UNIVERSIDAD DE GRANADA

NUI Galway
OÉ Gaillimh

Master's Thesis

Effect of weather conditions, atmospheric CO_2 and marine macroalgae on the seawater chemical conditions in Galway Bay (Ireland) during winter and summer

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September 10th, 2018

MSc in Geophysics and Meteorology (2017-2018)

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ACKNOWLEDGEMENTS

I would first like to thank my thesis supervisor Dr Rachel R. Cave of the Earth & Ocean Sciences Department at National University of Ireland Galway who has always assisting me with the work developed throughout the last nine months. Her positive attitude towards the technical problems we went through has been greatly encouraged me. She has showed me how a right balance between knowledge and practical skills are equally important. I am also gratefully indebted to her for her very valuable comments on this thesis.

I would also like to thank all the experts who were involved during both laboratory and fieldwork. Specially, thanks to Aedín McAleer, who has spent a considerable amount of time working at the laboratory to have all the samples processed on time, Katheryn Schoenrock, whose diving skills made possible to release all the devices attached to the mooring at Carraroe, and both Gerard Spain and Damien Martin, who provided me with the atmospheric pCO_2 data just on time.

Finally, I must express my very profound gratitude to my parents and to all my friends for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

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ABSTRACT

The effect of weather conditions, atmospheric carbon dioxide and marine macroalgae on the seawater chemical conditions in Galway Bay, in the west coast of Ireland, has been studied during winter and summer 2018. Data collected from a survey in the RV Celtic Explorer at both outside and inside Galway Bay on February 2018 were used as a wintertime representative sample. In addition, a mooring was set at Carraroe, north coast of Galway Bay, which was recording data during June and July 2018. The results of the present study shown a marked seasonal influence between winter and summer periods. Firstly, meteorological parameters, such as wind force, precipitation and the consequent river runoff, have governed the observed changes in the chemical conditions, mainly due to both vertical mixing drove by the wind force and the minimal influence of the biological activity during the winter period. On the other hand, changes in the surface ocean chemistry in summer were mostly driven by the marine macroalgae biological activity rather than the physical forcing. Daily seawater pH fluctuations were observed due to the uptake of dissolved inorganic carbon during the day via photosynthesis, driving an increase in pH in the surrounding seawater, and decreasing pH at night as a result of CO_2 release owing to respiration. Although overall the Atlantic Ocean has an extraordinary capacity to uptake CO_2 from the atmosphere, its coastal marine areas can either uptake or release CO_2 to the atmosphere. In this regard, the studied kelp bed was actively uptaking carbon during the summer sampling (maximum daily uptake rate of 3.307 $gC \cdot h^{-1}$), having become an effective carbon sink during this time period. Moreover, metabolic processes may were boosted by both the high seawater temperatures and solar radiation levels during this warm period.

Keywords: Ocean acidification, Climate change, Kelp bed.

1. INTRODUCTION

Earth's climate system is being altered as a result of an increase in the atmospheric CO_2 concentration from 280 to 387 ppm over the last two centuries (Burns, 2008) and continues to rise steadily. In 2016 atmospheric CO_2 concentration exceeded 400 ppm for the first time, and continues to rise. Over a third of net CO_2 emissions are being absorbed by the oceans (Sabine *et al*., 2004), leading to a rapid and persistent change in the chemistry of marine systems (Zeebe and Wolf-Gladrow, 2001). Ocean acidification (OA) is the decline in surface seawater pH caused by the sustained absorption of anthropogenically derived atmospheric CO_2 by the world's oceans (Caldeira, 2003). Carbon chemistry in seawater undergoes the following equilibrium reactions as CO_2 is uptaken by the ocean.

$$(1)\ CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+$$

The increased difference in partial CO_2 pressure between the atmosphere and the seawater boosts the absorption of anthropogenic CO_2 into the surface layer of the ocean. As shown in equation (1), when CO_2 dissolves in water it forms carbonic acid which easily dissociates to bicarbonate generating hydrogen ions, which make the ocean pH decrease. Thus CO_2 is stored in the oceans as dissolved inorganic carbon (DIC), which represents the sum of the concentrations of CO_2 (<1%), HCO_3^- (~90%) and CO_3^{2-} (~9%) (Ní Longphuirt *et al.*, 2010). It is predicted that surface water CO_2 concentration will rise by about a factor of three as a result of a projected increase in atmospheric CO_2 to about 750 ppmv by 2100 (Rost *et al.*, 2008). Significant changes in the seawater carbonate system are predicted to decrease the pH by 0.3 – 0.5 units due to the increased availability of dissolved CO_2 in the ocean by the end of the century (Riebesell, 2010).

Local wind patterns, horizontal ocean currents, vertical exchange, runoff and biological processes determine the amount of anthropogenic CO_2 which can be stored in the oceans (OSPAR, 2006). The 'biological pump' effectively removes CO_2 from the atmosphere by transferring organic material such as phytoplankton to the deep sea (Eppley and Peterson, 1979). Some of the material which reaches the ocean floor is stored into the sediments. The efficiency of the anthropogenic CO_2 uptake capacity in the global ocean appears to be reducing, resulting in a proportional increase of CO_2 in the atmosphere. Increases in both atmospheric temperature and stratification of the water column lead to a reduction of the CO_2 solubility in seawater as well as the transport of CO_2-rich surface water to the deep-ocean (Schubert *et al.*, 2006). Although overall the Atlantic Ocean has an extraordinary capacity to uptake CO_2 from the atmosphere (23% of the global oceanic anthropogenic CO_2 is stored in an ocean which covers only 15% of the global ocean area), its coastal marine areas can either uptake or release CO_2 to the atmosphere (Sabine *et al.*, 2004).

Future acidification may adversely impact marine ecosystems, reducing the net calcification rates of calcareous species (Appelhans, 2012) from the inshore and coastal zones to the open ocean. However, some species of non-calcareous kelp beds may benefit from the predicted future OA (Olischläger, 2012). Kelp beds can be found in any shallow coastal aquatic system between latitudes of ~35-65º, acting as an effective carbon sink

because of their large biomass as compared to phytoplankton as well as providing habitat, food, and nursery areas for numerous marine species (Smith, 1981). In the open ocean, pH does not vary greatly either in time nor space. By contrast, macrophytes which form the kelp beds have the capacity to elevate seawater pH as a result of their biological activity in some coastal ecosystems (Cornwall, 2013). Moreover, kelp beds are important autochthonous and allochthonous carbon sinks (Kennedy *et al.*, 2010), and this stored carbon can also be exported to the deep sea, latter ultimately results in a long-term storage sink (Laruelle *et al.*, 2010).

Laboratory studies indicate that daily seawater pH fluctuations within some kelp beds can be almost 1 pH unit due to the uptake of DIC during the day via photosynthesis, driving an increase in pH in the surrounding seawater, and decreasing pH at night as a result of CO_2 release owing to respiration (Hurd, 2011). Daily variations of partial pressure of CO_2 (pCO_2) and DIC are strongly influenced by the biological activity of the kelp, being significant in the spring and summer mainly, reflecting a seasonal pattern in which the biological activity is minor during winter (Delille, 2009). Elevated rates of growth and photosynthesis for kelp are expected due to the increased uptake of CO_2. Thus, warming is likely to stimulate a northward expansion for some marine plant species such as *Zostera marina* (Jueterbock *et al.*, 2013, Olesen *et al.*, 2015). In addition, predicted reductions in seawater pH may have little to no effect on photosynthesis and growth as carbon concentrating mechanisms (CCMs) uptake actively HCO_3^- from seawater (Hepburn, 2011).

The purpose of the present research is to examine how the meteorological parameters affect both the diel changes of pH during a survey on board the RV Celtic Explorer in February 2018 and the diel changes of pH and dissolved oxygen within a kelp bed located in the shallow waters in Galway Bay in summer 2018, and to use these data together with spot samples of total alkalinity (TA) and dissolved inorganic carbon (DIC), to determine (a) the natural variation in ocean alkalinity (OA) parameters in the kelp bed, (b) how much external control on these parameters is exerted by meteorological parameters and both the tidal and day-night regime and (c) the effects of kelp photosynthesis and respiration on OA parameters. The data collected are then considered alongside the expected changes in pH in ocean water due to climate change over the coming decades, to see if the observed local effects are greater or less than those expected from Climate Change. No study to date has examined the *in-situ* response of non-calcareous macroalgae to OA in the west of Ireland.

2. MATERIALS AND METHODS

2.1. Sites and sampling

Galway Bay is located on the west coast of Ireland between County Galway to the north and County Clare to the south, facing west into the Atlantic Ocean and in the path of the mid-latitude cyclones. There are three small islands offshore located at the mouth of the bay, known collectively as the Aran Islands. The surface area of the bay is approximately 800 km^2.

In February 2018, on board the RV Celtic Explorer both seawater samples and pH measurements were taken in 14 different locations in both Galway Bay on the 15th and 17th February and outside the Bay on the 16th February (Fig. 1). Surface water samples were collected at a depth of 3 to 5 metres using an underway system with which the vessel is equipped. A SeaFET™ pH sensor was set up in a tank with the seawater to the tank inlet supplied as a feed from the underway system, which recorded data during the whole survey. Temperature and salinity data were acquired from an onboard CTD (device used to measure conductivity, temperature and depth) built into the underway system. Seawater samples were taken from the tank using a siphon into DIC/TA bottles.

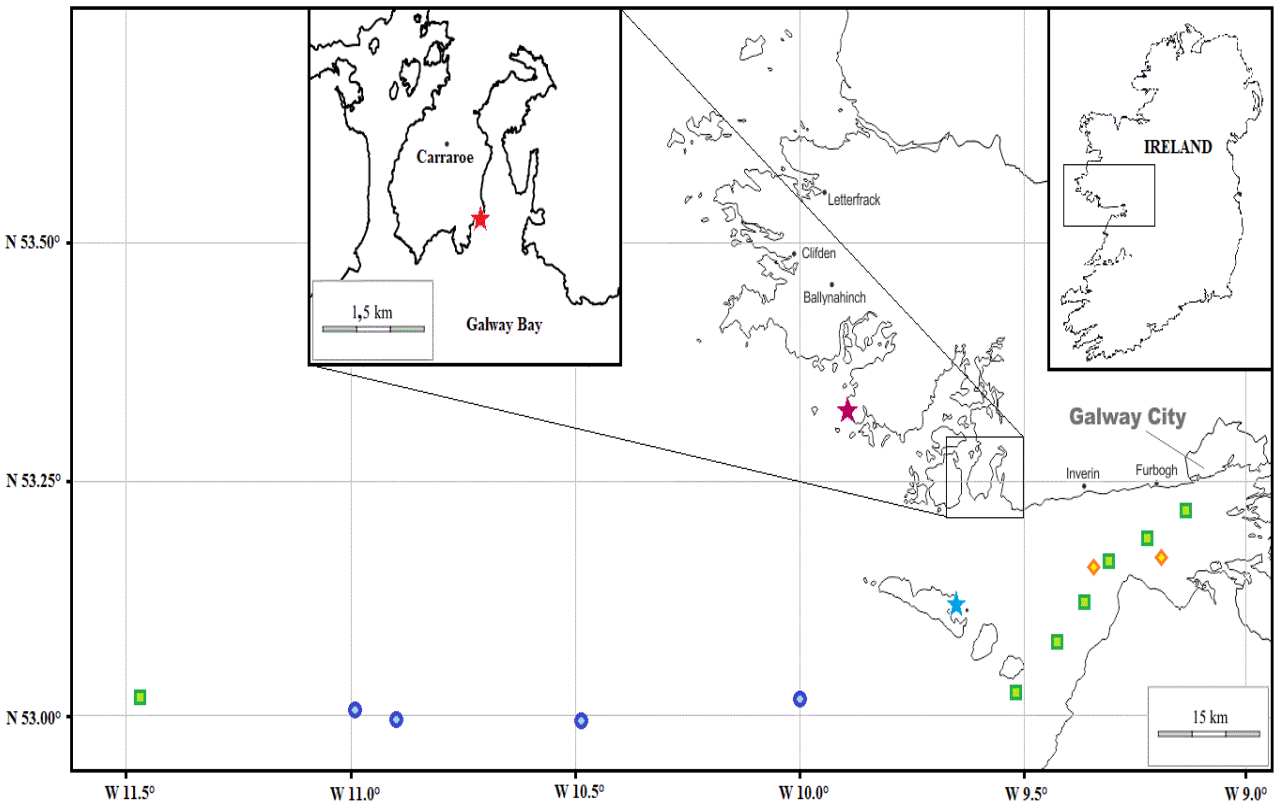

FIGURE 1. Sites where the samples were collected on board the RV Celtic Explorer. Orange rhombuses mark the sites where the samples were collected on the 15th February 2018. Sites where the samples were collected on the 16th February 2018 are marked on the map by blue circles and on the 17th February 2018 by green squares. The sampling site at Carraroe Peninsula is indicated by a red star. The atmospheric research station at Mace Head is indicated by a purple star. Buoy at the Inishmore harbour in Kilronan is indicated by a blue star.

In June 2018, a mooring was set up underwater on the east coast of Carraroe Peninsula in County Galway (53º 14' 38.04'' N, 9º 34' 48.36'' W) (Fig. 1). *Laminaria hyperborea* was the dominant species of the kelp bed which surrounds the mooring (estimated area of 23237 m^3). The structure consists of a triangular frame to which instruments were attached at one metre above the sea floor. Depth of water at the mooring varies between 5 and 7 metres at neap tides, and between 3.5 and 8 metres at spring tides.

A Hydrolab multi-parameter probe measuring temperature, salinity and pH was deployed on the mooring from 18th June, together with a Hobo oxygen and temperature data logger, sampling at 15 minutes intervals. At deployment and on a number of other dates both surface and bottom seawater samples were collected *in-situ* to determine both DIC/TA and salinity (Table 1). A SeaFET™ pH sensor was added to the frame and was recording pH data from the 2nd July. A Seabird SBE-37 CTD was added to the frame and was recording temperature data from the 11th July. The Hydrolab was retrieved on 11th July and the remaining instruments were retrieved on 16th July. A floating platform connected to the mooring was designed to carry out atmospheric CO_2, temperature and humidity measurements using a CO_2 logger which was tested on the 4th July. Data recorded by the CO_2 logger was not included as the instrument was damaged during the sampling, resulting in the loss of all recorded information at that moment.

2.2. Collection of water samples for chemical analysis

Seawater samples were taken from the RV Celtic Explorer underway system during the winter sampling. Both surface and bottom seawater samples were collecting in Niskin bottles at the Carraroe site during the summer sampling. Niskin bottles and taps were always checked for leaks. Samples which were taken during both samplings were used to analyse different chemical parameters such as dissolved inorganic carbon, total alkalinity and salinity.

2.3. Seawater temperature, salinity and depth measurements

Seawater temperature and salinity data were automatically recorded by the thermosalinograph onboard the RV Celtic Explorer, at about 3 metres below surface at a per minute rate, during the winter sampling. Thus, a continuous record of temperature and salinity was obtained along the whole survey in February 2018. In summer, seawater temperature and salinity data on the mooring were recorded by different devices such as the Hydrolab multi-parameter probe, Hobo O_2 and temperature logger and Seabird SBE-37 CTD. Proprietary software was used to load the raw data from the sensors (e.g. Hydrolab HL4 and HOBOware).

Seawater temperature and salinity was measured for both surface and bottom samples at the Carraroe site during the summer sampling (Fig. 1), making use of a thermosalinograph which carried out depth measurements as well. Water samples were taken to calculate the salinity during both the winter and the summer samplings.

2.4. Dissolved inorganic carbon and total alkalinity samples analysis

Dissolved inorganic carbon (DIC) and total alkalinity (TA) were analysed from the same seawater sample. The methods to sample and analyse both DIC and TA are described in *The Guide to Best Practices for Ocean CO_2 measurements* (Dickson *et al.*, 2007). 0.1 mL of saturated mercuric chloride solution was added to poison the sample and prevent any possible interference due to the biological activity. The sample bottle was inverted several times to disperse the chemical product and the sample was stored in a cool and dark location to be analysed at either the Marine Institute (Oranmore, County Galway) or the Ryan Institute (National University of Ireland Galway).

A VINDTA-3C (Versatile Instrument for the Determination of Titration Alkalinity) system with UIC coulometer was used to measure the DIC. Samples were acidified with phosphoric acid in order to convert all dissolved carbon to dioxide carbon. CO_2 was forced out of the sample using nitrogen as a carrier gas (Johnson et al., 1987, 1993, McGrath *et al.*, 2013).

TA was also analysed on the VINDTA 3C by potentiometric titration with 0.1 M hydrochloric acid. LabVIEW^{TM} proprietary software was used to control the process. The endpoint is determined by the change in pH against the volume of acid added to the solution (McGrath *et al.*, 2013). The result of the titration is evaluated with curve fitting (Mintrop *et al.*, 2000).

Analysis of duplicate certified reference materials (CRMs) were carried out to ensure the accuracy of both DIC and TA measurements. CRMs were provided by A. Dickson, Scripps Institution of Oceanography, USA (Dickson *et al.*, 2003).

2.5. Oceanic partial pressure of CO_2 calculation

The CO2Sys software (www.cdiac.ess-dive.lbl.gov/ftp/oceans/co2sys/) was used to calculate the oceanic partial pressure of CO_2 (pCO_2) concentration. The program uses two measurable parameters of the CO_2 system (such as total alkalinity, inorganic dissolved carbon, pH or fugacity of CO_2) to calculate the partial pressure of CO_2 at a set of both input and output conditions chosen by the user. This software essentially consists in an Excel macro which is a direct adaptation of the CO2Sys.BAS program, created by Dr. Ernie Lewis and Dr. Doug Wallace (Carbon Dioxide Information Analysis Centre, Oak Ridge National Laboratory, Tennessee). The software version which was used to process the data was the version number 2.1 (18th September 2012).

Input conditions data included salinity (PSU) and titration temperature (ºC). Seawater samples temperature data (ºC) were used as an output conditions data. Finally, total alkalinity (TA, µmol/Kg) and dissolved inorganic carbon (DIC, µmol/Kg) data obtained from the processed seawater samples were used as well to calculate the oceanic pCO_2 concentration (µatm). The CO_2 constants which were used for the pCO_2 calculations were K1 and K2 from Mehrbach *et al.*, 1973, refit by Dickson and Millero, 1987.

Oceanic pCO_2 concentration measurements were performed by the underway system onboard the RV Celtic Explore during the winter sampling both inside and outside Galway Bay.

2.6. pH measurements

Seawater pH can be measured both directly and indirectly. Direct measures can be taken making use of ocean pH sensors such as the SeaFET™ (measurement range of 6.5 – 9.0 pH units, accuracy of ± 0.05 pH units) or the Hydrolab multi-parameter probe (measurement range of 0 – 14 pH units, accuracy of ± 0.2 pH units). Moreover, pH can be indirectly determined from measurements of DIC, total alkalinity (TA), temperature and salinity data, and thus high precision monitoring of ocean acidification can be performed. Unfortunately, the number of water samples taken were insufficient to ensure a continuous record of pH data. Thus, direct pH measurements were taken making use of the SeaFET™ pH sensor during the winter sampling and both pH sensors during the summer sampling. This enabled us to examine the changes over the time in the pH on the basis of the continuous record obtained.

Raw data from the SeaFET™ pH sensor were processed using a specially designed software (SeaFETCom version 2.0.3.). Temperature and salinity data from either the Hobo O_2 logger or the Seabird SBE-37 CTD were used to perform pH corrections during both winter and summer samplings. In addition, pH data recorded by the Hydrolab multi-parameter probe was processed using the proprietary software (Hydrolab HL4).

2.7. Dissolved oxygen concentration measurements and calculations

Dissolved oxygen concentrations allows us to know the amount of oxygen that can be dissolved in water at a specified temperature. Some sources that can either increase or decrease the amount of oxygen in the seawater are the diffusion from the atmosphere, mixing of bodies of water with different dissolved oxygen concentrations, oxygenation boosted by wind and by photosynthesis of micro and macro-algae, including kelp. Dissolved oxygen concentration can vary due to numerous factors, such as, changes in the seawater temperature and in the barometric pressure, decomposing organic matter, anthropogenic pollution caused by fertilisers and pesticides and changes in the biological activity.

Dissolved oxygen was recorded automatically using a Hobo logger attached to the mooring on the 18th June. Moreover, the instrument was equipped with a temperature sensor which recorded data to make the necessary corrections for temperature. The percentage of dissolved oxygen saturation was calculated using both the dissolved oxygen and temperature recorded data. Raw data from the O_2 sensor was processed using the HOBOware proprietary software.

The dissolved oxygen concentration in seawater is a function of atmospheric pressure, water temperature and salinity, when physical processes are only taken into account. The equations to calculate the solubility values of dissolved oxygen were directly taken from Benson and Krause (1984). The following equation was used to obtain the dissolved oxygen concentration in micromole per litre, and then converted to mg L^{-1}.

$$(2)\ \ln DO\ (\mu mol \cdot L^{-1}) = A + B/T + C/T^2 + D/T^3 + E/T^4 - S \cdot (F + G/T + H/T^2)$$

The constants A to H are the following:

A = - 135.90205	E = - $8.621949 \cdot 10^{11}$	T = Temperature (K)
B = $+1.575701 \cdot 10^{5}$	F = + 0.017674	S = Salinity (PSU)
C = - $6.642308 \cdot 10^{7}$	G = -10.754	
D = $+1.243800 \cdot 10^{10}$	H= + 2140.7	

2.9. Meteorological data

The atmospheric research station at Mace Head (www.macehead.ie) operated by NUI Galway, is located on the west coast of Ireland, at Carna, County Galway (53º 20' N, 9º 54'' W) (Fig. 1). The climate of this area is mild and moist (annual rainfall is approximately 1200 mm) temperate maritime. The wettest months are October to December and the driest are April and May. This region has a high relative humidity of around 80 – 85% and an average air temperature of 10ºC (15ºC in summertime and around 5ºC in winter). May is the sunniest month with a maximum of 180 hours of sun, and December is the dullest month with less than 40 hours of sun. 2018 had unusually long dry hot spells during June and July (31.6 and 47.9 millimetres respectively, about half of the overall amount for these two months).

Wind speed, wind direction, solar radiation, UV levels, pressure, dry-bulb temperature, rainfall and relative humidity, are recorded continuously. Dry-bulb temperature is the temperature of air measured by a thermometer protected from moisture and solar radiation. In addition, atmospheric partial pressure of CO_2 is recorded by two different instruments running in parallel (Picarro G1301 and G2301 series, run by the EPA and LSCE, respectively). The G2301 instrument measures ambient air previously dried using a cold trap, while data from G1301 instrument is corrected using a formula to take into account the water vapour net effect on the pCO_2 measurements. Mace Head atmospheric research station is a part of some of the most important international research networks including the World Meteorological Organisation / Global Atmospheric Watch (WMO/GAW) and the Climate Monitoring and Diagnostics Laboratory / National Oceanic and Atmospheric Administration (CMDL/NOAA).

Meteorological data from the RV Celtic Explorer comes from the onboard weather station, at 10 metres above the sea level. Air temperature and wind speed and direction were recorded, as well as other meteorological parameters such as atmospheric pressure or relative humidity, along the whole survey in February 2018 at a per minute rate.

Real-time tide data was obtained from a buoy located at the Inishmore harbour in Kilronan (www.data.marine.ie), the biggest of the three Aran Islands (53º 7' 4.08'' N, 9º 40' 0.84'' W), at 15.12 kilometres from the sampling site (Fig. 1). Measured tide data was used instead of predicted data to considerer the effect of the local winds on the water level.

3. RESULTS

3.1. Winter sampling

RV Celtic Explorer departed from Galway Harbour on February 2018 for a survey across the Irish continental shelf and out across the Rockall Trough (northwest of Ireland). Weather conditions deteriorated rapidly and the vessel was forced to return to shelter in Galway Bay. This provided an opportunity to do some winter sampling in the bay. Seawater temperature and salinity data were recorded from the onboard thermosalinograph. Air temperature data comes from the onboard weather station. Precipitation data was obtained from the atmospheric research station at Mace Head, as the weather station from the RV Celtic Explorer does not record this meteorological parameter. Both oceanographic and meteorological data were recorded every minute.

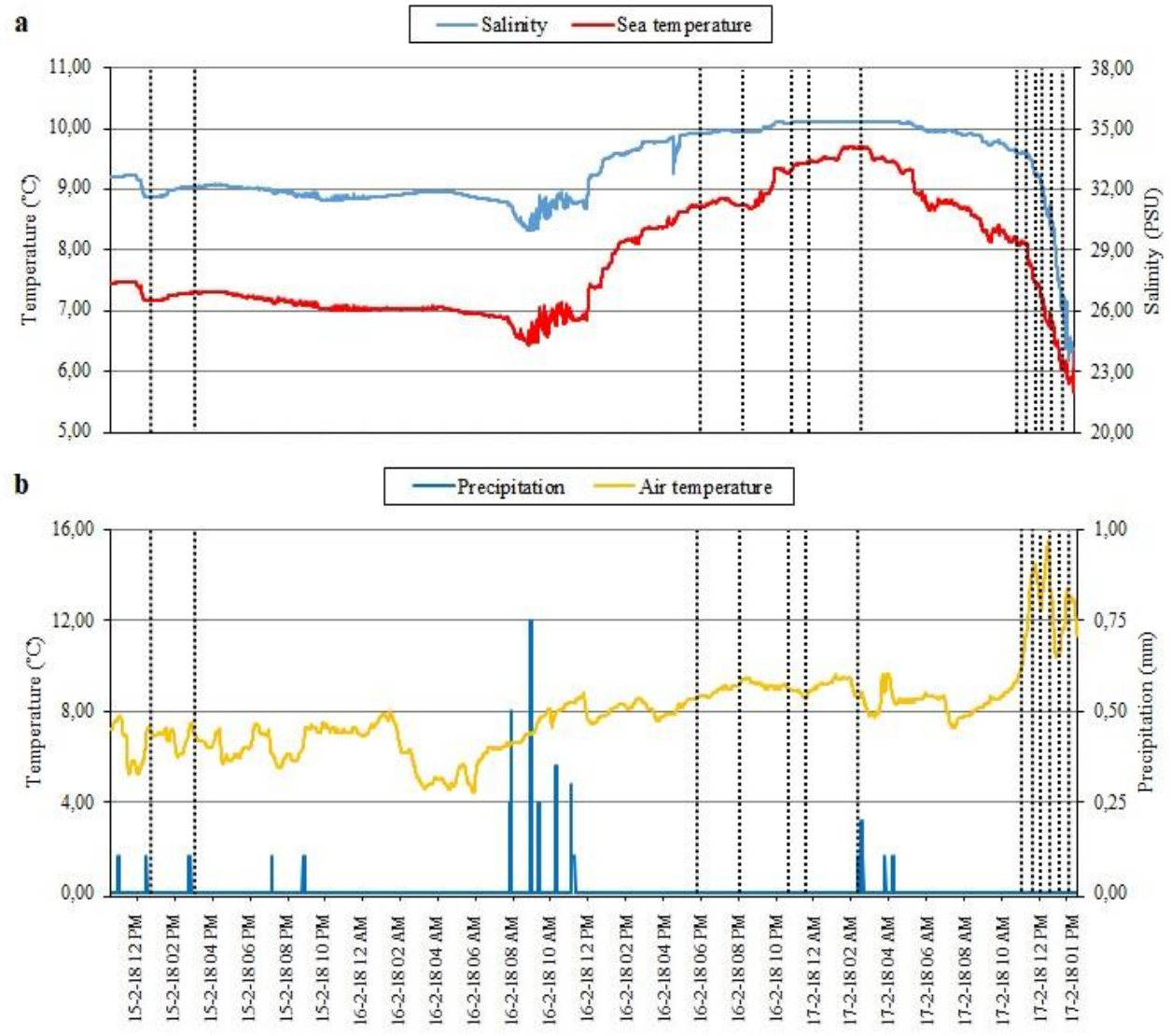

FIGURE 2. (a) Surface seawater temperature and salinity diagram from the data recorded on board the RV Celtic Explorer. Orange dotted lines mark the samplings carried out on the 15th February 2018. Samplings carried out on the 16th, 17th and 18th February 2018 are marked on the diagram by black dotted lines. (b) Air temperature data from the onboard weather station and precipitation data from the meteorological station in Mace Head.

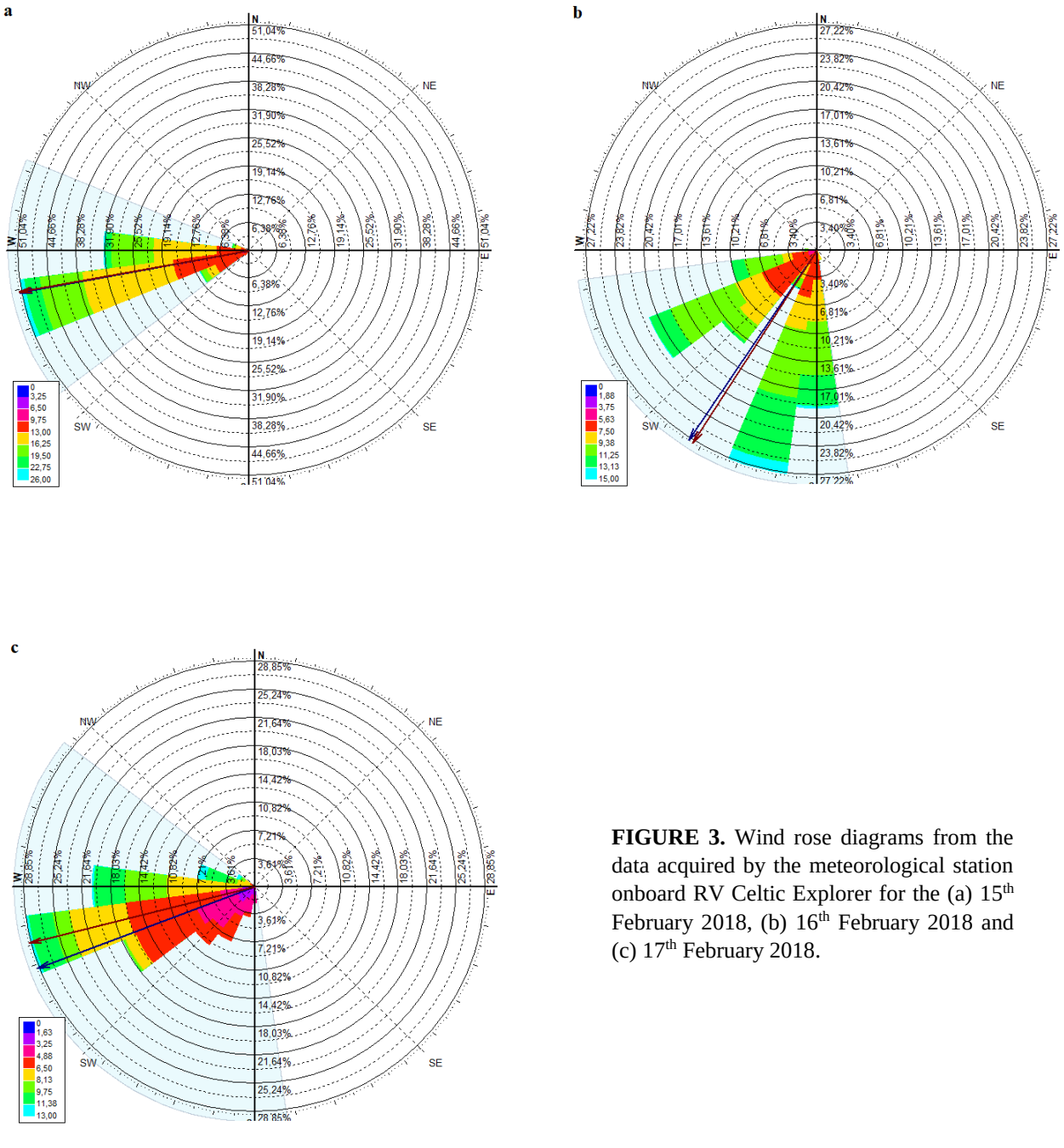

FIGURE 3. Wind rose diagrams from the data acquired by the meteorological station onboard RV Celtic Explorer for the (a) 15th February 2018, (b) 16th February 2018 and (c) 17th February 2018.

The first two water samples were taken from the underway system during the afternoon on the 15th February off the south coast in Galway Bay (Fig. 1). Seawater temperature was around 7.5ºC and salinity was under 33.0 PSU (Fig. 2a, Table 1). Air temperature ranged between 4.0 and 8.0 ºC, and precipitation was evenly distributed (Fig. 2b). Moreover, predominant winds came from the west with a mean speed value of 14.6 m/s and mean azimuth of 259.2º (Fig. 3a).

The next four samples were taken out of Galway Bay on the open shelf waters of the Atlantic Ocean on the 16th February. Samples sites were located at a minimum distance of 30 kilometres to the west of the Aran Islands at the mouth of Galway Bay (Fig. 1).

Temperature and salinity increased as the research vessel reached the open ocean (Fig. 2a). In addition, air temperature ranged between 4.0 and 10.0 ºC and a considerable amount of precipitation was measured between 8 AM and 12 PM (Fig. 2b), coinciding with the drop in salinity. Seawater temperature of 9.4ºC and salinity of 35.3 PSU were detected at 100 kilometres off the Aran Islands, where the effect of the local runoff is negligible (Table 1). Predominant winds came from the southwest with a mean speed value of 9.2 m/s and a mean azimuth of 213.2º (Fig. 3b).

The first of the final seven surface samples was collected at 130 kilometres to the west of the Aran Island on the 17th February. The next two were taken at the south entrance to Galway Bay close to Inisheer, the smallest and most eastern of the three Aran Islands. The last four samples were collected on the way back to Galway Harbour (Fig. 1). The strong influence of the fresh and cold water from the Corrib river runoff could be detected as the research vessel reached the coast (Fig. 2a). Lowest temperature and salinity were measured at less than 10 kilometres from Galway City (6.3ºC and 25.3 PSU, respectively) (Table 1). Air temperature reached almost 16.0 ºC and small amounts of precipitation were detected along the day (Fig. 2b). Westerly winds were predominant during the last sampling day with a mean speed value of 6.4 m/s and a mean azimuth of 248.9º (Fig. 3c).

Date	Latitude	Longitude	Depth (m)	Temp. (ºC)	Salinity (PSU)	DIC (µmol/kg)	TA (µmol/kg)	pCO_2 (ppm)
15/02/2018	53º 09' 35,40" N	09º 18' 36,60" W	5	7.46	32.69	2219.79	2354.45	475.45
15/02/2018	53º 10' 10,20" N	09º 11' 48,60" W	5	7.15	31.64	2228.62	2380.30	415.59
16/02/2018	53º 00' 09,66" N	09º 59' 58,81" W	3	8.62	34.71	2160.25	2328.94	414.66
16/02/2018	52º 59' 38,80" N	10º 29' 40,28" W	3	8.75	34.82	2155.61	2325.66	413.74
16/02/2018	52º 59' 52,80" N	10º 51' 19,09" W	3	9.33	35.29	2153.26	2327.76	418.46
16/02/2018	53º 59' 59,26" N	10º 59' 54,66" W	3	9.41	35.31	2144.96	2322.22	411.48
17/02/2018	53º 00' 03,72" N	11º 29' 39,38" W	3	9.69	35.35	2143.85	2330.97	395.72
17/02/2018	53º 00' 59,40" N	09º 31' 14,52" W	3	8.34	33.82	2167.20	2335.91	402.54
17/02/2018	53º 04' 17,04" N	09º 25' 24,96" W	3	8.28	33.77	2133.25	2335.09	328.70
17/02/2018	53º 07' 12,72" N	09º 21' 14,76" W	3	7.63	32.73	2175.86	2338.82	394.29
17/02/2018	53º 09' 41,76" N	09º 17' 33,36" W	3	7.24	31.48	2194.94	2349.38	399.42
17/02/2018	53º 11' 13,56" N	09º 13' 21,36" W	3	6.99	30.12	2226.29	2369.25	417.20

TABLE 1. Measured (temperature, salinity, DIC, TA) and calculated (pCO_2) data from the surface water samples taken from the underway system on board the RV Celtic Explorer on the 15th, 16th and 17th February 2018.

The SeaFET™ was recording data on a discontinuous basis on the 15th February and on a continuous basis from 5 PM on the 16th February to 1:30 PM on the 17th February, showing a range of variation of 0.2 pH units between 7.8 and 8.0 units (Fig. 4). A decline in pH of almost 0.2 units was observed as the RV Celtic Explorer reached the coast. By contrast, highest values were obtained on the open ocean, away from the influence of the freshwater plume from the river runoff in Galway Bay.

Both atmospheric and oceanic partial pressure of carbon dioxide (pCO_2) concentrations were measured on board RV Celtic Explorer on a discontinuous basis by the onboard weather station and underway system, respectively, from 15th to 17th February 2018. Atmospheric pCO_2 data was obtained from the atmospheric research station at Mace

Head. Moreover, pCO_2 processed data was calculated using the CO_2Sys software (version 2.1) from DIC/TA, temperature and salinity data from the collected samples on board (Fig. 4).

Atmospheric pCO_2 measurements from both Mace Head and RV Celtic Explorer ranged between 410 and 415 ppm, while oceanic pCO_2 concentrations obtained from both Celtic Explorer and the DIC/TA samples had greatest variations. Furthermore, oceanic pCO_2 concentrations were below 425 ppm during the survey, except when the vessel was approaching the inner part of Galway Bay. At that point, the oceanic pCO_2 concentration reached a maximum value of 491.19 ppm, coinciding with the minimum value in pH of 7.81.

FIGURE 4. pH data from the SeaFET™ and oceanic pCO_2 data processed from the DIC/TA samples (green bards) and measured from the underway system onboard RV Explorer (blue bars). Atmospheric pCO_2 data from Mace Head (black dotted line) and from the weather station onboard the RV Explorer on February 2018 (orange bars). Accuracy range is indicated by shaded area (SeaFET™ ± 0.05 pH).

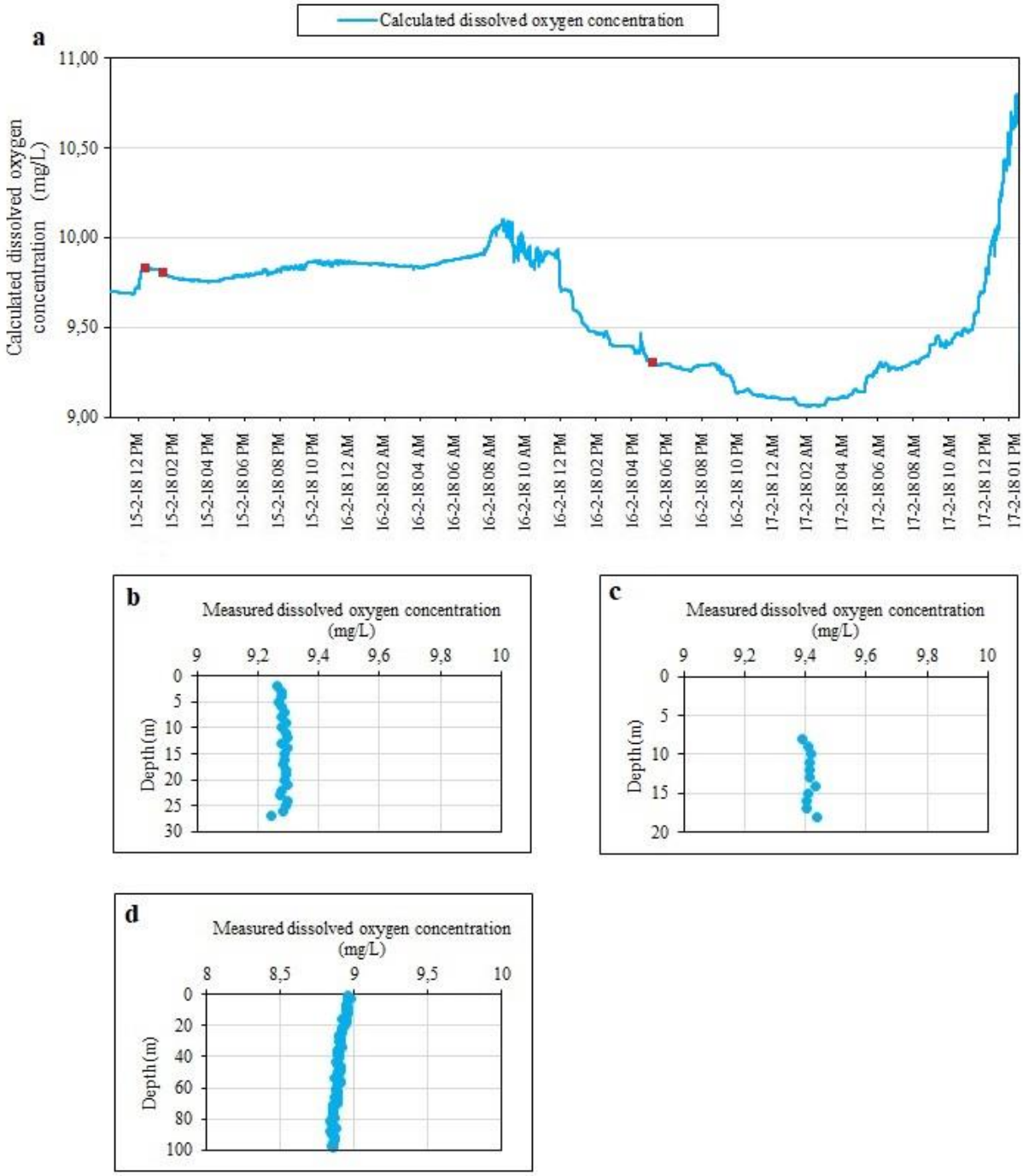

FIGURE 5. (a) Calculated dissolved oxygen concentration at saturation from the equation (2), using the underway surface seawater temperature and salinity data recorded on board the RV Celtic Explorer, from 15th February at 12 PM to 17th February at 1 PM. Measured dissolved oxygen concentration depth profile from the CTD casts on (b) 15th February at 12:52 PM, (c) 15th February at 1:53 PM, and (d) on 16th February at 5:38 PM. The CTD cast times are marked on (a) by red squares.

Dissolved oxygen concentrations at saturation have been calculated from the equation (2), using the seawater temperature and salinity data recorded on board the RV Celtic Explorer (Fig. 5a). Surface seawater could have held a maximum dissolved oxygen concentration if saturated of between 9.05 and 10.80 milligrammes per litre. Changes in calculated saturated dissolved oxygen concentration between 8 AM and 12 PM on the 16th February were mainly due to the heavy rainfall measured that day. Moreover, seawater out of Galway Bay was relatively saltier and warmer, allowing to hold slightly less dissolved oxygen than the cold and fresh seawater in the bay.

Actual dissolved oxygen concentration depth profiles were obtained from CTD casts during the three first samplings carried out on the 15th and 16th February (Fig. 5b, c and d). The first two CTDs were cast in Galway Bay (53° 13.44' N; 09° 15.79' W, 53º 9' 35.4''N, 9º 18' 36.6''W and 53º 10' 10.2''N, 9º 11' 48.6''W, respectively), while the third was cast out of the bay (53º 0' 9.66''N, 9º 59' 58.81''W). Homogenous profiles were obtained from all casts, showing a well mixed water column. Maximum concentrations have been measured from the CTDs casted in Galway Bay (9.2 to 9.5 mg/L), while minimum concentrations have been measured outside of the bay (< 9 mg/L). In all cases, the water column was oxygen undersaturated as the dissolved oxygen concentration measured is lower than the maximum dissolved oxygen concentration that the water could have held at the given temperature and salinity (saturation was 90-91% for the CTD casts).

3.2. Summer sampling

A continuous record of the seawater temperature and salinity was carried out using a combination of the Hydrolab multi-parameter probe, Hobo O_2 and temperature logger and Seabird SBE-37 CTD recorder attached to the mooring which was set up underwater on the east coast of Carraroe Peninsula in County Galway (53º 14' 38.04'' N, 9º 34' 48.36'' W) (Fig. 1). The Hydrolab probe was recording seawater temperature, salinity and pH data from the 18th June to the 11th July. The Seabird SBE-37 CTD was recording seawater temperature data from the 11th July to the 16th July, while the SeaFET™ V2 simultaneously recorded pH from the 2nd July to the 16th July. The Hobo O_2 and temperature logger was recording seawater temperature and oxygen concentration and saturation from 18th June to 16th July. Air temperature data were obtained from the Mace Head atmospheric research station. All data were recorded at fifteen minutes intervals (Table 2). Precipitation data was considered despite the shortage of rain along the time series (6.7 millimetres from the 18th June to the 11th July). All data from the samples collected in June and July 2018 is shown in Table 3.

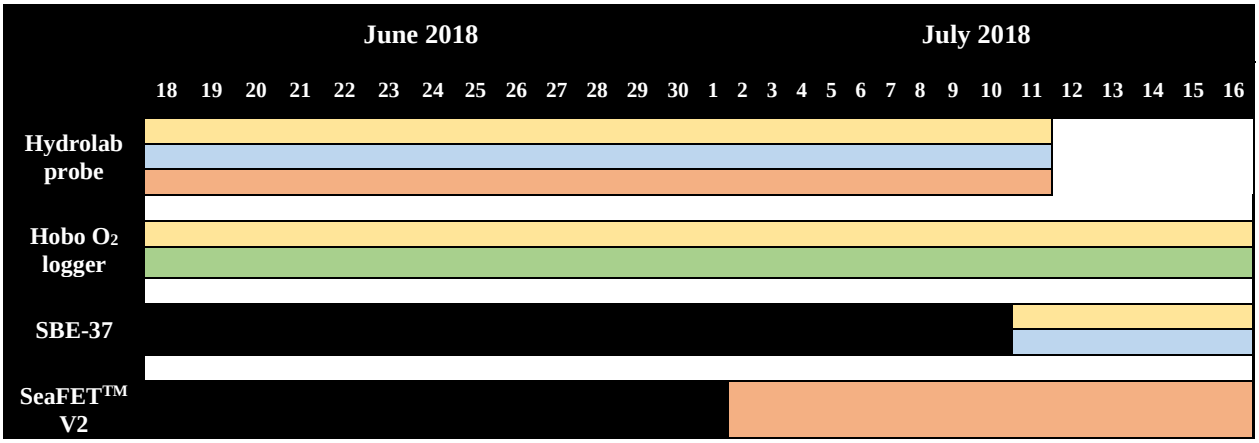

TABLE 2. Summer sampling schedule by date, instrument and measured parameter (yellow and blue colours indicate seawater temperature and salinity measurements, respectively; red and green colours indicate pH and dissolved oxygen concentration measurements, respectively; pink colour indicate pCO_2 atmospheric measurements).

Seawater temperature varied between 12.5ºC and 20.0ºC, and the salinity reached a minimum value of around 33 PSU and a maximum value of 34.5 PSU (Fig. 6a). Air temperature showed a greater variation due to the differences between day and night, ranging between 7.5ºC and 28ºC, and small amounts of precipitation were measured along the whole time series (Fig. 6b). Highest air temperatures are found from the 26th June to the 2nd July, coinciding with the first heat wave of 2018 and the total absence of precipitation (long dry period of approximately 24 days, from 20th June to 14th July). Rainfall was detected only four out of twenty nine days, being the wettest period of the whole time series between 14th to 16th July. Seawater reached a maximum value of 20.0ºC on the 30th June, with a time lag of between two and three days with regard to the maximum air temperature value. The minimum salinity value was found on the 30th June as well.

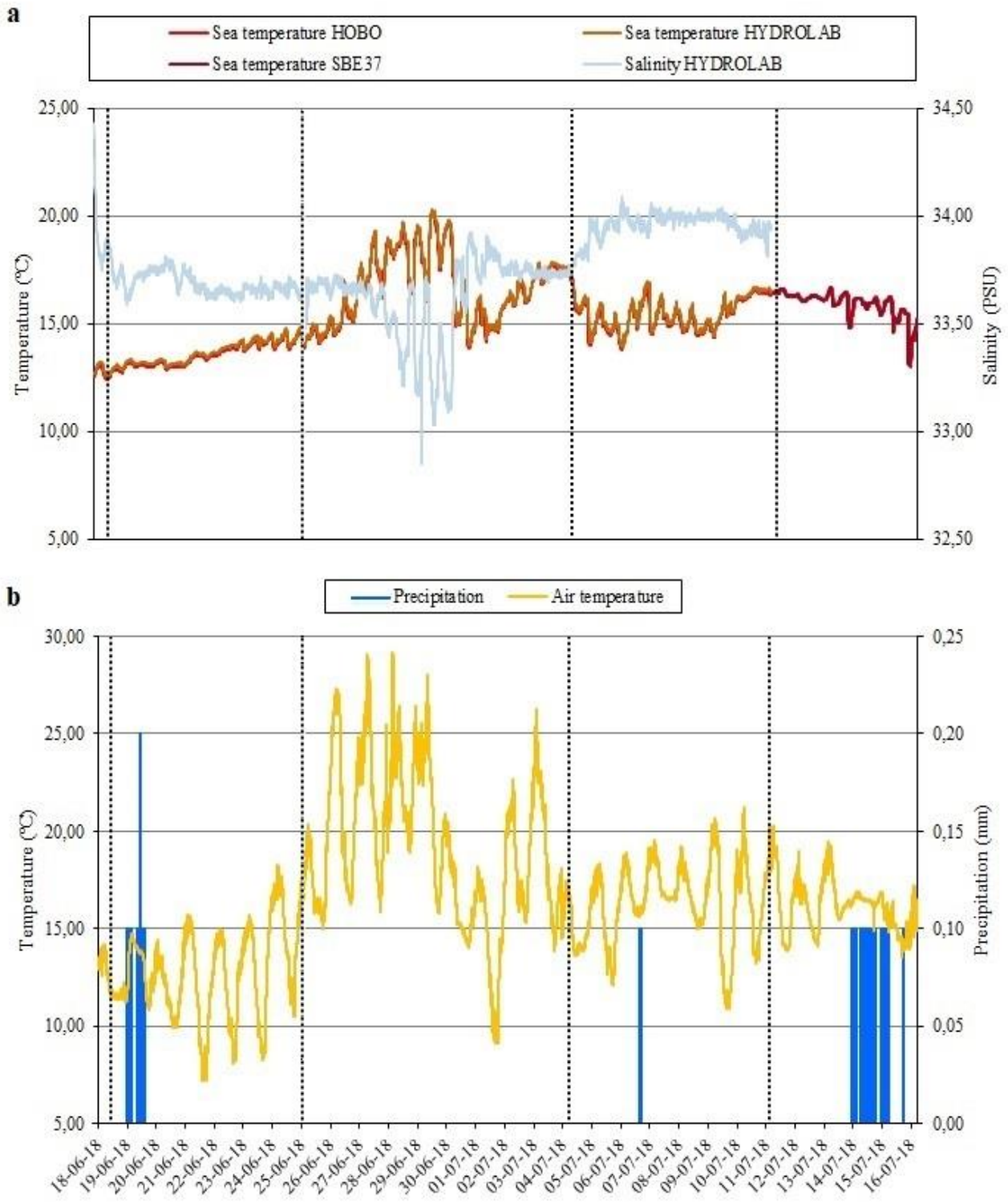

FIGURE 6. (a) Surface seawater temperature and salinity diagram from the data recorded in the mooring from 18th June 2018 to 16th July 2018. Seawater temperature data from Hobo logger, Hydrolab probe and Seabird SBE-37 CTD. Salinity data from Hydrolab probe. Samplings carried out on the June and July 2018 are marked on the diagram by black dotted lines. (b) Air temperature and precipitation data from the meteorological station at Mace Head.

Date	Time	Depth (m)	Temperature (ºC)	Salinity (PSU)	DIC (µmol/kg)	TA (µmol/kg)	pCO_2 (ppm)
18/06/2018	11:41 AM	7.30	12.80	34.10	2111.07	2328.48	367.60
18/06/2018	12:36 PM	6.50	14.00	32.90	2106.82	2322.94	375.90
18/06/2018	01:32 PM	5.70	13.70	33.30	2100.82	2320.21	367.50
18/06/2018	02:31 PM	5.50	13.70	33.20	2096.87	2321.99	355.60
18/06/2018	03:27 PM	4.90	13.70	33.30	2100.36	2321.65	364.10
25/06/2018	09:40 AM	5.00	15.00	34.20	2024.30	2307.77	281.30
25/06/2018	10:31 AM	4.40	15.00	34.30	2027.43	2304.47	290.50
25/06/2018	11:25 AM	5.00	15.40	34.10	2016.08	2305.45	276.60
25/06/2018	12:25 PM	5.00	15.30	33.90	2003.36	2304.20	258.60
25/06/2018	01:28 PM	6.50	15.40	33.70	2013.14	2312.03	262.60
25/06/2018	02:29 PM	7.20	14.50	33.90	2044.80	2317.65	290.60
25/06/2018	03:29 PM	7.10	14.10	33.90	2025.58	2307.10	271.00
25/06/2018	04:30 PM	8.00	14.70	33.90	2037.91	2318.61	282.00
25/06/2018	05:17 PM	8.00	14.80	34.00	2038.79	2319.22	284.50
25/06/2018	06:31 PM	7.40	14.80	34.00	2031.50	2317.16	276.70
25/06/2018	07:31 PM	6.60	14.60	33.90	2032.68	2323.20	268.50
25/06/2018	08:32 PM	5.70	14.90	33.90	2009.92	2313.19	253.30
25/06/2018	09:29 PM	5.40	14.60	33.80	2016.58	2346.23	226.70
25/06/2018	10:24 PM	3.40	15.10	33.80	2011.42	2308.32	261.70
04/07/2018	11:40 AM	5.10	19.20	33.20	2065.81	2325.49	373.89
04/07/2018	01:15 PM	5.20	19.10	33.10	2052.26	2328.67	307.30
04/07/2018	01:45 PM	SURFACE	19.00	33.00	2044.56	2326.71	342.10
04/07/2018	02:33 PM	5.30	19.30	33.00	2038.42	2339.38	307.87
04/07/2018	02:58 PM	SURFACE	18.90	34.00	2023.34	2324.05	329,70
04/07/2018	03:55 PM	5.60	18.50	33.70	2027.61	2327.88	301.45
04/07/2018	04:15 PM	SURFACE	19.00	33.60	2027.15	2326.45	308.01
11/07/2018	12:19 PM	3.00	16.40	34.20	2027.44	2322.26	285.91
11/07/2018	02:16 PM	SURFACE	16.90	34.00	2017.83	2319.16	280.62
11/07/2018	03:30 PM	SURFACE	17.00	34.00	2029.65	2319.25	298.40

TABLE 3. Measured (temperature, salinity, depth, DIC, TA) and calculated (pCO_2) data from the samples taken at Carraroe site during the summer sampling in June and July 2018.

Wind speed and direction data were recorded at the atmospheric research station at Mace Head every fifteen minutes (23.36 kilometres from the mooring site) (Fig. 7). In general, weak winds prevailed during the whole time series. Wind speeds lower or equal to 8 metres per second (28.80 kilometres per hour) prevailed during 88.29% of the summer sampling time period. Wind speed did not exceed 6 metres per second from the 24th June to the 30th June, allowing the warming of surface seawater. Thermal stratification was favoured by weak winds and high air temperatures during that period. In addition, rainy days at both the beginning and the end of the summer sampling were concentrated when southerly winds prevailed.

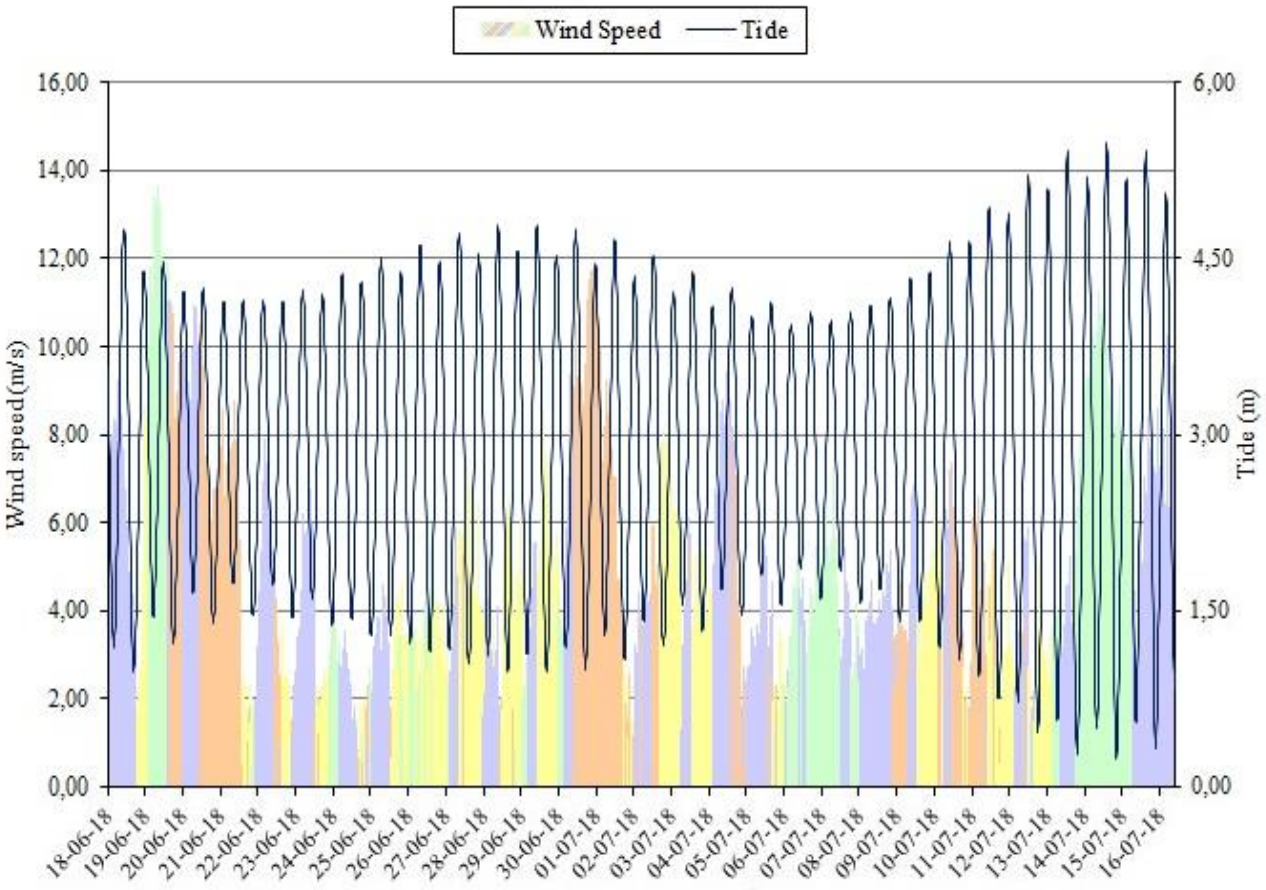

FIGURE 7. Wind speed data from Mace Head atmospheric research station and tide data from a buoy at the Inishmore harbour in Kilronan from the 18th June 2018 to 16th July 2018. Red colour areas on the chart indicate northerly winds (315º – 45º), yellow areas indicate easterly winds (45º - 135º), green areas indicate southerly winds (135º - 225º) and blue areas indicate westerly winds (225º – 315º).

pH data were recorded by the Hydrolab probe from 18th June to 11th July. The SeaFET™ V2 started recording pH data on the 2nd July till 16th July (Fig. 8a). It has been observed that while the magnitude of the pH variation was the same, there was an offset of around 0.20 pH units between the pH data recorded by the SeaFET™ V2 and the Hydrolab probe. This could be explained by the differences in the accuracy ranges in both instruments (SeaFET™ V2 ± 0.05 pH units and Hydrolab probe ± 0.20 pH units) however it is more likely to be due to the internal device pH calculation processes, since the pH for the SeaFET™ V2 was calculated using the Hydrolab probe temperature and salinity data during the period where they were deployed together. However since the magnitude and pattern of the Hydrolab probe is identical to the SeaFET™ V2 while they overlap, there is high confidence in the accuracy and precision of the Hydrolab pH (a statistically significant positive correlation was found between the two pH data sets of 0.875, N=851). Regardless, maximum and minimum peaks and amplitudes match in both data sets from the 2nd July to the 11th July. The whole data set was recorded every fifteen minutes.

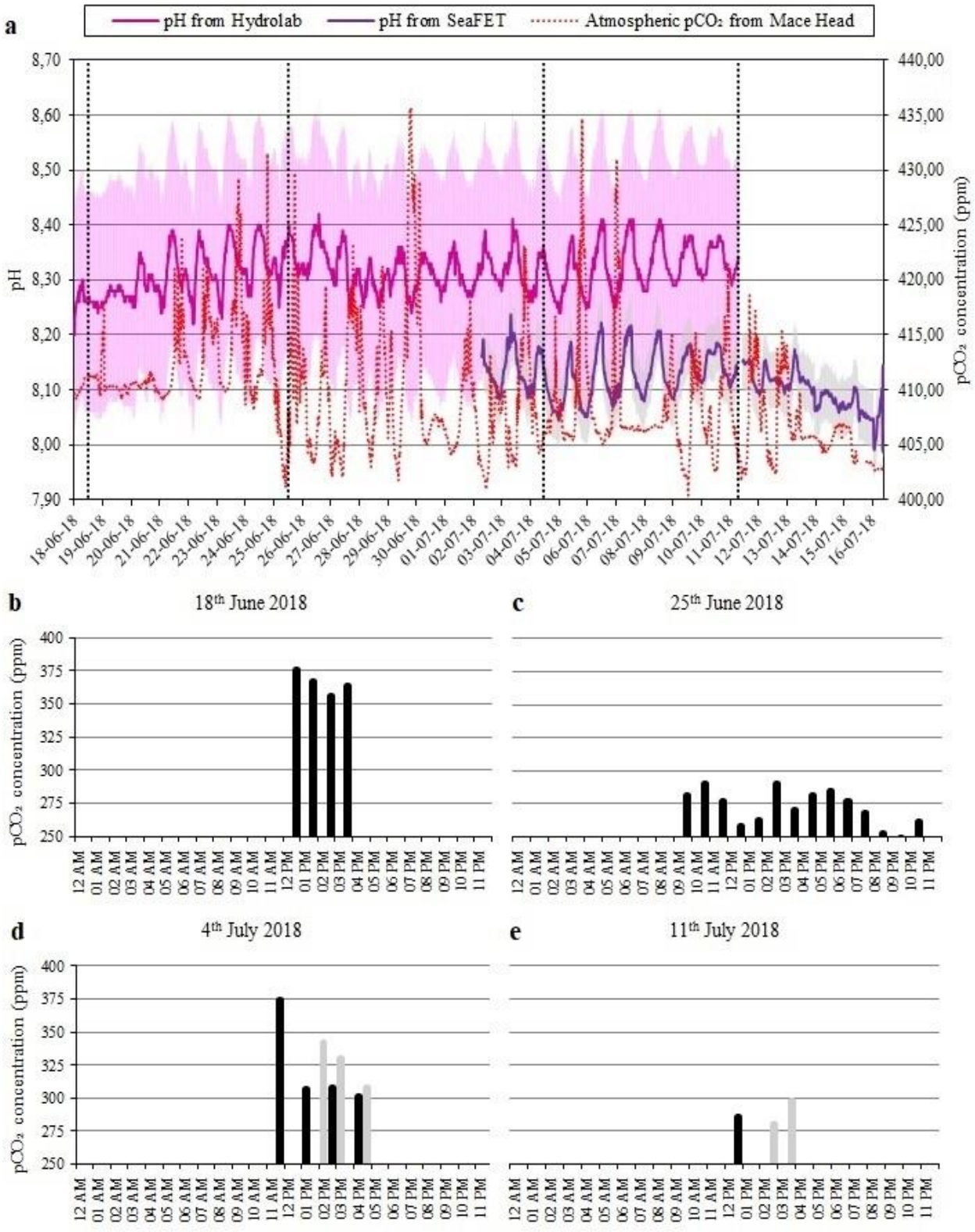

FIGURE 8. (a) pH data from the SeaFET™ V2 instrument from 18th June to 11th July 2018 and Hydrolab probe from the 2nd July to 11th July 2018. Accuracy ranges are indicated by shaded areas (SeaFET™ V2 ± 0.05 pH units and Hydrolab probe ± 0.20 pH units). Atmospheric pCO_2 concentration data from the atmospheric research station at Mace Head is marked on the diagram by a red dotted line. Samplings carried out on the June and July 2018 are marked on the diagram by black dotted lines. Oceanic pCO_2 concentration data from the DIC/TA samples collected at both the mooring (black bars) and the sea surface above it (grey bars) on the (b) 18th June, (c) 25th June, (d) 4th July, and (e) 11th July 2018.

pH data recorded by the Hydrolab probe ranged between 8.20 and 8.40 pH units. pH decreased around 0.05 units on the 28th June, coinciding with an easterly winds prevailing period. SeaFET™ V2 pH data ranged between 8.00 and 8.25 pH units, reaching a minimum value of 8.00 units on the 16th July. SeaFET™ V2 pH sensor was retrieved from the mooring for a short period of time, between 11:45 AM to 4:15 PM on 11th July, in order to download data and check instrument was working correctly.

Atmospheric pCO_2 concentrations ranged between 400 and 437 ppm, reaching maximum peaks between 4 and 8 AM and minimum peaks during the evening, specifically between 6 and 8 PM (Fig. 8a). Maximum variability was found during three different time periods: from 21st to 30th June, from 2nd to 7th July, and from 9th to 13th July. Furthermore, easterly winds predominated during these time periods of maximum variability, while prevailing winds from north, south and west drove minor changes in the atmospheric pCO_2 concentration (Fig. 9). In addition, wind speed does not seem to be related to the scale of the atmospheric pCO_2 concentration changes.

On the other hand, the greatest variability was found in the oceanic pCO_2 concentration from DIC/TA samples as compared with the atmospheric pCO_2 concentration (Fig. 8b, c and d). Oceanic pCO_2 concentrations ranged between 250 and 375 ppm, and all concentrations values were below the minimum atmospheric concentration of 400 ppm (Table 3). Highest concentrations were measured on 18th June and 4th July, while the lowest were measured in the samplings carried out on 25th June and 11th July.

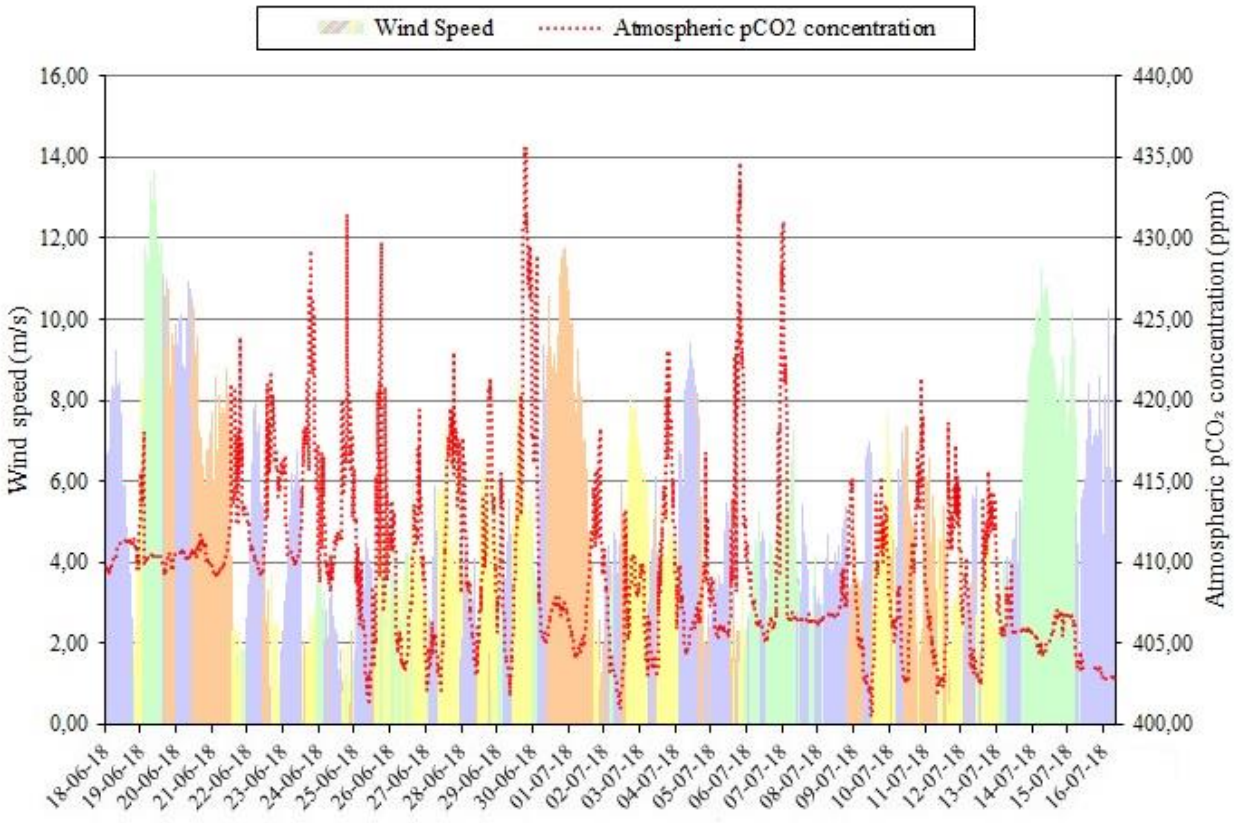

FIGURE 9. Wind speed data and atmospheric pCO_2 concentration from Mace Head atmospheric research station from the 18th June 2018 to 16th July 2018. Red colour areas on the chart indicate northerly winds (315º – 45º), yellow areas indicate easterly winds (45º - 135º), green areas indicate southerly winds (135º - 225º) and blue areas indicate westerly winds (225º – 315º).

The Hobo O_2 and temperature logger was recording dissolved oxygen data along the whole time series, from 18th June to 16th July (± 0.5 milligrammes per litre) (Fig. 10). Hobo probe was retrieved from the mooring for a short period of time, between 11:45 AM to 4:15 PM on 11th July, in order to download the data. Dissolved oxygen ranged between 9.5 and 14.0 milligrammes per litre. A large daily variation of around 4.0 milligrammes per litre was observed, partly due to temperature variation and partly due to biological activity, mainly because of the kelp beds photosynthesis. Dissolved oxygen concentration increases along the morning, reaching its maximum value in the early evening.

Dissolved oxygen concentration and saturation maximum and minimum peaks match the maximum and minimum pH values. Daily maximum dissolved oxygen values were under 13 milligrams per litre between 28th June and 3rd July, coinciding with a period in which temperature reached 20ºC (Fig. 6a). Minimum dissolved oxygen values were found within last three days of the time series, that is between the 14th July and the 16th July.

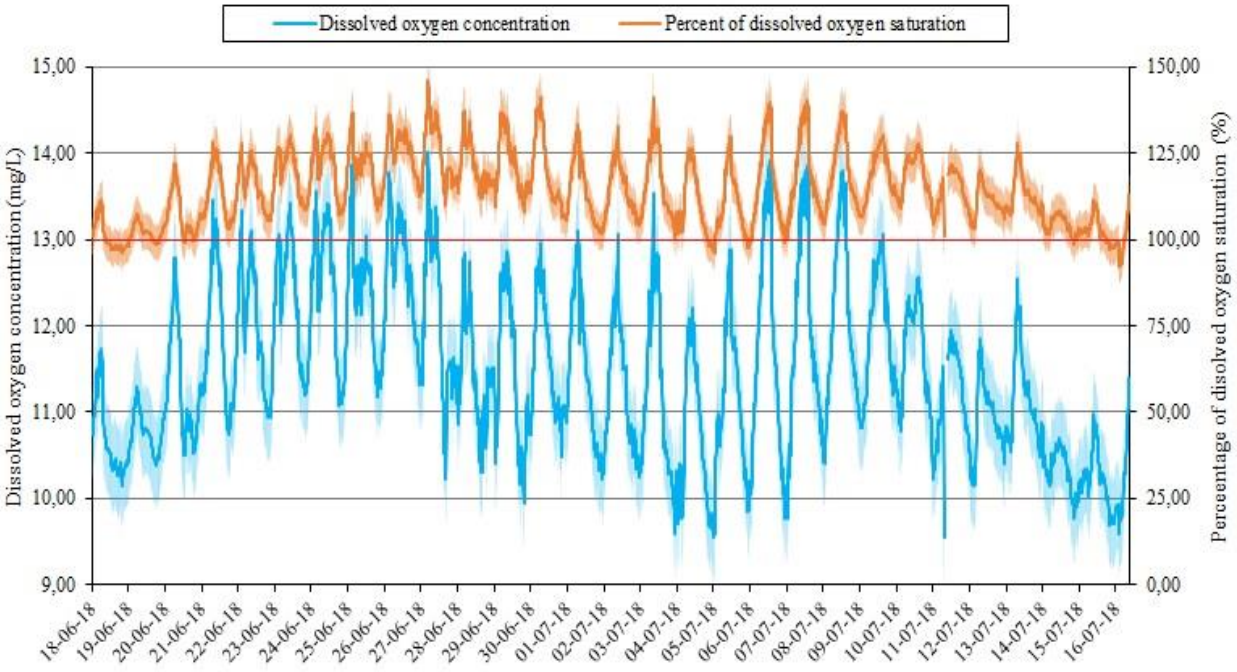

FIGURE 10. Dissolved oxygen and percentage of dissolved oxygen saturation data from the Hobo O_2 and temperature logger from the 18th June 2018 to 16th July 2018. Accuracy range is indicated by shaded areas (Dissolved oxygen ± 0.5 milligrams per litre and percentage of dissolved oxygen saturation ± 5.0%). Percentage of 100% dissolved oxygen saturation is highlighted in red.

Seawater oxygen saturation is a ratio of the concentration of dissolved oxygen in the seawater as a proportion of the maximum amount of oxygen that can be dissolved at a specified temperature and pressure. Seawater can become supersaturated with oxygen when it reaches more than 100% saturation, due to a combination of a high photosynthetic rate and a slow equilibration after a change of the atmospheric conditions. Dissolved oxygen percent saturation ranged from a minimum of 92% at the end of the time series, to a maximum of over 145% on the 27th June (Fig. 10). Oxygen supersaturated conditions were prevailing during 24 out of the 29 days of the sampling, even at night. Diel

fluctuations reached a maximum value of ± 40% due to diel changes in both the oxygen production by the aquatic organisms and seawater temperature.

Seawater dissolved oxygen fluctuations caused by the biological activity of the kelp bed surrounding the mooring have been calculated from 18th June to 11th July (Fig. 11a). To do this, dissolved oxygen concentration directly measured by the Hobo O_2 logger has been subtracted from the theoretical amount of dissolved oxygen which the seawater can hold at a given temperature and pressure, the latter calculated from the oxygen saturation data directly measured by the Hobo O_2 logger.

Photosynthesis is a process used by plants and algae to convert solar radiation into chemical energy that can be used in several biological processes such as tissue growth. Chemical energy is stored in organic molecules, such as glucose ($C_6H_{12}O_6$), which are synthesized from water and CO_2, releasing O_2 as a result. Conversely, the metabolic process which converts the organic molecules into chemical energy, consuming O_2 and releasing CO_2 and H_2O, is called aerobic respiration (see equation 3).

$$(3)\ 6CO_2 + 6\ H_2O \leftrightarrow C_6H_{12}O_6 + 6O_2$$

Solar radiation from the weather station in Mace Head has been plotted in the Figure 11a, in order to know if there is any relation between solar radiation and dissolved oxygen fluctuations due to the kelp bed biological activity. Maximum values around 6 J/cm^2 were reached between noon and 2 PM in both June and July. Solar radiation is zero during nighttime, which in summer ranges from approximately 9 PM to 4 AM (around 7 hours of darkness). During summertime, when are more daylight hours and the incident solar radiation is strong, daily cycles are observed.

Maximum dissolved oxygen concentration levels are reached with a lag of a few hours with regard to the maximum solar radiation values. Maximum oxygen concentrations from 18th to 22nd June were measured in the evening between 5 PM and 7 PM, matching the solar radiation high peaks in the afternoon from 23rd to 30th June, in the evening between 5 PM and 7 PM from 1st to 5th July and at night between 8 PM to 10 Pm from 6th to 11th July. Two different maximum values were measured between 23rd and 28th June, the highest in the afternoon and the second highest at night. Unique maximum values were observed along the rest of the time period. Minimum dissolved oxygen values were reached just before the dawn. Spikes in dissolved oxygen concentrations during nighttime have been observed from 27th June to 1st July. Maximum daily variations in dissolved oxygen concentration of around 4.0 milligrammes per litre were found.

Percentages of biological dissolved oxygen concentration regarding the dissolved oxygen concentration measured by the Hydrolab probe were plotted in the Figure 11b. Values over zero indicate the proportion of dissolved oxygen concentration that can be attributed to the biological activity. A maximum value of 31.51% was reached on the 27th June, while the lowest value of -4.28% was reached on the 18th June. Moreover, values below zero were only reached during 6 out of the 24 days, and they indicate that the oxygen which the seawater can hold at a given temperature and pressure is more than the measured dissolved oxygen concentration.

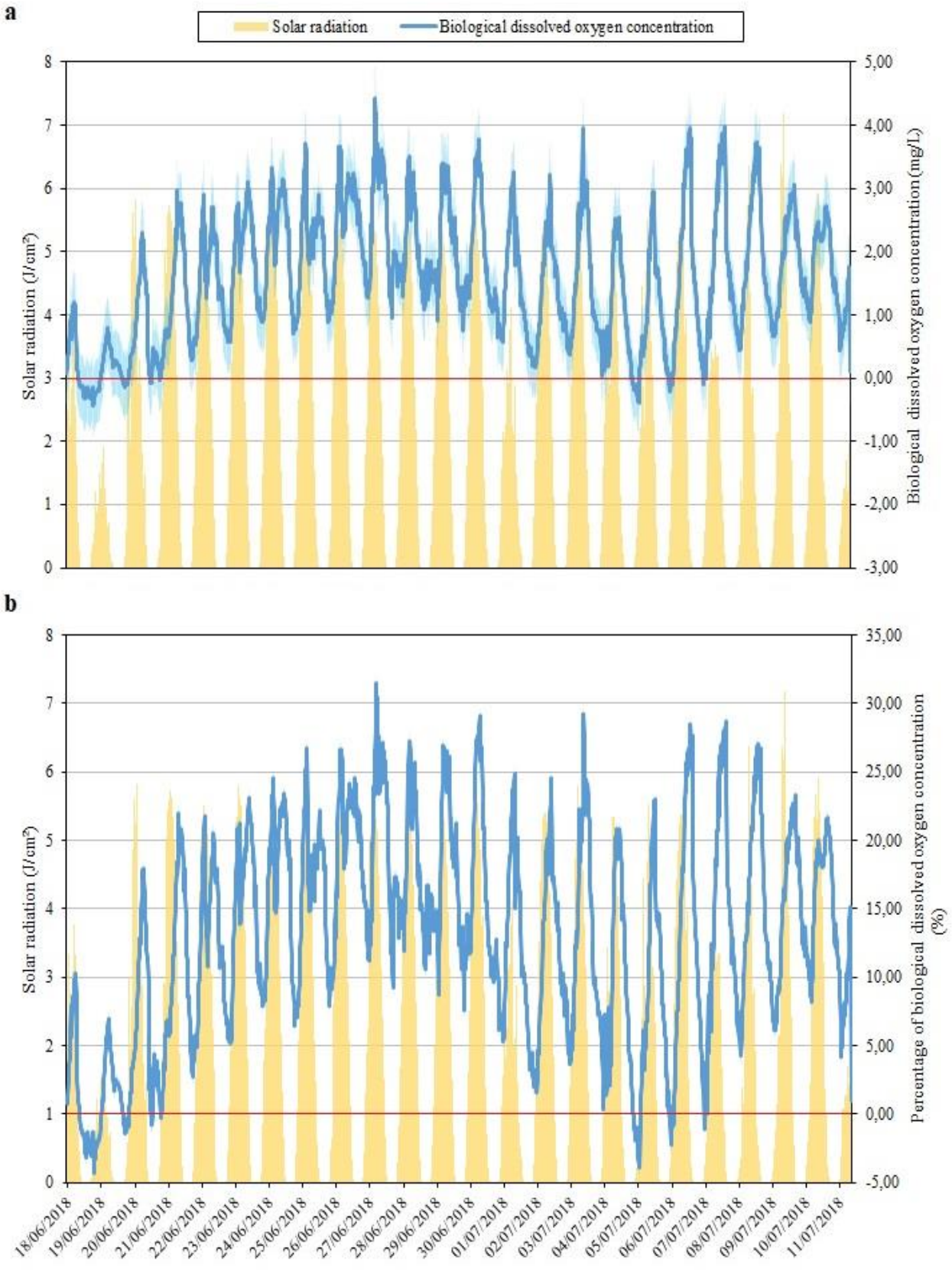

FIGURE 11. (a) Biological oxygen concentration calculated from the dissolved oxygen saturation data measured by the Hydrolab probe, and solar radiation data obtained from the weather station in Mace Head from 18th June to 11th July 2018. Accuracy range is indicated by shaded areas (Dissolved oxygen ± 0.5 milligrams per litre). Biological dissolved oxygen concentration of 0 mg/L is highlighted in red. (b) Percentage of biological dissolved oxygen concentration regarding the dissolved oxygen concentration measured by the Hydrolab probe. Percentage of biological dissolved oxygen concentration of 0% is highlighted in red.

Both pH data from Hydrolab multi-parameter probe and solar radiation data have been plotted in the Figure 12. Maximum pH values were measured at night between 7 PM and 10 PM, at least 5 hours later than the solar radiation maximum. With the exception of the maximum pH value on 30th June which matches the solar radiation maximum. Minimum pH values were matching the maximum solar values from 21st to 29th June, while during the rest of the time period minimum values were reached just after the dawn.

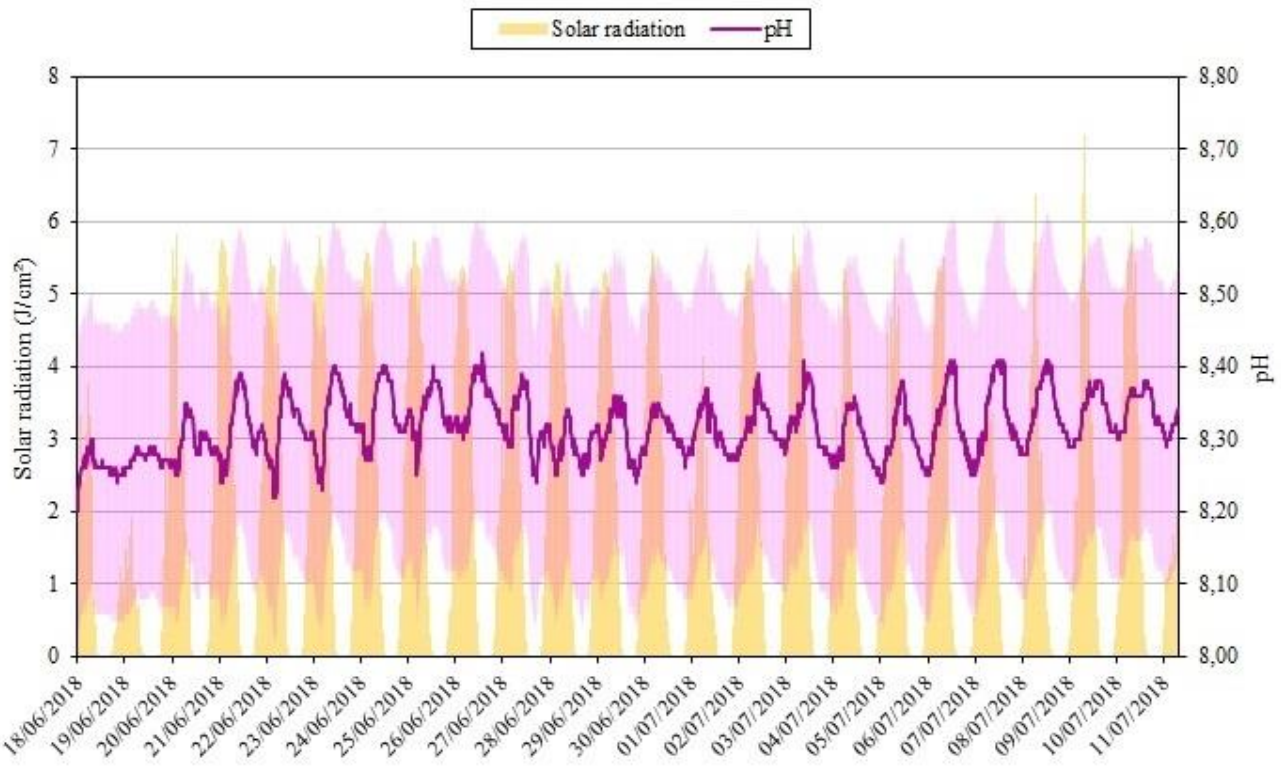

FIGURE 12. pH from Hydrolab multi-parameter probe and solar radiation data from the weather station in Mace Head from 18th June to 11th July 2018. Accuracy ranges are indicated by shaded areas (Hydrolab probe ± 0.20 pH units).

In order to quantify the potential of the kelp bed uptaking carbon from the water column, a set of calculations were carried out taking into account the following assumptions: (1) oxygen production as a result of the photosynthesis process was calculated as the difference between the maximum and minimum peak of dissolved oxygen concentrations due to biological activity while photosynthesis was the dominant process, (2) oxygen consumption as a result of the respiration process was calculated as a the difference between the maximum and minimum peak of dissolved oxygen concentrations due to biological activity while respiration was the dominant process, (3) the water column volume in which the kelp bed was active has been calculated using the kelp bed area calculated using GIS software and a depth water column of 1 metre, resulting in a total volume of 23237 m^3.

Kelp bed photosynthetic and respirations rates were calculated making use of the assumptions described above from 19th June to 11th July (Fig. 13a). Photosynthetic rates ranged between 0.10 and 0.65 $mgO_2 \cdot L^{-1} \cdot h^{-1}$, while respiration rates ranged between 0.05

and 0.40 $mgO_2 \cdot L^{-1} \cdot h^{-1}$. In addition, oxygen production rate, when photosynthesis was the dominant process, was higher than the oxygen consumption rate, when respiration was the dominant process, 18 out of 23 days.

Furthermore, carbon production and uptake rates were calculated taking into account a 1:1 proportion between the oxygen production / consumption and the carbon dioxide consumption / production as a result of the photosynthesis and respiration processes, respectively (equation 3). Kelp bed actively took up carbon from the water column 16 out of 23 days, reaching a maximum uptake rate of 3.307 $gC \cdot h^{-1}$ (Fig. 13b). Note that carbon production and uptake rates were calculated using the proportion of carbon in a carbon dioxide molecule.

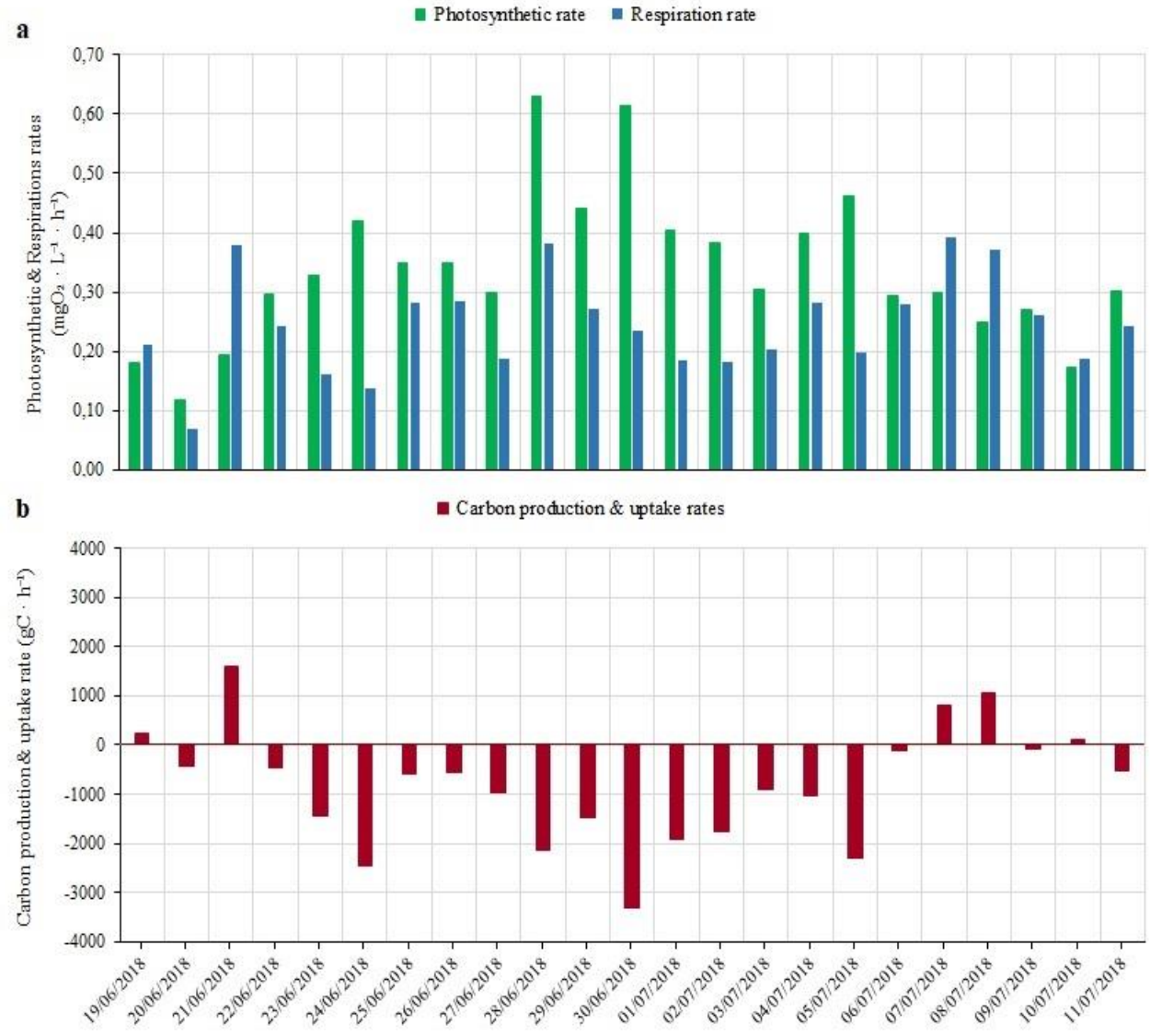

FIGURE 13. (a) Kelp bed photosynthetic and respirations rates calculated making use of the assumptions described above from 19th June to 11th July. (b) Carbon production and uptake rates calculated for the whole time period.

4. DISCUSSION

4.1. Winter sampling

A statistical analysis was carried out using salinity, seawater temperature and pH data recorded every minute on board the RV Celtic Explorer, as well as air temperature and wind speed data from the onboard meteorological station recorded at the same rate. Note that wind speeds have not been separately analysed based on their wind directions, due to the marked homogeneity of wind data along the whole time series during the winter sampling (winds from the west and southwest were prevailing during the three-day survey). The data set included on the statistical analysis from 5 PM on the 16th February to 2 PM on the 17th February, coinciding with the SeaFET^{TM} continuous data recording. Data did not follow a normal distribution, so data were analysed using the Spearman correlation (N = 1263, Table 4). Correlations were statistically significant for levels of significance lower than 0.01.

Seawater temperature and salinity followed a similar pattern during this sampling. In winter, the surface seawater which can be found in Galway Bay is greatly affected by the cold freshwater plume from the Corrib river runoff, as well as by cold fresh submarine groundwater discharge from the South-eastern part of the bay, whereas the ocean water outside the bay has a higher temperature and higher salinity as it is not affected by fresh water runoff. A strong positive correlation between seawater temperature and salinity data of 0.990 reflects this (Table 4).

Westerly and southwesterly winds prevailed during the whole survey, contributing to corral the relatively fresh surface water from the Corrib river plume in Galway Bay, making horizontal ventilation of the cold and fresh water difficult. Consequently, the stronger the winds were the higher the contrast was between salinity and seawater temperature from both in and outside Galway Bay (0.807 and 0.793 correlation coefficients, respectively).

On the other hand, air temperature did not have a great effect on the oceanographic conditions during the winter sampling as none of the correlation coefficients is greater than 0.250, mainly due to vertical mixing caused by strong winds. Therefore, physical forcings driven by both wind force on the west-east direction and runoff due to the winter precipitation on the east-west direction governed changes in salinity and seawater temperature on this coastal area.

pH data also has a strong and positive correlation with both salinity and seawater temperature (0.661 and 0.641 correlation coefficients, respectively). This can be explained by the fact that open ocean seawater has a higher pH compared to the water bodies in Galway Bay due to its higher salinity and to the lower pH of the Corrib inflow. The latter is supported by the study carried out by McGrath *et al.* in 2012 in which both inorganic carbon and pH levels were measured on the offshore surface waters of the Rockall Trough (northwest of Ireland). Open ocean pH levels on this area ranged between 8.05 and 8.15 units in wintertime, while values in Galway Bay in February 2018 ranged between 8.00 and 7.80.

In addition, terrigenous materials interactions as well as anthropogenic activities such as fossil fuel combustion and agriculture produce inputs of dissociation products of strong acids (HNO_3 and H_2SO_4) and bases (NH_3) which cause decreases in surface seawater pH (Doney *et al.*, 2007), while strong rainfall over the bay can also potentially lower the pH of surface waters. For this reason, as the RV Celtic Explorer was reaching Galway harbour, pH dropped reaching a minimum value of 7.8 units.

		Seawater temperature	Salinity	pH	Air temperature
Salinity	**Correlation coefficient**	**0.990**			
	Sig.	0.000			
pH	**Correlation coefficient**	**0.641**	**0.661**		
	Sig.	0.000	0.000		
Air temperature	**Correlation coefficient**	-0.173	-0.169	-0.238	
	Sig.	0.000	0.000	0.000	
Wind speed	**Correlation coefficient**	**0.793**	**0.807**	0.480	-0.089
	Sig.	0.000	0.000	0.000	0.002

TABLE 4. Spearman correlation coefficients for the data collected on board the RV Celtic Explorer from 4:50 PM on the 16th February 2018 to 1:55 PM on the 17th February 2018 (N = 1263). Salinity data (PSU), seawater temperature data (ºC) and pH data recorded on board the RV Celtic Explorer, as well as air temperature data (ºC) and wind speed data (m/s) from the onboard meteorological station. Correlations were statistically significant for levels of significance lower than 0.01. Statistically significant correlations above 0.500 are highlighted in green.

Correlations between pCO_2 data and the other oceanic and atmospheric measured parameters were not calculated due to the lack of a continuous record in both oceanic and atmospheric pCO_2 concentrations. In any case, oceanic pCO_2 concentration changes are mainly attributed to the differences in the oceanographic conditions between the water bodies inside and outside Galway Bay, however biological activity does constitute a small but significant source of carbon dioxide variability during this time of the year. Figure 4 shows that atmospheric pCO_2 from Mace head and Celtic Explorer are in very good agreement, with values of 410-415 ppm. Underway system pCO_2 from the surface water indicates higher values of 415-225 ppm, indicating that respiration and decomposition are driving up the CO_2 in the water column, so a positive output of CO_2 to the atmosphere during winter would be expected, even in a well mixed water column. The pCO_2 calculated from the DIC/TA samples also indicate higher water column pCO_2. Cold fresher water found inside the bay could have held more carbon dioxide rather than the relatively warmer saltier water which is located outside the bay. Furthermore, low pH found in Galway Bay could be attributed to the combined effect of the cold water which

could have held a considerable amount of carbon dioxide and the inputs of lower alkalinity waters from the river Corrib.

Taking into account the difference between the theoretical dissolved oxygen concentration that seawater could have held and the measured dissolved oxygen concentration, it has been observed that seawater is oxygen undersaturated both inside and outside Galway Bay. This can be explained by the fact that, regardless how well wind speed could have oxygenated the sea surface, oxygen production rates from biological activity during winter are the lowest throughout the year due to the combined effect of low seawater temperature and solar radiation, but consumption through respiration/decomposition still occurs, reducing the oxygen saturation.

On the other hand, the four dissolved oxygen concentration depth profiles (Fig. 5) have shown how well mixed the water column was during winter. Strong wind speeds are expected during wintertime at this latitude, preventing thermal stratification from developing, which would have been detected with these depth profiles if it had occurred.

4.2. Summer sampling

A statistical analysis was carried out using the data recorded every fifteen minutes from the 11:45 AM on the 18th June to the 11:30 AM on the 11th July (Table 5). Salinity data was obtained from Hydrolab multi-parameter probe and seawater temperature data comes from the Hobo O_2 and temperature logger. Wind speeds have been separately analysed based on their wind directions (Fig. 3), due to the marked heterogeneity of wind data along the whole time series during the summer sampling. In this way, wind directions between 315º to 45º were considered as northerly winds, between 45º to 135º as easterly winds, between 135º to 225º as southerly winds, and between 225º to 315º as westerly winds. Tide data was obtained from a buoy at the Inishmore harbour in Kilronan. Air temperature and wind speed were recorded at the atmospheric research station at Mace Head (Fig. 7). Data did not follow a normal distribution, so data were analysed using the Spearman correlation coefficient. Correlations were statistically significant for levels of significance lower than 0.01.

Summer sampling was carried out during one of the most severe droughts in Northwest Europe, reaching minimum night temperatures of 18.0ºC and no precipitation during the 82.75% of the sampling time. Changes in seawater temperature data had a positive correlation with the air temperature data (0.654 correlation coefficient), as well as with the easterly winds speed data (0.578 correlation coefficient). In this way, displacement of the relatively warm seawater in Galway Bay to the open ocean has been favoured by the easterly winds, when the seawater temperature maximum was reached.

On the other hand, salinity changes appears not to be linked with any of the measured parameters for the whole time period as none of the calculated correlations coefficients were higher than 0.200. Westerly winds prevailed along the whole time period (35.17% of the time series). Conversely, they were not strong enough to boost the entry of saltier open ocean water and break the thermal stratification (0.096 correlation coefficient). In general, it was not observed any strong correlation between wind speed and salinity data, presumably due to average wind speed did not exceed 6 metres per second.

The time period when the greatest change in salinity has been observed was between 27th and 30th June (~ 1 PSU), during spring tide. In order to know why this changes in salinity occurred, correlations were recalculated for this 3-day time period (N=384, data did not follow a normal distribution, so data was analysed using the Spearman correlation coefficient). Tide data had a negative statistically significant correlation with seawater temperature data (-0.601 correlation coefficient) and a positive correlation with salinity data (0.447 correlation coefficient). Wind speed data did not have a statistically significant correlation with both seawater temperature and salinity data. Thus, spring tide was the main physical forcing which favoured the entry of saltier seawater and favoured the horizontal ventilation to the open ocean during these three days. Consequently, seawater temperature changes were driven mainly by changes in air temperature and tide forcing. By contrast, salinity was only affected by the changes in the oceanographic conditions caused by tidal cycle.

		Seawater temp.	Salinity	Tide	Air temp.	Atmosp. pCO_2	pH
Salinity (N=2208)	**Correlat. coeff.**	-0.135					
	Sig.	0.000					
Tide (N=2208)	**Correlat. coeff.**	-0.135	0.088				
	Sig.	0000	0.000				
Air temp. (N=2208)	**Correlat. coeff.**	**0.659**	-0.122	**0.018**			
	Sig.	0.000	0.000	0.404			
pH (N=2208)	**Correlat. coeff.**	0.161	0.075	**0.026**	0.281	-0.373	
	Sig.	0.000	0.000	0.227	0.000	0.000	
Northerly wind speed (N=525)	**Correlat. coeff.**	-0.210	-0.192	**0.034**	**-0.054**	-0.282	-0.215
	Sig.	0.000	0.000	0.435	0.218	0.000	0.000
Easterly wind speed (N=581)	**Correlat. coeff.**	**0.578**	**-0.042**	-0.126	0.424	-0.253	-0.194
	Sig.	0.000	0.310	0.002	0.000	0.000	0.000
Southerly wind speed (N=330)	**Correlat. coeff.**	-0.202	**0.107**	**0.073**	**-0.099**	**-0.025**	-0.206
	Sig.	0.000	0.051	0.188	0.071	0.646	0.000
Westerly wind speed (N=772)	**Correlat. coeff.**	-0.174	0.096	0.161	-0.254	**-0.062**	**-0.035**
	Sig.	0.000	0.007	0.000	0.000	0.085	0.323

TABLE 5. Spearman correlation coefficients for the data collected from the 18th June to the 11th July 2018. Seawater temperature data (ºC) was obtained from Hobo probe. Salinity data (PSU) and pH data from Hydrolab multi-parameter probe. Air temperature data (ºC), wind speed data (m/s) and pCO_2 data (ppm) from the atmospheric research station at Mace Head. Tide data (m) was obtained from a buoy at the Inishmore harbour. Correlations were statistically significant for levels of significance lower than 0.01. Statistically significant correlations above 0.500 are highlighted in green. Non-statistically significant correlations are highlighted in red.

Atmospheric pCO_2 concentration does not have a strong correlation with either the atmospheric or the oceanic measured parameters. However, maximum pCO_2 concentrations have been found while winds from the east prevailed. This can be explained by the fact that easterly winds could have brought both carbon dioxide produced inland by anthropogenic activities, as Galway city is approximately 56.5 kilometres away, and the daily pCO_2 fluctuations caused by the inland vegetation biological activity, as maximum peaks were measured when respiration was the dominant process. On the other hand, a negative correlation was found between pH and atmospheric pCO_2 concentration of -0.373. Further studies would be required to quantify how much of the decrease in pH is due to either the atmospheric CO_2 diffusion into seawater or the CO_2 production from the aquatic photosynthetic organisms' biological activity, especially during summertime when the highest photosynthetic rates were measured. On the other hand, oceanic pCO_2 concentrations from DIC/TA samples ranged between 250 and 375 ppm, and all concentrations values were well below the minimum atmospheric concentration of 400 ppm. Taking into account that all the samples were taken in the daytime, the kelp bed was effectively removing carbon dioxide from the water column

via photosynthesis. This is in contrast to the winter sampling, where pCO_2 in the water column was higher than in the atmosphere. There are no water samples from the kelp mooring in summer which were taken at night, so it cannot be definitively said that the system has net uptake of CO_2 form the atmosphere in summer, however the dissolved oxygen data (Fig. 11) indicate that this is most likely the case.

Another statistical analysis was carried out using the data recorded every fifteen minutes from 18th June to the 11th July (Table 6). Correlations were calculated for both day and nighttime to quantify the effect of solar radiation on the biological activity of the kelp bed surrounding the mooring for each analysed parameter. This 24-day time series was chosen as it matches with the longest continuous pH data set recorded by only one stand-alone device. Seawater temperature and dissolved oxygen data were obtained from Hobo probe. Salinity and pH were measured by Hydrolab multi-parameter probe. Air temperature and solar radiation data were recorded at the atmospheric research station at Mace Head. Seawater dissolved oxygen data caused by the biological activity of the kelp bed have also been included. Moreover, wind speed and tide data have not been included as they had not such a big effect on the oceanographic conditions during the summer sampling, as we have seen above. Data did not follow a normal distribution, so data was analysed using the Spearman correlation coefficient. Correlations were statistically significant for levels of significance lower than 0.01.

pH and dissolved oxygen concentration changed in the same direction during both daytime and nighttime (0.719 and 0.917 correlations coefficients, respectively), as well as dissolved oxygen concentration and the fluctuations in dissolved oxygen concentration due to the biological activity of the kelp bed. In order to know why these changes have happened and if they can be attributed to the biological activity of the kelp bed, correlations between the fluctuations in dissolved oxygen concentration and the rest of the measured parameters must be analysed.

Respiration is the dominant process from the end of the evening to first early morning hours, when complete absence of solar radiation occurs. This metabolic process consumes oxygen at the same rate as carbon dioxide is produced, increasing the dissolved inorganic carbon, and hence lowering the pH. Consequently, a strong positive correlation was found between pH data and the fluctuations in dissolved oxygen concentration produced by the biological activity of the kelp bed during nighttime 0.775, so as the dissolved oxygen concentration reduced, so the pH lowered also. The fact that the correlation is lower than 1.000 can be explained because of the lag of a few hours between when the minimum dissolved oxygen concentration and the minimum pH values were reached. Note that as oxygen is consumed, carbon dioxide is produced at the same rate during respiration, decreasing the pH.

As soon as the solar radiation begins to increase, giving rise to the solar-radiation-dependent process known as photosynthesis, respiration ceases to be the dominant process. Oxygen is produced as metabolic waste during photosynthesis at the same rate as carbon dioxide is consumed. Dissolved oxygen concentration reach maximum values during the evening, coinciding with a drop of pH due to the CO_2 consumption and consequent removal from the water column. As in the previous case, a strong positive correlation was found between pH data and the fluctuations in dissolved oxygen

concentration produced by the biological activity of the kelp bed during daytime of 0.737. Again the imperfect correlation can also be explained by the fact that there is a lag of a few hours between when the maximum dissolved oxygen concentration and the maximum pH values were reached. The lag which was observed during nighttime is shorter than the daytime lag. It should be borne in mind that some of this change could have been caused by mixing of water bodies with either different dissolved oxygen or DIC concentrations, due to the combined action of tide and wind forcings. However, since there is no correlation between tide and seawater temperature or salinity (Table 5), and since the salinity changes throughout the period are so small, we can be confident that the changes are due to biological activity.

		Seawater temperature		Salinity		pH		Dissolved oxygen concentration		Biological disolved oxygen concentration	
pH	**Correlation coefficient**	0.258	-0.102	0.112	**0.001**						
	Sig.	0.000	0.009	0.000	0.975						
Dissolved oxygen concentration	**Correlation coefficient**	0.073	-0.121	-0.145	**-0.021**	**0.719**	**0.917**				
	Sig.	0.004	0.002	0.000	0.609	0.000	0.000				
Biological disolved oxygen concentration	**Correlation coefficient**	0.373	0.335	-0.195	-0.213	**0.737**	**0.775**	**0.948**	**0.862**		
	Sig.	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Air temperature	**Correlation coefficient**	**0.680**	**0.753**	-0.097	-0.175	0.418	**-0.036**	0.405	**0.012**	**0.584**	0.382
	Sig.	0.000	0.000	0.000	0.000	0.000	0.374	0.000	0.767	0.000	0.000

TABLE 6. Spearman correlation coefficients for the data collected from the 18th June to the 11th July 2018. Seawater temperature data (ºC), and both total and biological dissolved oxygen concentration data (mg/L) were obtained from Hobo probe. Salinity data (PSU) and pH data from Hydrolab multi-parameter probe. Air temperature data (ºC) from the atmospheric research station at Mace Head. Correlations were statistically significant for levels of significance lower than 0.01. Daytime data are in yellow background columns (N = 1596). Nighttime data are in grey background columns (N = 619). Statistically significant correlations above 0.500 are highlighted in green. Non-statistically significant correlations are highlighted in red.

Seawater temperature and salinity data appear not to have a great effect on pH and dissolved oxygen concentration changes during the summer sampling. This is due to dissolved oxygen concentrations related to temperature alone, calculated at the saturation of 100%, vary by only 1.6 milligrammes per litre, while the additional variation due to biological activity is not larger than 5.0 milligrammes per litre. In addition, dissolved oxygen concentration changes due to biological activity have a small positive correlation with seawater temperature data regardless of whether it is day or night (0.373 and 0.335 correlation coefficients, respectively), inasmuch as high seawater temperatures boost the metabolic activity during both respiration and photosynthesis. Consequently, increasing seawater temperature during daytime may have led to a slight increase in oxygen production during the photosynthesis phase. Conversely, decreasing of the biological

dissolved oxygen concentration during night could have related to the effect of decreasing seawater temperature on the respiration metabolic process. Further control-environment studies may help to understand whether these variations are due to a natural trend or seawater temperature may also be involved.

In addition, correlations were recalculated for the time period between 23rd and 26th June, when the maximum double peaks were found during daytime. Strong positive correlations between pH and both total dissolved oxygen concentration and dissolved oxygen concentration from the biological activity were found during nighttime (N = 159, 0.950 and 0.778 correlation coefficients, respectively), while weak positive correlations were found when the photosynthesis was the dominant process (N = 417, 0.343 and 0.264 correlation coefficients, respectively). Photosynthetic reaction centres might have been oversaturated due to exposure to high levels of solar radiation along the day. In any case, further studies in strictly controlled environment conditions could confirm this hypotheses.

It is important to note two results from the pH measurements. One is that relatively large variations in the pH of surface waters of the order of 0.2 pH units, occur in Galway Bay which are driven by the saltwater-freshwater regime in the bay, varying with the strength of the river outflow, and the wind strength and direction. This is clearly seen in the winter data. The second is that within the kelp bed, with no change in salinity, similarly large changes in pH occur on a daily basis, driven by photosynthesis/respiration cycles, this is seen in the summer data. This contrasts with the deep sea environment, where a change of only 0.1 pH unit per decade is observed (McGrath et al, 2012).

To sum up, it can be concluded that the changes in pH and dissolved oxygen concentration are governed more by the biological activity of the kelp bed during the summer period rather than physical forcing, although the latter may not be insignificant as they may have an important role on the observed lags during both day and night. This has been reflected in the great capacity of the kelp bed uptaking carbon from the water column (maximum uptake rate of 3.307 $gC \cdot h^{-1}$), providing an effective carbon sink during summertime.

5. CONCLUSIONS

Meteorological parameters, such as wind speed and direction, air temperature or precipitation, affect differently the water bodies which can be found in Galway Bay during winter and summer. On the one hand, strong westerly winds during winter drive saltier surface seawater into Galway Bay, retarding horizontal dispersion of the cold and fresh water from the river Corrib outflow. Thus, physical forcing, driven by both wind force and runoff due to the winter precipitation, governed changes in salinity and seawater temperature in this coastal area. Moreover, low pH found in Galway Bay could be attributed to the combined effect of the cold water which could have held a considerable amount of carbon dioxide and the inputs of lower alkalinity waters from the river Corrib. Furthermore, oceanic pCO_2 concentration changes are mainly attributed to the differences in the oceanographic conditions between the water bodies inside and outside Galway Bay in winter as biological activity does not constitute a significant source of carbon dioxide variability during this time of the year due to the combined effect of low seawater temperature and solar radiation, which minimises photosynthesis but also reduces respiration and decomposition. However the winter water column was oxygen undersaturated, despite the high winds and well mixed conditions. This could be also explained by the fact that stormy winter weather, would have saturated the seawater with oxygen, some of which was then consumed by metabolic processes as respiration and decomposition of the organic matter from both the disturbed sediments and debris brought in by the river runoff.

Conversely, the development of a strong thermal stratification during summertime was possible due to the weak winds, that were not strong enough to boost the entry of saltier open ocean, and the almost total absence of precipitation as well as the continuous high temperature during one of the most severe droughts in Northwest Europe. Thus, the main physical forcing which favoured the entry of saltier seawater and favoured the horizontal ventilation to the open ocean was the tide. On the other hand, pH and dissolved oxygen concentration are governed more by the biological activity of the kelp bed during this period rather than physical forcing, taking into account the great capacity of the kelp bed uptaking carbon from the water column and producing oxygen. In any case, further studies to quantify how much of the decrease in pH is due to either the atmospheric CO_2 diffusion into seawater or the CO_2 production from the aquatic photosynthetic organisms' biological activity are required. Therefore, the main factor governing the changes in the chemical conditions of seawater in summer is the biological activity, which is boosted by both the high seawater temperature and the long daylight period during summer.

Ultimately, we have come to the conclusion that the pH and oxygen concentration changes in seawater during winter are mainly due to the physical forcing, specially wind force and precipitation, while during summer these changes were governed by the biological activity of the kelp bed rather than the relatively minor effect caused by physical forcing during this time period. However in winter it is clear that some respiration/decomposition is taking place in the water column, as there is about 10% undersaturation of oxygen. The magnitude of the pH changes in Galway Bay that are driven by the physical forcing and biological activity are similar (about 0.2 pH units in each case), and are much greater and more rapid than anything currently being experienced in deep waters offshore. This implies that coastal biota are well adapted to

rapid (diurnal) pH changes, something not experienced by deep ocean fauna. Finally, the indications are that Galway Bay is a source of CO_2 to the atmosphere in winter, and, at least areas where macroalgae grow, is a sink in summertime.

Further studies are required to throw light on (1) how the pH and oxygen concentration change due to both the effect of biological activity and physical forcing in the area in which the mooring was set, (2) what is the magnitude of these changes during a similar length period of time during the four seasons, and last but not least, (3) what proportion of the pH changes in the seawater in Galway Bay is being driven by atmospheric CO_2 during the different seasons throughout the year, increasing knowledge about how Climate Change is affecting OA in this particular area.

6. REFERENCES

Appelhans, Y. S., Thomsen, J., Pansch, C., Melzner, F., Wahl, M., 2012. *Sour times: seawater acidification effects on growth, feeding behaviour and acid-base status of Asterias rubens and Carcinus maenas.* Mar Ecol Prog Ser **459**, 85-97.

Benson, B. B., Krause, D. Jr., 1984. *The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with the atmosphere*. Limnology and Oceanography, **29**, 620-632.

Burns, W. C. G., 2008. *Anthropogenic carbon dioxide emissions and ocean acidification*. In Saving Biological Diversity: Balancing protection of endangered species and ecosystems. Eds. Askins R.A., Dreyer G.D., Visgilio G.R., Whitelaw D.M. Springer, 190-196.

Caldeira, K. & Wickett, M. E., 2003. *Anthropogenic carbon and ocean pH.* Nature **425**, 365. (doi: 10.1038/425365a).

Cornwall, C. E. *et al*., 2013. *Diurnal fluctuations in seawater pH influence the response of a calcifying macroalga to ocean acidification*. Proc R Soc Biol Sci Ser B **280**. (doi: 10.1098/rspb.2013.2201).

Delille, B., Borges, A. V., Delille, D., 2009. *Influence of giant kelp beds (Macrocystis pyrifera) on diel cycles of pCO_2 and DIC in the Sub-Antartic coastal area.* Estuarine, Coastal and Shelf Science **81**, 114-122. (doi: 10.1016/j.ecss.2008.10.004).

Dickson, A. G., Millero, F. J., 1987. *A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media*. Deep Sea Research Part A, Oceanographic Research Papers, **34**, 1733-1743. (doi: 10.1016/0198-0149(87)90021-5).

Dickson, A. G., Afghan, J. D., Anderson, G. C., 2003. *Reference materials for oceanic CO_2 analysis: a method for the certification of total alkalinity*, Mar. Chem., **80**, 185–197.

Dickson, A. G., Sabine, C. L., Christian, J. R., 2007. *Guide to best practices for ocean CO_2 measurements*, PICES Special Publication, **3**, 1–191.

Doney, S. C., Mahowald, N., Lima, I., Feely, R. A., Mackenzie, F. T., Lamarque, J. F., Rasch, P. J., 2007. *Impact of anthropogenic atmospheric nitrogen and sulphur deposition on Ocean Acidification and the inorganic carbon system.* Proceeds National Academy of Science, USA 104 (**37**), 14580-14585.

Eppley, R.W. & Peterson, B. J., 1979. *Particulate organic matter flux and planktonic new production in the deep ocean.* Nature **282**, 677-680.

Hepburn, C. D. et al., 2011. *Diversity of carbon use strategies in a kelp forest community: implications for a high CO_2 ocean*. Glob Change Biol **17**, 2488-2497.

Hurd, C. L., Cornwall, C. E., Currie, K. I., Hepburn, C. D., McGraw, C. M., Hunter, K. A., Boyd, P., 2011. *Metabolically-induced pH fluctuations by some coastal calcifiers exceed projected 22nd century ocean acidification: a mechanism for differential susceptibility?* Glob. Change Biol. **17**, 3254-3262.

Johnson, K. M., Sieburth, J. M., Williams, P. J. L., Brändström, L., 1987. *Coulometric total carbon dioxide analysis for marine studies: Automation and calibration*, Mar. Chem., **21**, 117–133.

Johnson, K. M., Wills, K. D., Butler, D. B., Johnson, W. K., Wong, C. S., 1993. *Coulometric total carbon dioxide analysis for marine studies: maximizing the performance of an automated gas extraction system and coulometric detector*, Mar. Chem., **44**, 167–187.

Jueterbock, A., Tyberghein, L., Verbruggen, H., Coyer, J. A., Olsen, J. L., Hoarau, G., 2013. *Climate change impact on seaweed meadow distribution in the North Atlantic rocky intertidal*. Ecol. Evol., **3**, 1356–1373.

Kennedy, H., Beggins, J., Duarte, C. M., Fourqurean, J. W., Holmer, M., Marbà, N., Middelburg, J. J., 2010. *Seagrass sediments as a global carbon sink: isotopic constraints*. Glob. Biogeochem. Cycles, **24**. (doi: 10.1029/2010GB003848).

Laruelle, G. G., Dürr, H. H., Slomp, C. P., Borges, A. V., 2010. *Evaluation of sinks and sources of CO_2 in the global coastal ocean using a spatially-explicit typology of estuaries and continental shelves: global CO_2 fluxes in coastal waters*. Geophys. Res. Lett., **37**. (doi: 10.1029/2010GL043691).

McGrath, T., Kivimäe, C., Tanhua, T., Cave, R. R., McGovern, E., 2012. *Inorganic carbon and pH levels in the Rockall Trough 1991-2010 (1991-2010)*. Deep-Sea Research, **68**, 79–91. (doi: 10.1016/j.dsr.2012.05.011).

McGrath, T., Kivimäe, C., McGovern, E., Cave, R. R., Joyce, E., 2013. *Winter measurements of oceanic biogeochemical parameters in the Rockall Trough (2009-2012)*. Earth Syst. Sci. Data, **5**, 375–383. (doi: 10.5194/essd-5-375-2013).

Mehrbach, C., Culberson, C. H., Hawley, J. E., Pytkowicx, R. M., 1973. *Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure*. Limnology and oceanography, **18**, 897-907. (doi: 10.4319/lo.1973.18.6.0897).

Mintrop, L., Pérez, F. F., Gonzalez-Dávila, M., Santana-Casiano, J. M., Körtzinger, A., 2000. *Alkalinity determination by potentiometry: intercalibration using three different methods*, Cienc. Mar., **26**, 23–37.

Ní Longphuirt, S., Stengel, D., O'Dowd, C., McGovern, E., 2010. *Ocean acidification: An emerging threat to our marine environment.* Marine foresight series, **6**.

Olesen, B., Krause-jensen, D., Marbà, N., Christensen, P. B., 2015. *Eelgrass Zostera marina in subarctic Greenland : dense meadows with slow biomass turnover in cold waters*. Mar Ecol. Prog. Ser., **518**, 107–121.

Olischläger, M., Bartsch, I., Gutow, L., Wiencke, C., 2012. *Effects of ocean acidification on different life-cycle stages of the kelp Laminaria hyperborean (Phaeophyceae)*. Bot Mar **55**, 511-515.

OSPAR, 2006. *Effects on the marine environment of Ocean Acidification resulting from elevated levels of CO_2 in the atmosphere.* Biodiversity Series **285/2006.**

Riebesell, U., Fabry, V. J., Hansson, L., Gattuso, J-P., 2010. *Guide to best practices for ocean acidification research and data reporting*, p. 260. Luxembourg: Publications Office of the European Union.

Rost, B., Zondervan, I., Wolf-Gladrow, D., 2008. *Sensitivity of phytoplankton to future changes in ocean carbonate chemistry: current knowledge, contradictions and research directions.* Marine Ecology Progress Series **373**, 277-237.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T. H., Kozyr, A., Ono, T., Rios, A. F., 2004. *The oceanic sink for anthropogenic CO_2.* Science **305**, 367–371.

Schubert, R., Schellnhuber, H. J., Buchmann, N., Epiney, A., Grießhammer, R., Kulessa, M., Rahmstorf, S., Schmid, J., 2006. *The future oceans - Warming up, rising high, turning sour.* Special Report by the German Advisory Council on Global Change (WBGU), p 123.

Smith, S. V., 1981. *Marine macrophytes as global carbon sink*. Science **211**, 838-840.

Zeebe, R. E., Wolf-Gladrow, D., 2001. *CO_2 in seawater: Equilibrium, kinetics, isotopes.* Elsevier Oceanographic Series **65**, 346.