Marine Environmental Research 116 (2016) 51-60

Contents lists available at ScienceDirect

Marine Environmental Research

journal homepage: www.elsevier.com/locate/marenvrev

Time variability of the north-western Mediterranean Sea pH over 1995–2011

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A R T I C L E I N F O

Article history: Received 4 December 2015 Received in revised form 12 February 2016 Accepted 18 February 2016 Available online 4 March 2016

Keywords: Ocean acidification Anthropogenic CO₂ Mediterranean sea

ABSTRACT

Factors controlling ocean acidification and its temporal variations were studied over the 1995–2011 period at the Dyfamed site at 10 m depth, in the North Mediterranean Sea. The results indicated a mean annual decrease of 0.003 \pm 0.001 pH units on the seawater scale. The seasonal variability was characterized by a pH decrease during springtime and a strong pH increase in late fall. Anthropogenic CO₂ (C_{ANT}) absorption by the ocean was the key driver of seawater acidification in this region, accounting for about 70% of the observed drop in pH, followed by water temperature (about 30%). The total inorganic carbon (C_T) data showed a C_T increase of 30.0 \pm 1.0 µmol kg⁻¹ per decade. This decadal increase is mainly due to the C_{ANT} penetration (43.2 µmol kg⁻¹ per decade) in surface waters, which is mitigated for by relatively small opposing changes in C_T due to physical and biological processes.

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1. Introduction

Understanding the temporal evolution of ocean waters acidification is of outmost importance especially to quantify its potential environmental impacts. Therefore it is necessary to first determine and understand all the processes affecting the ocean pH.

Many models have shown that ocean pH has already declined with increases in atmospheric CO_2 by approximately 0.1 unit since the beginning of the industrial era and is expected to decrease by an additional 0.4 units by the end of this century (Brewer, 1997; Caldeira and Wickett, 2003; Orr et al., 2005; Blackford and Gilbert, 2007; Doney et al., 2009; Feely et al., 2009; Touratier and Goyet, 2011; Flecha et al., 2015; Hassoun et al., 2015; Palmiéri et al., 2015). Furthermore, recent studies indicate that, in some areas, the rates of decline are substantially faster than inferred by previous predictions (Wootton et al., 2008). At present, sustained time-series observations from 15 to 30 years show that surface ocean pH decreases regionally at different rates, ranging from 0.0013 to 0.0026 per year (Dore et al., 2009; Olafsson et al., 2009, 2010; Gonzales-Davila et al., 2010; Astor et al., 2013; Midorikawa et al., 2012, Bates, 2007, 2012; Bates et al., 2014). Observations

* Corresponding author. E-mail address: markcelklindr@gmail.com (K. Marcellin Yao). from other long-term monitoring stations have also revealed a decreasing trend, with higher values near shores (Hauri et al., 2013; Lauvset and Gruber, 2014; Xue et al., 2014). Although many efforts have been made, still more regions should be evaluated to better understand the various regional trends as well as the global trend.

It is known that ocean acidification may affect metal speciation; hence its bioavailability (Millero et al., 2009; Lacoue-Labarthe et al., 2009; Shi et al., 2010) and adversely impacts marine biota, but little is known on what the gradual long term of pH lowering will be on marine organisms (Feely, 2004; Comeau et al., 2009; Milligan et al., 2009; Bates et al., 2010; Fujita et al., 2011; Hurd et al., 2011; Andersson and Mackenzie, 2012, 2012; Flynn, 2012; Beare et al., 2013). Actually, laboratory experiments have shown that a low carbonate saturation state can lead to the dissolution of calcium carbonate (both calcite and aragonite) skeletons of multiple calcifying plankton species, corals, coralline algae and mollusks. However, a relatively recent paper (Wootton et al., 2008) has pointed out the positive response to pH declining both by calcareous acorn banarcles and non-calcareous fleshy algae, as well as the lack of response by coralline algae crollina vancouveriensis. Nevertheless, the same study also predicted that increasing H⁺ ion concentrations will negatively affect large dominant calcifying organisms. The authors related these counter behaviors to the web of species interactions (e.g., competition, predation, grazing) that may complicate the response. As pH changes may have detrimental







effects on marine ecosystems, it is essential to improve our understanding of the dynamics of ocean pH.

Though several data and available literature deal with pH decrease and distributions in the world ocean, our knowledge of factors controlling ocean acidification and its temporal trend is still relatively unclear. First and foremost, the obvious source is the unmastered variability of anthropogenic CO2 (CANT). It has been relatively well estimated (Sabine et al., 2004; Canadell et al., 2007) that globally the ocean has taken up about 30% of atmospheric carbon from anthropogenic origin during the last few decades. The increasing uptake of atmospheric CO₂, at least in some parts of the ocean, is expected to significantly affect the sea water chemistry, which includes an increase in both partial pressure of CO_2 (p CO_2) and total inorganic carbon (C_T) , a decrease in the carbonate ion (CO_3^{2-}) concentration, and subsequently a decrease in pH (Riebesell et al., 2009a,b). These changes, particularly with respect to pH, vary strongly among ocean basins and depend mainly on the variation of the concentration of total inorganic carbon (C_T) , which is known to be linked to variable physical and biological processes (Bégovic and Copin-Montégut, 2002; Copin-Montégut and Bégovic, 2002; Riebesell et al., 2009a,b; Archer et al., 1996; Touratier and Goyet, 2009; Dore et al., 2009; González-Dávila et al., 2010). Thus, studies on factors controlling C_T variations can provide fundamental information on ocean pH variations. Another major source of uncertainties is that while the CO₂ fugacity and total alkalinity (A_T) have been extensively measured regionally and globally over several decades with high precision and accuracy (Lauvset and Gruber N., 2014), high quality measured pH are scarce (Touratier et al., 2005: Lauvset and Gruber N., 2014), especially in the Mediterranean Sea (Touratier and Goyet, 2011). Furthermore, problems associated with the calculations of the carbonate system parameters include the choice of the pH scale and the high-precision determination of all relevant dissociation constants in natural seawater (Friis et al., 2004; Marion et al., 2011). As a result, it is a great challenge to have any specific idea of pH long-term trend in many areas of the global ocean.

In the Mediterranean Sea, considerable efforts have been made over the last decade to estimate pH decline in deep waters with respect to the preindustrial levels using various CANT models. While some researchers have simulated a total pH decline between -0.055 and -0.156 pH units based on CANT estimation by the tracer combining oxygen, inorganic carbon and total alkalinity (TrOCA) method (Touratier and Goyet, 2011; Hassoun et al., 2015), others pointed out values ranging from -0.005 to -0.06 pH units using the transit time distribution (TTD) model (Palmiéri et al., 2015; Flecha et al., 2015). These conclusions are based on the differences in the amount of CANT calculated through these various models (Huertas et al., 2009; Schneider et al., 2010; Rivaro et al., 2010; Flecha et al., 2012). Moreover, no data is available for surface waters because the aforementioned approaches could not distinguish the C_{ANT} from the bulk of CO_2 in surface layer (>300 m), except Palmiéri et al. (2015) who estimated a total pH change of -0.08 pH units since the beginning of the preindustrial era and concluded that the pH reduction in the Mediterranean Sea is similar to the one of the global ocean.

The two main objectives of this study are first to determine and understand the seasonal variability of near surface (10 m depth) seawater pH from 1995 to 2011, at the Dyfamed site located in the North Mediterranean Sea and second, to determine and quantify the main factors driving the long term trends of both pH and C_T in this area which may influence the carbon inventories of the North Atlantic Ocean (Huertas et al., 2009).

2. Methods

2.1. Data

The time series of pH values over the 1995–2011 period were estimated at 10 m depth based on the observational records of salinity, temperature, pressure, total alkalinity (A_T), and C_T at the Dyfamed site, which is located in the central part of the Ligurian Sea (42°25 N, 7°59 E), in the North-Western of the Mediterranean Sea (Fig. 1). These data are available from the DYFAMED database at http://www.obs-vlfr.fr/dyfBase/, but not all the used data are publicly accessible at this moment. Details concerning the measurements of the carbonate properties can be found at http://www. obs-vlfr.fr/jgofs2/sodyf/home.htm/. Measurements of C_T and A_T were performed by potentiometry according to the DOE handbook of methods for CO₂ analysis (DOE, 1994). The accuracy of C_T and A_T measurements, based on measurements of certified reference material (Dickson et al., 2003), were $\pm 2 \mu mol kg^{-1}$ and $\pm 2 \ \mu$ mol kg⁻¹, respectively. The DYFAMED time series station has been sampled approximately once a month from 1995 to 2011. However, measurements for practical salinity, AT and CT were not available from 1995 to 1997 as well as those for temperature from 2003 to 2008. Thus, as the computation of pH required these properties, it was necessary to reconstruct them.

2.2. Reconstruction of near surface (10 m depth) water salinity and temperature

Since measurements of temperature, salinity and pressure corresponding to the sampling time at the same site were carried out for hydrobiological studies (http://www.obs-vlfr.fr/jgofs2/sodyf/ hydrolo.htm/), we used the software package TABLE CURVETM 3Dv4.0 which tests thousands of equations to determine appropriate functions that best fit the measured temperatures, salinities and pressures. The goodness of fit of the multiple linear regressions was assessed by the standard deviation (SD_R) of the residuals R (i.e., the difference between the measured and estimated property). Once equations that best fit these properties were determined for each sampling period, missing data where calculated and the statistical analysis of the residuals showed that SD_R values were within ± 0.002 °C and ± 0.0004 , for temperature and salinity, respectively, with R² values greater than 0.99 (Figs. 2 and 3). Thus, the resulting errors for A_T and C_T appeared insignificant. Since hydrobiological and biogeochemical samplings were carried out both at the same time, these results show that temperature and salinity data from hydrobiological data base could then be used to calculate the carbonate system properties in biogeochemical samples. Data reconstruction was not performed for a data gap over 2000-2003 because biogeochemical sampling was not carried out during this period.

2.3. Reconstruction of A_T and C_T values from 1995 to 1997

From 1995 to 1997, among the carbonate properties, only the CO_2 fugacity (f CO_2) data were available. We estimated surface A_T with an uncertainty of 6 µmol kg⁻¹ using calculated salinity and measured water temperature in the empirical relationship provided by Touratier and Goyet (2011; Eq. (1)) for the whole Mediterranean Sea:

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