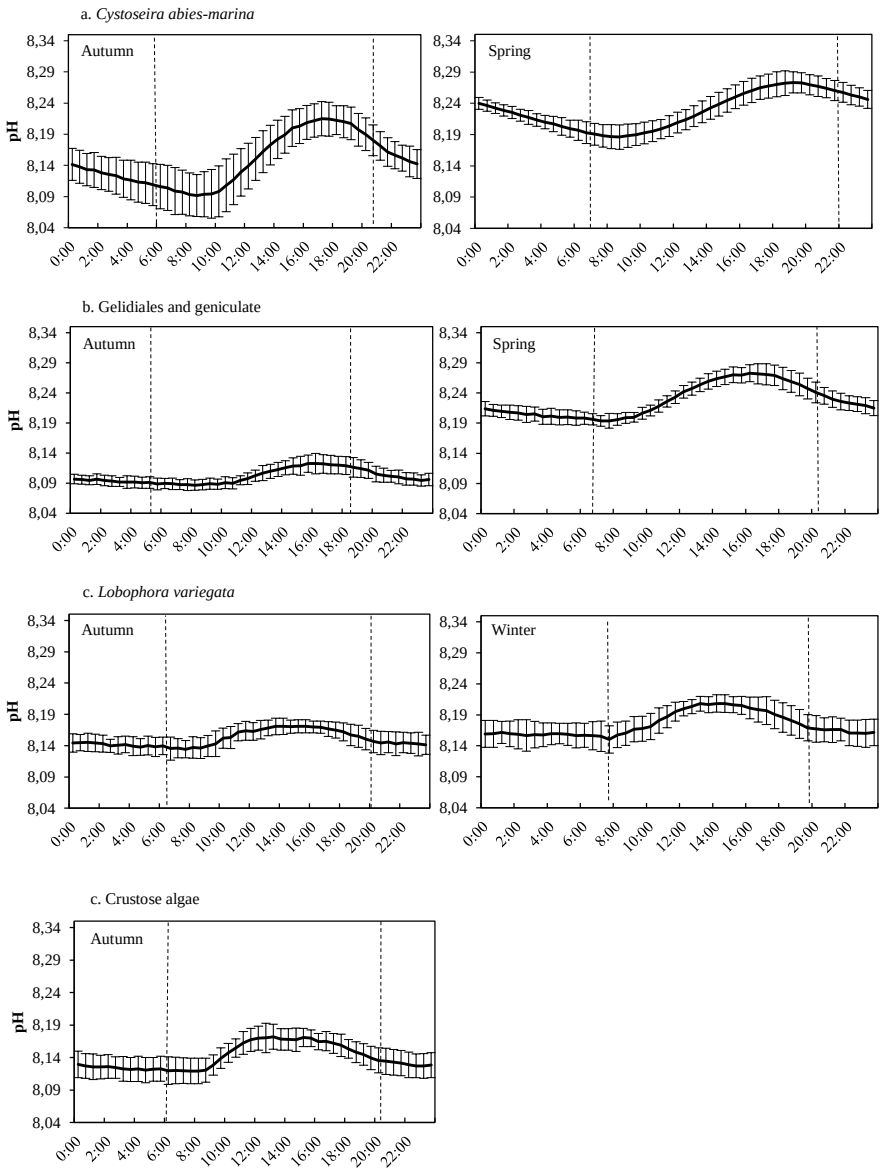


Figure 22. Mean pH per hour of the day at each site: a) *Cystoseira abies-marina;* b) Gelidiales and geniculate corallines; c) *Lobophora variegata;* d) Crustose algae. The vertical dotted lines indicate the time of sunrise and sunset.

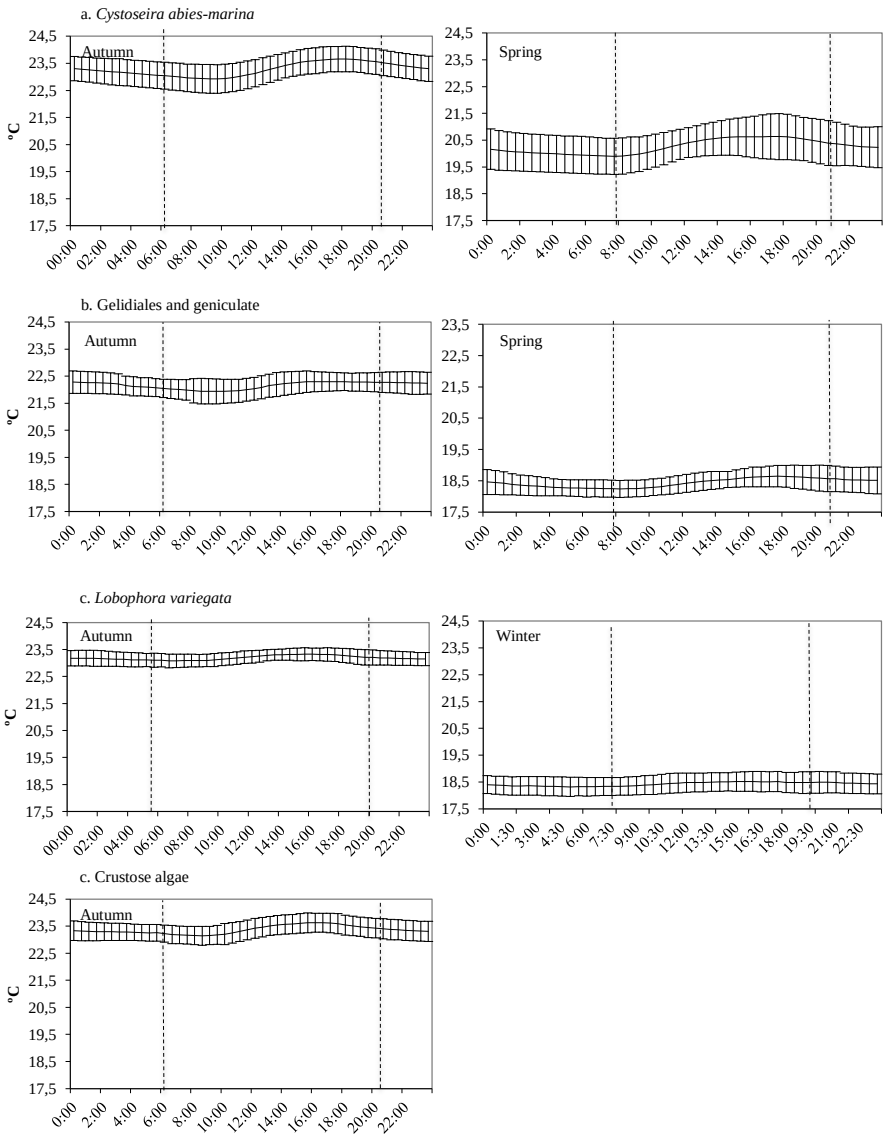


Figure 3~~2~~. Mean sea surface temperature (SST) per hour of the day at each site: a) *Cystoseira abies-marina;* b) Gelidiales and geniculate corallines; c) *Lobophora variegata;* d) Crustose algae. The vertical dotted lines indicate the time of sunrise and sunset.

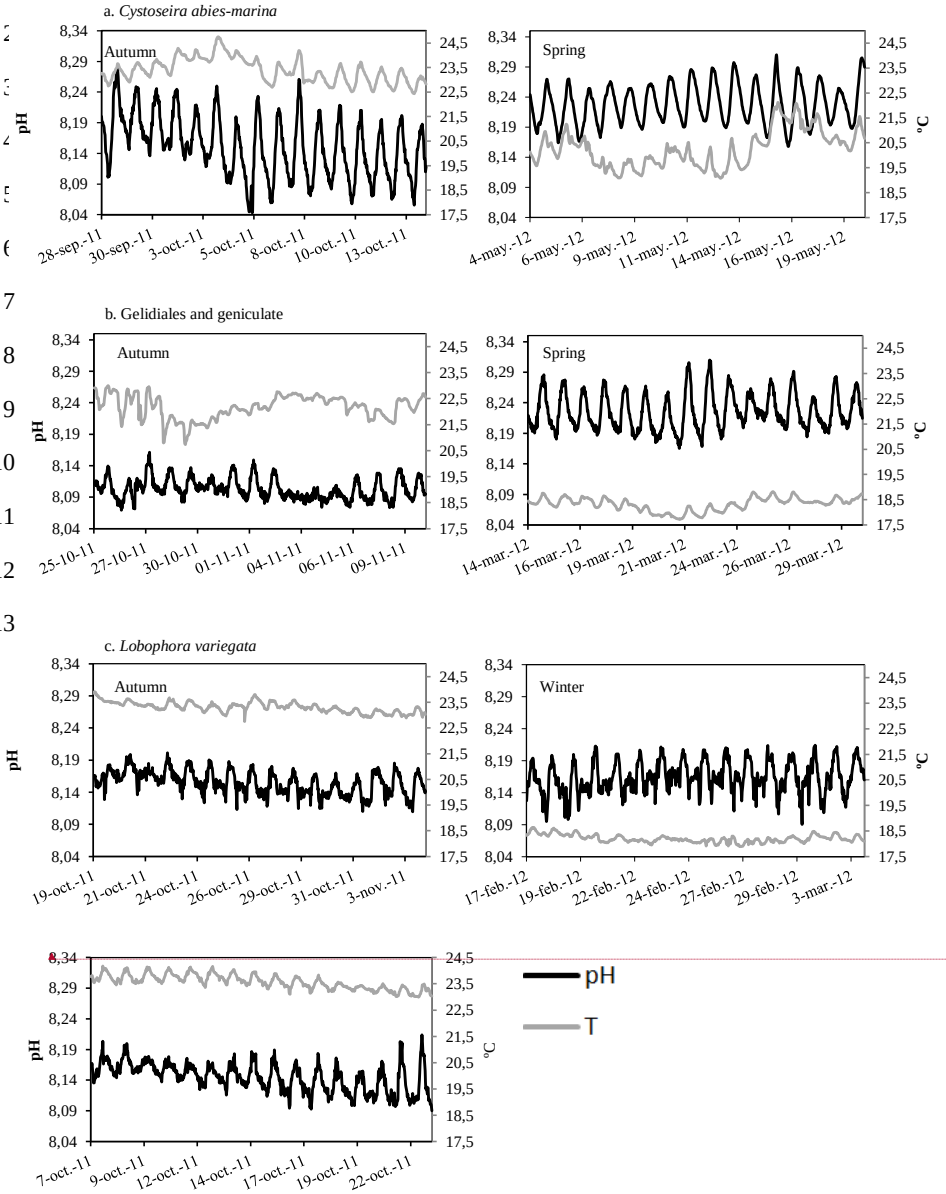


Figure 43. Variation in seawater pH and temperature at each site: a) *Cystoseira abies-marina;* b) Gelidiales and geniculate corallines; c) *Lobophora variegata;* d) Crustose algae.

Con formato: Inglés (Estados Unidos)