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### ► To cite this version:

Cathy Wimart-Rousseau, Thibaut Wagener, Marta Álvarez, Thierry Moutin, Marine Fourier, et al.. Seasonal and Interannual Variability of the CO<sub>2</sub> System in the Eastern Mediterranean Sea: A Case Study in the North Western Levantine Basin. *Frontiers in Marine Science*, 2021, 8, pp.649246. 10.3389/fmars.2021.649246 . hal-03227218

**HAL Id: hal-03227218**

**<https://hal.science/hal-03227218v1>**

Submitted on 17 May 2021

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# Seasonal and Interannual Variability of the CO<sub>2</sub> System in the Eastern Mediterranean Sea: A Case Study in the North Western Levantine Basin

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### Specialty section:

This article was submitted to  
Marine Biogeochemistry,  
a section of the journal  
Frontiers in Marine Science

Received: 04 January 2021

Accepted: 09 April 2021

Published: 17 May 2021

### Citation:

Wimart-Rousseau C, Wagener T, Álvarez M, Moutin T, Fourier M, Coppola L, Niclas-Chirurgien L, Raimbault P, D'Ortenzio F, Durrieu de Madron X, Taillandier V, Dumas F, Conan P, Pujo-Pay M and Lefèvre D (2021) Seasonal and Interannual Variability of the CO<sub>2</sub> System in the Eastern Mediterranean Sea: A Case Study in the North Western Levantine Basin. *Front. Mar. Sci.* 8:649246. doi: 10.3389/fmars.2021.649246

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The seasonal variability of the carbonate system in the eastern Mediterranean Sea (EMed) was investigated based on discrete total alkalinity ( $A_T$ ), total dissolved inorganic carbon ( $C_T$ ), and pH measurements collected during three cruises around Crete between June 2018 and March 2019. This study presents a detailed description of this new carbonate chemistry dataset in the eastern Mediterranean Sea. We show that the North Western Levantine Basin (NWLB) is unique in terms of range of  $A_T$  variation vs.  $C_T$  variation in the upper water column over an annual cycle. The reasons for this singularity of the NWLB can be explained by the interplay between strong evaporation and the concomitant consumption of  $C_T$  by autotrophic processes. The high range of  $A_T$  variations, combined to temperature changes, has a strong impact on the variability of the seawater  $pCO_2$  ( $pCO_2^{SW}$ ). Based on Argo float data, an entire annual cycle for  $pCO_2^{SW}$  in the NWLB has been reconstructed in order to estimate the temporal sequence of the potential “source” and “sink” of atmospheric CO<sub>2</sub>. By combining this dataset with previous observations in the NWLB, this study shows a significant ocean acidification and a decrease in the oceanic surface  $pH_{T=25}$  of  $-0.0024 \pm 0.0004$   $pH_{T=25}$  units.a<sup>-1</sup>. The changes in the carbonate system are driven by the increase of atmospheric CO<sub>2</sub> but also by unexplained temporal changes in the surface  $A_T$  content. If we consider that the EMed will, in the future, encounter longer, more intense and warmer summer seasons, this study proposes some perspectives on the carbonate system functioning of the “future” EMed.

**Keywords:** carbonate system, Mediterranean Sea, acidification, CO<sub>2</sub> fluxes, Levantine Sea, inorganic carbon

## INTRODUCTION

Since the beginning of the industrial era, the rise in atmospheric CO<sub>2</sub> due to anthropogenic activities is considered to be the main factor responsible for current climate change (IPCC, 2018). The ocean plays a significant role in modulating atmospheric CO<sub>2</sub> as it has sequestered *ca.* 31% of the global anthropogenic CO<sub>2</sub> emissions in the past few decades (Gruber et al., 2019). Between 2009 and 2018, the ocean CO<sub>2</sub> sink was estimated to be equal to  $2.5 \pm 0.6 \text{ PgC.a}^{-1}$  (Friedlingstein et al., 2019). Ocean CO<sub>2</sub> uptake induces an increase in hydronium ion concentration (*i.e.*, a decrease in oceanic pH) commonly referred as ocean acidification (Doney et al., 2009). This ocean acidification represents a significant threat to marine organisms (Kroeker et al., 2013) and is likely to affect marine ecosystems (Feely et al., 2004).

The marginal Mediterranean Sea (MedSea) is a singular oceanic basin in terms of carbonate chemistry and deserves specific study. Due to the relatively short residence time of its water masses, this semi-enclosed basin is considered to be more reactive to external forcing than other oceanic areas (Durrieu de Madron et al., 2011). The warm and highly alkaline waters absorb CO<sub>2</sub> from the atmosphere and transport it to the interior by active overturning circulation (Schneider et al., 2010; Álvarez et al., 2014). Indeed, while representing only 0.3% of the global oceanic volume, the anthropogenic carbon content of the MedSea was estimated to represent 1.1% of the world's ocean content in 1994 (Schneider et al., 2010; Lee et al., 2011). Moreover, several studies have reported a marked decline in the pH of the MedSea over the last few decades (*e.g.*, Touratier and Goyet, 2011; Hassoun et al., 2015b; Palmiéri et al., 2015; Flecha et al., 2019).

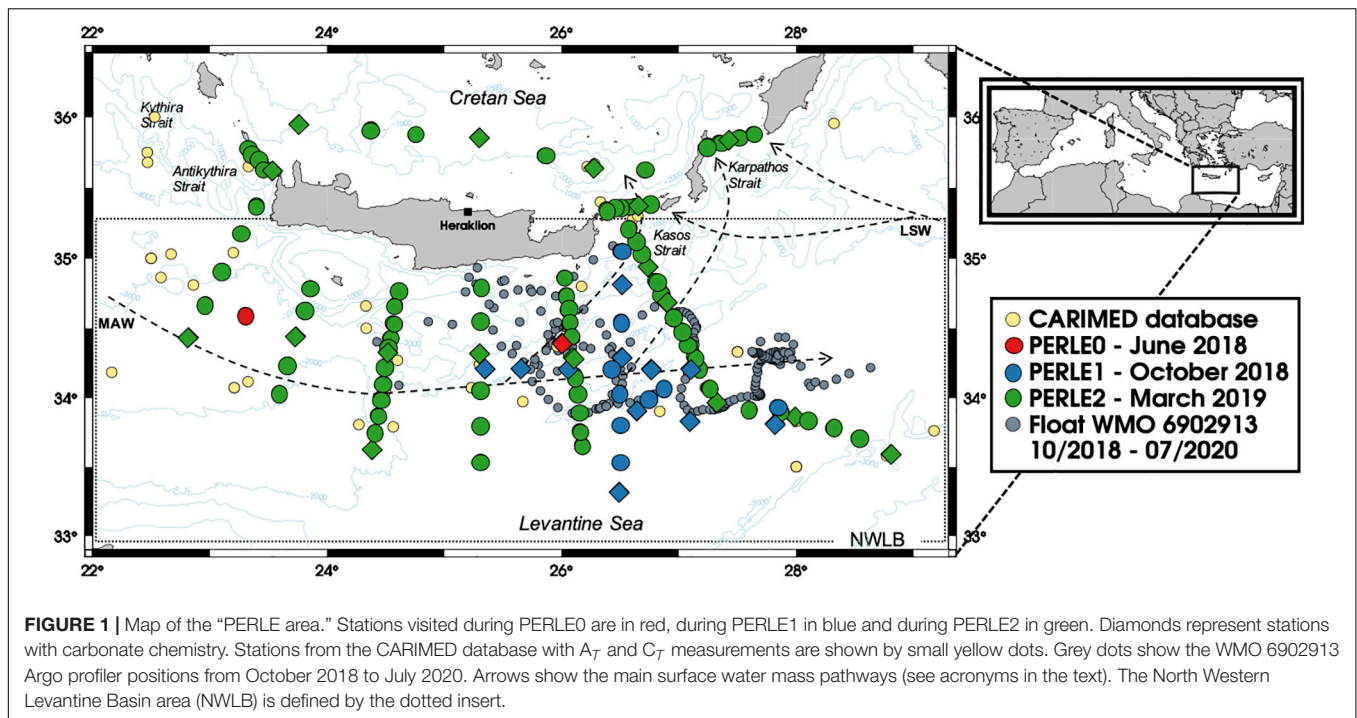
Detailed descriptions of the circulation and water masses of the MedSea can be found in Millot and Taupier-Letage (2005), Bergamasco and Malanotte-Rizzoli (2010), and Durrieu de Madron et al. (2011). The water masses of the Eastern Mediterranean Sea (EMed) are warmer, more haline, more oxygenated and more alkaline than those in the Western Mediterranean Sea (WMed) (Álvarez et al., 2014). The EMed water column can be schematically divided into three layers: (1) The surface layer, filled with Modified Atlantic Waters (MAW) with specific regional and seasonal characteristics [*e.g.*, Levantine Surface Waters (LSW)]; (2) Intermediate waters characterised, in the presence of MAW, by a local salinity maximum and generally described by the generic name Levantine Intermediate Waters (LIW); (3) The Eastern Mediterranean Deep Waters (EMDW), mostly retained in the EMed, consisting of a mixture of Adriatic Deep Waters (AdDW) and Aegean Deep Waters (AeDW). EMDW have undergone drastic changes over the last few decades (known as the Eastern Mediterranean Transient; Roether et al., 1996).

The MedSea is already exhibiting a consistent ocean acidification trend as a direct consequence to oceanic CO<sub>2</sub> uptake. It is therefore important to observe carbonate chemistry over sustained time-series to understand the long-term changes

in ocean chemistry. The seasonal dynamics of the carbonate system, crucial in understanding the variability in the air-sea CO<sub>2</sub> exchanges, also requires these important time-series observations. When compared to other oceanic areas, including the WMed, the oligotrophic EMed (Pujo-Pay et al., 2011) is characterised by low primary production rates (Moutin and Raimbault, 2002). This low productivity reduces the vertical gradients of dissolved inorganic carbon, making the detection and understanding of decadal and seasonal changes in the carbonate system particularly challenging in this area. Over the last few decades, a considerable amount of work has been devoted to the EMed (*e.g.*, Schneider et al., 2010; Álvarez et al., 2014; Hassoun et al., 2015b; Hainbucher et al., 2019), however, these cruises do not cover a full seasonal cycle leading to biased observations. Most of the time-series measurements recorded in the MedSea have been taken in the coastal (*e.g.*, De Carlo et al., 2013; Ingrosso et al., 2016; Kapsenberg et al., 2017) and oceanic WMed (Lefèvre, 2010; Coppola et al., 2018). In the EMed, time-series measurements are scarce and mostly based in the Cretan Sea (Petihakis et al., 2018) or coastal sites such as the Lebanese coast (Hassoun et al., 2019) or the Israeli coast (Sisma-Ventura et al., 2017), precluding a rigorous description of the temporal variability of the carbonate system in the open-ocean EMed. In the MedSea open-ocean, studies based on data derived from satellite observations have been conducted to decipher, over a seasonal and interannual scale, the variations in *p*CO<sub>2</sub> (D'Ortenzio et al., 2008; Taillandier et al., 2012). Nonetheless, understanding the variability in the seasonal carbonate system in the EMed is required to evaluate the effects of the increasing threats in this area, such as warming (Nykjær, 2009) and ocean acidification.

In the frame of the PERLE project (the Pelagic Ecosystem Response to deep water formation in the Levant Experiment), an intense *in situ* survey of the Levantine area was carried out during 2018–2019 (D'Ortenzio et al., 2020). This study reports on a new oceanic inorganic carbon dataset acquired over three different periods of the year in the South Cretan area (described as the North Western Levantine Basin or NWLB hereafter) (**Figure 1**).

This study gives a detailed description of this new dataset and the oceanographical context (section “Descriptive Carbonate Chemistry in the Context of the PERLE Cruises”). In section “Atypical Drivers of the Seasonal Dynamics of the Carbonate Chemistry Within the Mixed Layer of the North Western Levantine Basin,” using these new annual observations in the NWLB, the physical and biological drivers explaining the seasonal variability of the carbonate parameters in the upper water column will be investigated and the impact of the variations on air-sea CO<sub>2</sub> fluxes will be discussed. In section “Long Term Temporal Changes in Carbonate Chemistry in the North Western Levantine Basin,” the main drivers of carbonate chemistry changes will be considered on longer timescales, based on the estimated trends in the surface carbonate chemistry of the NWLB derived from existing data over the last 20 years. Some hypotheses on the future of the carbonate system functioning of the EMed will be discussed.



## MATERIALS AND METHODS

### Cruise and Sampling Strategy

This study focuses on three PERLE cruises: PERLE0, PERLE1, and PERLE2 (Figure 1). These cruises were carried out in the EMed between 2018 and 2019. At all stations, a CTD-Rosette was deployed (1) to acquire data with sensors (Conductivity Temperature and Depth–CTD and associated parameters) along vertical profiles and (2) to collect discrete seawater samples from Niskin bottles for chemical analysis. Over the 11, 31, and 125 casts performed during the PERLE0, PERLE1, and PERLE2 cruises, seawater was sampled from 1, 12, and 17 casts, respectively, for carbonate parameter analysis (see Supplementary Table 1 and Supplementary Figure 1). Details for the cruises and parameters measured during each PERLE cruise are summarised in Table 1.

### Parameters Measured CTD and Seawater Sampling

A SeaBird<sup>TM</sup> 911+ underwater unit was used to interface a pressure sensor, an external temperature probe (SBE3plus) and an external conductivity cell (SBE4C). Sensors were calibrated by the manufacturer. Additional sensors were interfaced and data from a fluorescence (Chelsea Aqua 3) and an oxygen (SBE43) sensor are used in this study. Fluorescence and oxygen are expressed in A.U. (Arbitrary Unit) and  $\mu\text{mol.kg}^{-1}$ , respectively, in this study. For vertical profiles, 24 Hz data on the downcast were averaged on 1 dbar bins by the SeaBird<sup>TM</sup> dedicated software. Water samples were collected from CTD-Rosette casts with a carousel equipped with 22 Niskin bottles (12 L). Water was sampled from 10 to 21 depths, from a few meters above the seafloor up to the surface (0–5 dbars). From 0 to 200 dbars, a

higher sampling resolution was applied (every *ca.* 20 dbars) than below 200 dbars (every *ca.* 200 dbars).

In addition, the “Real-time” CTD data from the WMO 6902913 Argo float (Argo, 2000) deployed during the PERLE1 cruise were used in this study to complete the hydrological data. Data collected from October 2018 to July 2020 were used (Figure 1). Because the Argo float considered in this study is still operational, no “Delayed Mode” data were available at this stage. The Argo real-time quality control procedures have been applied by the Coriolis data centre (Wong et al., 2020). A visual comparison of the Argo CTD data with collocated PERLE cruise CTD data was carried out on two profiles to exclude major deviations in the Argo data. Salinity measurements (derived from conductivity—SBE41CP sensor, Seabird<sup>TM</sup>) were recorded with an accuracy of 0.005 psu.

### Total Alkalinity and Total Dissolved Inorganic Carbon

Samples for total dissolved inorganic carbon ( $C_T$ ) and total alkalinity ( $A_T$ ) were collected into acid-washed 500  $\text{cm}^3$  borosilicate glass bottles, poisoned with 200  $\text{mm}^3$  of a 36  $\text{g.dm}^{-3}$   $\text{HgCl}_2$ , as recommended by Dickson et al. (2007) and stored in the dark at 4°C. Analyses were performed after 5 months of storage. Measurements of  $C_T$  and  $A_T$  were performed simultaneously by potentiometric acid titration using a closed cell following the methods described by Edmond (1970) and Dickson and Goyet (1994). Analyses were performed at the National Facility for Analysis of Carbonate System Parameters (SNAPO-CO<sub>2</sub>, LOCEAN, Sorbonne University—CNRS, France) with a prototype developed at LOCEAN. The average accuracy of  $A_T$  and  $C_T$  analysis (estimated from repeated measurements of Certified Reference Material provided by Prof. Dickson’s laboratory from the Scripps Institution of Oceanography, San

**TABLE 1** | Summary of the cruise information and the parameters measured during each PERLE cruises including availability, number of samples (n) and their associated accuracy.

		PERLE0	PERLE1	PERLE2
Cruise information	Date	8 <sup>th</sup> –24 <sup>th</sup> June 2018	10 <sup>th</sup> –21 <sup>st</sup> October 2018	27 <sup>th</sup> February–16 <sup>th</sup> March 2019
	Research Vessel	<i>Téthys II</i>	<i>L'Atalante</i>	<i>Pourquoi Pas?</i>
Carbonate parameters	DOI	10.17600/18000550	No DOI available	10.17600/18000865
	$A_T/C_T$	Parameter sampled [ $n = 12$ ] QC test ok [ $\pm 1.8/2.1 \mu\text{mol.kg}^{-1}$ ]	Parameter sampled [ $n = 164$ ] QC test not ok–Derived** [ $\pm 19/19 \mu\text{mol.kg}^{-1}$ ]	Parameter sampled [ $n = 341$ ] QC test ok [ $\pm 4.6/4.7 \mu\text{mol.kg}^{-1}$ ]
	pH	Parameter not sampled Derived* [ $\pm 0.012$ ]	Parameter sampled [ $n = 156$ ] QC test ok [ $\pm 0.007$ ]	Parameter sampled [ $n = 361$ ] QC test ok [ $\pm 0.003$ ]
Ancillary data	Oxygen	Parameter sampled QC test ok	Parameter sampled QC test ok	Parameter sampled QC test ok
	Nutrients	Parameter sampled QC test ok	Parameter sampled QC test ok	Parameter sampled QC test ok

\*  $pH_T^{25}$  values were calculated with the  $A_T/C_T$  couple.

\*\*  $A_T$  values deduced from the  $A_T$ -S relationship proposed by Hassoun et al. (2015a, see section 3.2.2).  $C_T$  values were calculated with the  $A_T/pH_T^{25}$  couple.

Stations where carbonate parameters were studied are represented by diamonds on **Figure 1**. Nutrients were used at these stations to calculate the derived carbonate parameters. Errors for the derived carbonate parameters have been computed by propagating the standard uncertainties of the thermodynamic constants and associated errors of the environmental variables (Orr et al., 2018).

Diego) was 1.8 and 2.1  $\mu\text{mol.kg}^{-1}$ , respectively, for PERLE0 and 4.6 and 4.7  $\mu\text{mol.kg}^{-1}$ , respectively, for PERLE2. Although  $A_T$  and  $C_T$  measurements were carried out during the PERLE1 cruise, the accuracy of the dataset did not conform to the quality control procedure (see section “Primary Quality Control of the Measured Data”) therefore the measured PERLE1  $A_T/C_T$  dataset was not used in this study. However,  $A_T$  values were reconstructed for PERLE1 based on a published  $A_T$ -S relationship (see section “Derived Parameters”).

## pH

The pH was measured directly on board. Samples for pH measurements were collected in cylindrical optical glass vials and analyses were performed manually using purified m-Cresol Purple (mCP) following the spectrophotometric protocol (at 25°C) described by Clayton and Byrne (1993) (see details in **Supplementary Material**). This method is based on the dissociation of the pH-sensitive mCP dye (provided by Prof. Byrne, University of Southern Florida) in the water sample. pH is reported on the total scale at 25°C ( $pH_T^{25}$ ) using the equation by Liu et al. (2011). The reproducibility of measurements was estimated to be  $\pm 0.0009$  by measuring replicates from the same Niskin bottle. The accuracy was determined to range within  $\pm 0.007$  for PERLE1 and  $\pm 0.003$  for PERLE2 by analysing replicates of TRIS solution (provided by Prof. Dickson, Scripps Institution of Oceanography, San Diego). No direct pH measurements were carried out during the PERLE0 cruise. The effect of the addition of the indicator on the seawater pH was evaluated and corrected (see details in the **Supplementary Material**).

## Oxygen

For all three PERLE cruises, dissolved oxygen concentrations ( $[O_2]_{mes}$ ) were analysed on board following the Winkler method (Winkler, 1888; modified Carritt and Carpenter, 1966) using photometric endpoint detection (Williams and Jenkinson, 1982).

The recommendations of Langdon (2010) were followed for sampling, reagent preparation and sample analysis. The thiosulfate solution was calibrated by titrating it against a potassium iodate certified standard solution of 0.0100 N (CSK standard solution—WAKO). The reproducibility of measurements, calculated by measuring replicates from the same Niskin bottle, was estimated to be  $\pm 0.86 \mu\text{mol.kg}^{-1}$  ( $n = 42$ , PERLE2).

Oxygen measurements from the SBE43 sensor from the CTD rosette were systematically adjusted for all cruises with the “Winkler” values on the whole water column. Based on the raw data processing algorithm (Owens and Millard, 1985), 3 calibration coefficients were adjusted (the oxygen signal slope, the voltage at zero oxygen signal and the pressure correction factor) by minimising the sum of the square of the difference between the Winkler oxygen values and oxygen derived from the sensor signal. The accuracy of the SBE43 adjusted values is around  $\pm 2 \mu\text{mol.kg}^{-1}$ .

## Nutrients

Samples for dissolved inorganic nutrients were collected from Niskin bottles in 20 mL polyethylene bottles. Samples were analysed directly on board during PERLE2 and frozen before analysis on land for PERLE0 and PERLE1. Analyses were performed after less than a month of storage. All nutrient samples were analysed by a standard colorimetric method on a segmented flow analyser (Autoanalyser II Seal Bran& Luebbe®) following Aminot and Kerouel (2007). The relative precision of these analyses ranged from 5 to 10% (Aminot and Kerouel, 2007).

## Primary Quality Control of the Measured Data

Systematic primary quality control of the measured data was performed on each PERLE dataset. No significant problems have been detected for Winkler oxygen and pH measurements. During PERLE1, for a few casts, a CTD pump dysfunction

significantly altered the quality of the CTD oxygen: oxygen measurements from these casts were disregarded. A systematic quality control procedure for  $A_T$  and  $C_T$  was conducted based on internal consistency tests between  $A_T$ ,  $C_T$  and  $pH_T$  (see details in the **Supplementary Material**). Following these steps, only 15 PERLE2 casts were validated, leading to the loss of *ca.* 60% of the PERLE2  $A_T/C_T$  dataset. All the  $A_T/C_T$  PERLE1 dataset was lost. A comparison of the quality controlled PERLE dataset with previously collected data does not reveal systematic biases for  $A_T$ ,  $C_T$ , or  $pH_T^{25}$  (**Figure 2A–C**).

## Statistical Tests on the Linear Model

Relationships between years and carbonate parameters ( $A_T$ ,  $C_T$ , and  $pH_T^{25}$ ) and between  $A_T$  and salinity were computed using a linear regression model. Linear regression statistics, including the standard error of the slope (*i.e.*, the error of the estimated trend), the coefficient of determination ( $r^2$ ) and the significance of the trend ( $p$ -value) were calculated using the R software. Linear relationships have been tested using the Pearson coefficient for parametric test (Sokal and Rohlf, 1969) with a significance level of 95%.

Parameters derived from the  $A_T$ -S linear relationship were tested against previously published  $A_T$ -S relationships in the area using a Student's  $t$ -test for the slope and intercept. The null hypothesis,  $H_0$ , was that our observations were not significantly different from these linear models.

## Derived Parameters

Absolute salinity ( $S_A$ ), conservative temperature ( $\Theta$ ) and potential density ( $\sigma_\theta$ ) were derived from practical salinity, temperature and pressure and the geographic position based on the TEOS-10 (The International Thermodynamic Equation of Seawater-2010). In this study, following the recommendations of the Intergovernmental Oceanographic Commission (Valladares et al., 2011),  $S_A$  and  $\Theta$  were used to study the hydrological context ( $\Theta - S_A$  diagrams). Calculations were made with the “oce” R package (Kelley et al., 2017). Note that practical salinity (labelled Salinity) and *in situ* temperature (labelled Temperature) were used in this study to facilitate comparisons with previous studies in particular, for  $A_T$ -S relationships.

Apparent Oxygen Utilisation ( $AOU - \mu\text{mol.kg}^{-1}$ ) was calculated from the difference between oxygen solubility concentration (at  $P = 0$  dbar) estimated with the “Benson and Krause coefficients” (Garcia and Gordon, 1992) and *in situ*  $[O_2]_{mes}$ .

A density threshold of  $0.03 \text{ kg.m}^{-3}$  with a reference depth of 10 dbars was used to compute the Mixed Layer Depth (MLD) (D'Ortenzio et al., 2005).

Salinity data were used to reconstruct an  $A_T$  time-series using the sub-surface  $A_T$ -S relationship proposed by Hassoun et al. (2015a) (see discussion in section “Total Alkalinity and Salinity Relationships Within the Mixed Layer”). In this study, the PERLE1 and the Argo float  $A_T$  datasets were reconstructed following this  $A_T$ -S relationship. Considering the standard deviation of the  $A_T$ -S relationship proposed by Hassoun et al. (2015a), the accuracy of the calculated  $A_T$  values is  $\pm 19 \mu\text{mol.kg}^{-1}$ .

Salinity-normalised changes in  $A_T$  ( $NA_T^{39.3}$ ) and  $C_T$  ( $NC_T^{39.3}$ ) were calculated dividing by *in situ* salinity and multiplying by 39.3 (*i.e.*, the mean PERLE salinity above 200 dbars).

Seawater carbonate system parameters were derived from  $A_T$  and  $C_T$  values. Calculations were made with the software program CO2SYS-MATLAB (van Heuven et al., 2011) using silicate and phosphate concentrations. When nutrient data was not available, silicate and phosphate mean concentrations for each depth were used. As recommended for the MedSea by Álvarez et al. (2014), the carbonic acid dissociation constants  $K_1$  and  $K_2$  from Mehrbach et al. (1973) as refitted by Dickson and Millero (1987) and the dissociation constant for  $HSO_4^-$  from Dickson (1990) were used. Uppström (1974) was used to calculate the ratio of total boron to salinity and Dickson and Riley (1979) to calculate the hydrogen fluoride constant  $K_F$ .

The buffer factors  $\gamma_{A_T}$  ( $\gamma_{C_T}$ ),  $\beta_{A_T}$  ( $\beta_{C_T}$ ) and  $\omega_{A_T}$  ( $\omega_{C_T}$ ) provide an estimation of the seawater's ability to buffer changes in the aqueous  $CO_2$  [ $CO_2$ ], protons [ $H^+$ ] and the carbonate saturation state ( $\Omega$ ) when  $A_T$  ( $C_T$ ) changes at constant  $C_T$  ( $A_T$ ) (Eggleston et al., 2010). The calculations were performed following the formula proposed by Álvarez et al. (2014).

## Quantification of Biological Processes

Net Ecosystem Production (NEP) is defined as the sum of biotic and abiotic carbon fluxes in the ecosystem (Borges et al., 2008). Net Ecosystem Calcification (NEC) is a measure of the balance between  $CaCO_3$  formation (calcification) and dissolution (Smith and Kinsey, 1978). Based on the  $NA_T^{39.3}$  and  $NC_T^{39.3}$  plot, the reaction path can take on variable slopes depending on the ratio of different processes, such as photosynthesis/respiration, carbonate dissolution/formation and  $CO_2$  release/invasion (Zeebe, 2012). Temporal changes in  $NA_T^{39.3}$  ( $\Delta NA_T^{39.3}$ ) and  $NC_T^{39.3}$  ( $\Delta NC_T^{39.3}$ ) between each PERLE cruise can be calculated according to NEP and NEC processes as:

$$\Delta NC_T^{39.3} = -0.15 * NEP + 0.9 * NEC \quad (1)$$

$$\Delta NA_T^{39.3} = 0.02 * NEP + 1.8 * NEC \quad (2)$$

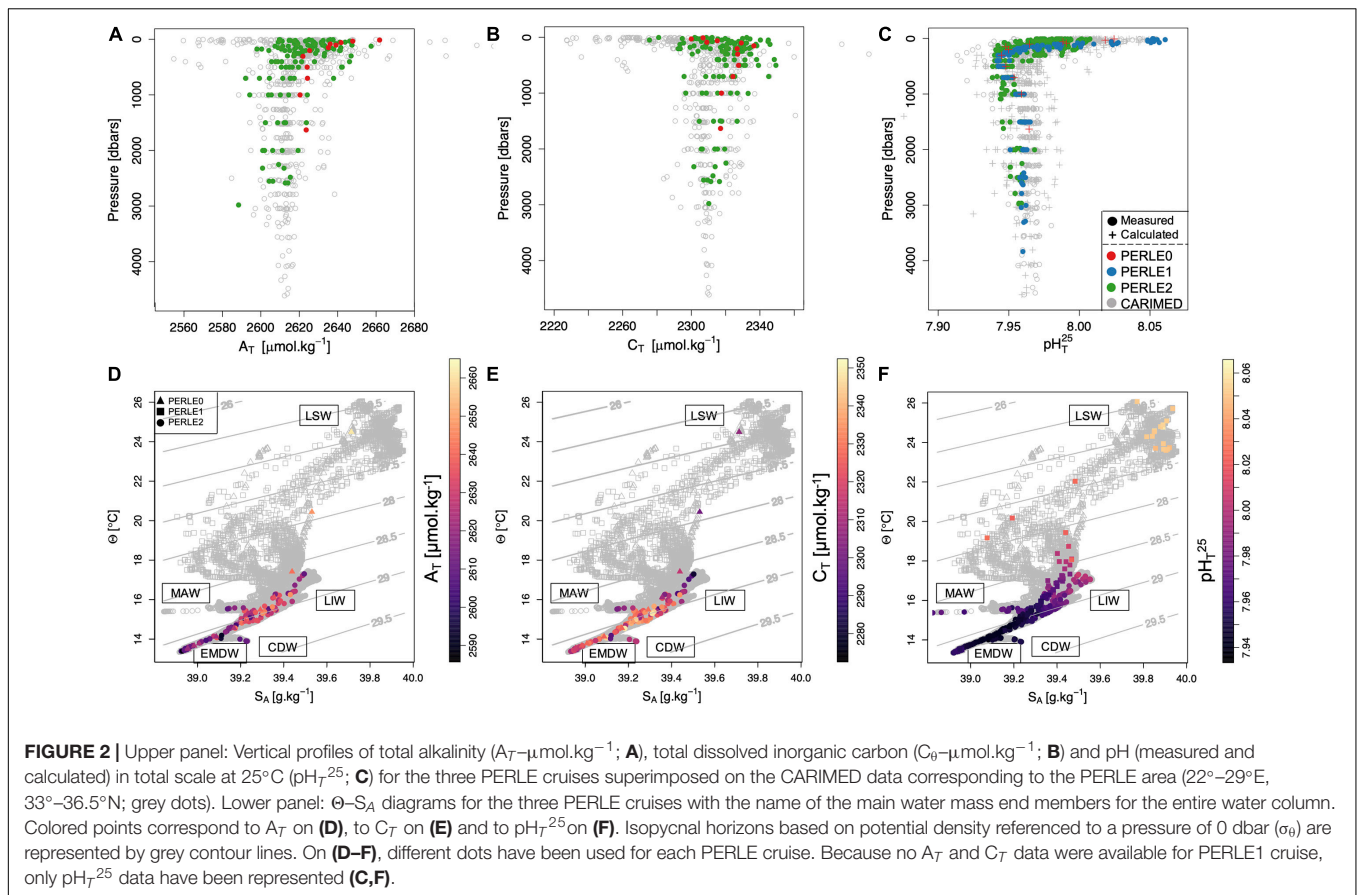
Following equation (2), NEP can be expressed according to NEC as:

$$NEP = \frac{\Delta NA_T^{39.3} - 1.8 * NEC}{0.02} \quad (3)$$

Then, by replacing the NEP term in equation (1) by equation (3), NEC can be calculated as:

$$NEC = \frac{\Delta NC_T^{39.3} + \frac{(0.15 * \Delta NA_T^{39.3})}{0.02}}{14.4} \quad (4)$$

NEC and NEP are expressed in  $\mu\text{mol.C.kg}^{-1}.\text{d}^{-1}$ . Salinity-normalised  $A_T$  and  $C_T$  values “exclude” the “precipitation-evaporation” influence in the layer where biological activity is at a maximum. It is assumed that the layers considered (MLD-200 dbars) to estimate the NEP and NEC processes are not influenced by air-sea  $CO_2$  fluxes, which were therefore not considered.



## CARIMED Database

CARIMED (CARbon, tracer and ancillary data In the MEDsea) aims to be an internally consistent database containing inorganic carbon data relevant for this basin (Álvarez et al., in preparation). Ancillary (hydrographic, inorganic nutrients and dissolved oxygen),  $\text{CO}_2$  (pH,  $A_T$ , and  $C_T$ ) and transient tracer (CFC-11 and 12, Tritium,  $\text{SF}_6$ , Neon,  $\text{CCl}_4$ , and  $\Delta\text{He}^3$ ) data from several cruises in the MedSea from 1976 until 2018 were assembled. Primary and secondary quality control procedures following the GLODAP (Global Ocean Data Analysis Project) philosophy (Tanhua et al., 2010) are locally adapted to this marginal sea. This work only uses data collected in the Levantine basin (Supplementary Table 2).

## DESCRIPTIVE CARBONATE CHEMISTRY IN THE CONTEXT OF THE PERLE CRUISES

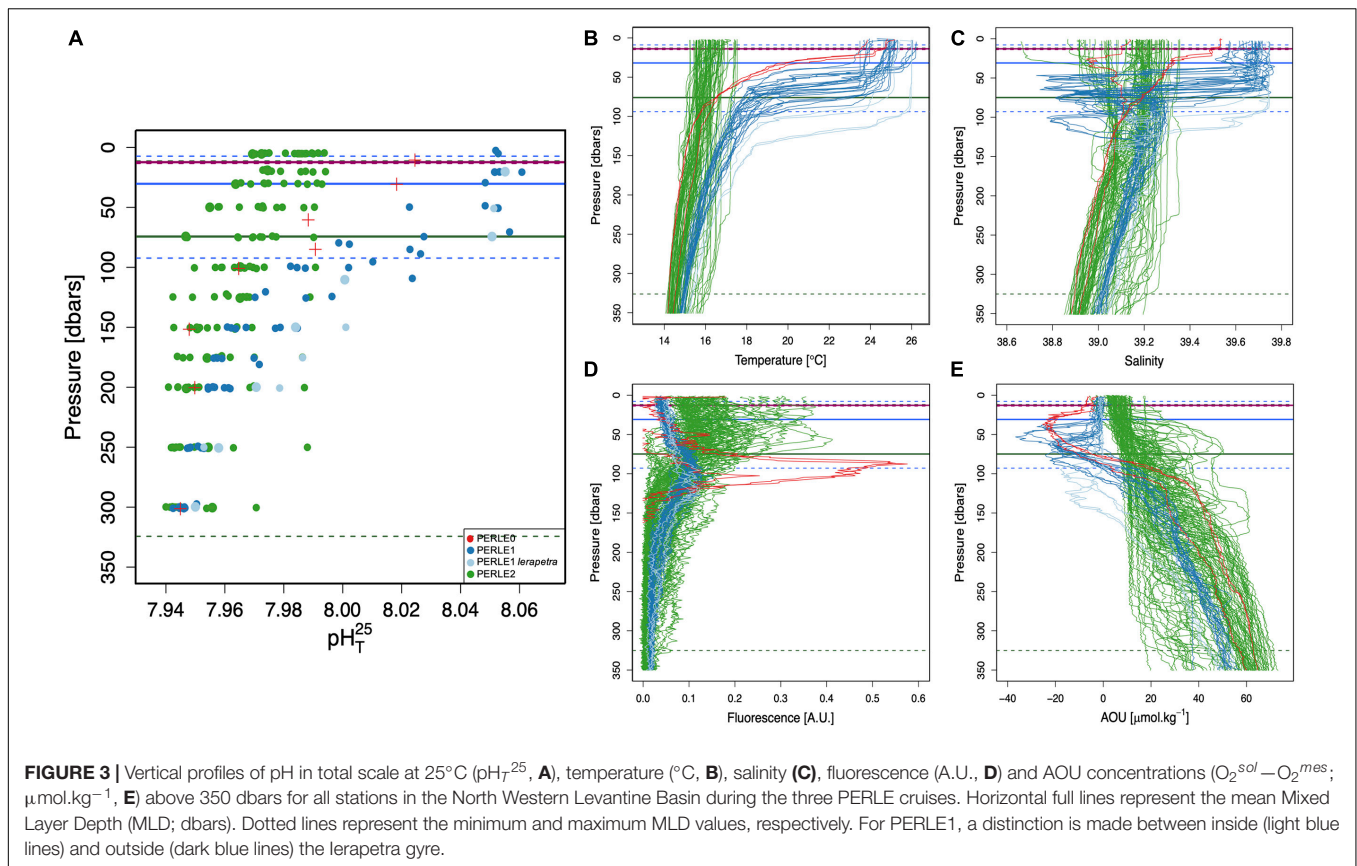
### Carbonate Chemistry Along the Water Column Below the Surface Layer

All vertical profiles for  $A_T$ ,  $C_T$  and  $\text{pH}_{T^{25}}$  measured during the PERLE cruises are presented in Figures 2A–C, respectively. All the  $A_T$  profiles presented maximum values in the surface, minimum values between 500 and 700 dbars and remained

almost constant (or slightly decreasing) below 1000 dbars. Most of the  $C_T$  vertical profiles presented the lowest values in surface waters, reaching maximum values between 500 and 700 dbars and then remaining relatively invariable below 1000 dbars.  $\text{pH}_{T^{25}}$  presented maximum values at the surface (with values around 8.060 measured during PERLE1 cruise), minimum values close to 700 dbars and nearly constant values under 1000 dbars (Figure 2C). The main water masses are identified in Figures 2D–F and detailed in Supplementary Figure 1.

Intermediate waters (mostly LIW) were located around the 29.0  $\text{kg.m}^{-3}$  isopycnal layer (Lascaratos and Nittis, 1998; see Supplementary Figure 1) and were characterised by an  $A_T$  maximum evolving from 2,600 to 2,640  $\mu\text{mol.kg}^{-1}$  (Figures 2A,D). As observed by Álvarez et al. (2014), the LIW was located above the layer of maximum organic matter mineralisation in the EMed and was associated with low  $C_T$  concentrations (ca. 2,290  $\mu\text{mol.kg}^{-1}$ ) and high  $\text{pH}_{T^{25}}$  values (ca. 8.000) in contrast to the deepest water masses. It can be observed that slightly colder, more haline and denser Cretan Intermediate Waters (Velaoras et al., 2019) were detected during PERLE2 in the western part of the Cretan Sea with the highest  $A_T$  value for PERLE2 cruise (ca. 2,660  $\mu\text{mol.kg}^{-1}$ , Figure 2A).

In the deep-water layer (i.e., EMDW), both AeDW and AddW presented similar  $C_T$  values (Figure 2E) while slightly higher  $\text{pH}_{T^{25}}$  (Figure 2F) and  $A_T$  (Figure 2D) values were measured in the AeDW (see Supplementary Figure 2). On the Cretan



shelf, deep waters were comprised of dense EMDW with high  $A_T$  ( $\approx 2,650 \mu\text{mol.kg}^{-1}$ ) and  $C_T$  values ( $\approx 2,350 \mu\text{mol.kg}^{-1}$ ). Deep waters of the Cretan Sea were filled with CDW with low  $\text{pH}_T^{25}$  ( $\approx 7.950$ ) values resulting from relatively low  $A_T$  and high  $C_T$  content (**Figures 2D–F**).

This description of the carbonate chemistry in the deep and intermediate water masses in the PERLE area is in good agreement with previous studies (Schneider et al., 2010; Álvarez et al., 2014). However, the PERLE strategy based on an intense observation period over a year is not appropriate to describe changes in deep-water masses. For the rest of this study, in order to tackle the seasonal dynamics of the surface waters, only data in the NWLB (**Figure 1**) where all three PERLE cruises were conducted, will be discussed further.

## Seasonal Variability in the Upper Water Column

The highest spatial and temporal variability in carbonate chemistry parameters was encountered in the upper water layer which has been defined to be approximately the first 200 dbars. Discrete  $\text{pH}_T^{25}$  values (measured and calculated), taken from the southern part of the PERLE sampling area (the NWLB) illustrate the seasonal variability of the carbonate chemistry in the upper layer (**Figure 3A**). The  $\text{pH}_T^{25}$  was the most measured carbonate parameter in this study and, when normalised to 25°C, can be considered as an indicator of the carbonate

chemistry status by including the changes in  $A_T$  and  $C_T$ . An overview of the upper layer seasonal dynamics is also presented for temperature, salinity, fluorescence, and AOU profiles in **Figures 3B–E**, respectively.

The lowest  $\text{pH}_T^{25}$  values were encountered in March 2019 during the PERLE2 cruise and correspond to the relatively higher  $C_T$  values and lower  $A_T$  values. During this cruise, a significant range in the MLD was encountered with the deepest values observed. This cruise coincided with the abrupt stratification observed in the EMed after the deepening of the MLD from November to February–March (D’Ortenzio et al., 2005). Increased fluorescence values were observed in shallow waters at the end of the cruise (in the eastern part of the area) in comparison to the beginning of the cruise (in the western part).

Intermediate  $\text{pH}_T^{25}$  values were measured in June 2018 during the PERLE0 cruise corresponding to increased surface alkalinity and a moderate depletion in inorganic carbon. The PERLE0 cruise is an early summer cruise characterised by a shallow MLD. The highest fluorescence values were recorded during this cruise well below the MLD (*ca.* 90 dbars) and light oxygen supersaturation ( $\text{AOU} \approx -20 \mu\text{mol.kg}^{-1}$ ) just beneath the MLD.

Finally, high  $\text{pH}_T^{25}$  values ( $>8.000$ ) were measured up to 100 dbars during the PERLE1 cruise, probably in association with a high  $A_T$  content due to evaporation. During this late summer cruise, the deepest Deep Chlorophyll Maximum (DCM)



with the lowest fluorescence values but also the deepest negative AOU concentrations were encountered. Moreover, during this cruise, the mesoscale Ierapetra Eddy (IE) was crossed (see **Supplementary Figure 3** and Ioannou et al., 2019). The core of this warm and salty eddy (**Figures 3B,C**) was characterised by a deepening of the MLD associated with a deep DCM and negative AOU values. Nonetheless, no clear IE signal was observed on the  $\text{pH}_T^{25}$  values (**Figure 3A**).

In the EMed, spring and autumn seasons need to be considered as short transition periods between the summer and winter, which come later than on the continent (Özsoy et al., 1989). Moreover, in the EMed, summer is characterised by maximum heat in the surface layer that can remain up until November, whereas winter is identified with minimal heat that can occur until April. Considering each cruise as representative of a period within the annual cycle, the PERLE0 cruise (June 2018) associated with intermediate  $\text{pH}_T^{25}$  values corresponds to the early summer period with decreasing biological activity associated with the strengthening of stratification. PERLE1 (October 2018) is associated with the highest  $\text{pH}_T^{25}$  values and corresponds to the end of the summer period characterised by a warm and stratified water column with deep and low fluorescence maximum. PERLE2 (March 2019), associated with the lowest  $\text{pH}_T^{25}$  values and shallow fluorescence maximum, corresponds to the end of the winter period, with the beginning of the seasonal stratification of the water column in the eastern part. These features agree with the analysis of the seasonal patterns of surface chlorophyll *a* concentration (Chl *a*) (based on remote sensing). The lowest values of surface Chl *a* were observed during the summer period, whereas an increase in surface Chl *a* was observed in winter, concomitantly to the deepening of MLD (Bosc et al., 2004; D'Ortenzio and Ribera d'Alcalá, 2009).

## Total Alkalinity and Salinity Relationships Within the Mixed Layer

When no  $A_T$  values were available (see section “Primary Quality Control of the Measured Data”),  $A_T$  can be estimated based on an  $A_T$ - $S$  relationship. In the MedSea, several linear relationships between  $A_T$  and salinity in the surface waters have been proposed for different sub-basins (e.g., Schneider et al., 2007; Cossarini et al., 2015; Hassoun et al., 2015a; Gonzalez-Daivila et al., 2016).

During the PERLE cruises, in the NWLB,  $A_T$  was significantly ( $n = 14$ ,  $p$ -value = 0.014,  $r^2 = 0.36$ ) influenced by salinity variations within the mixed layer (**Figure 4**). **Figure 4** also displays the  $A_T$ - $S$  distribution in the Cretan Sea (grey dots on **Figure 4**). The mixing of high alkalinity Black Sea waters (values of ca.  $2,967 \mu\text{mol.kg}^{-1}$ ; Hiscock and Millero, 2006) in the Cretan Sea shifts the  $A_T$ - $S$  characteristics of surface waters in agreement with Schneider et al. (2007) who demonstrated that freshwater and Black Sea inputs affect the  $A_T$ - $S$  relationship. More pronounced deviations from the expected linear  $A_T$ - $S$  relationship are observed for stations with deeper mixed layers (**Figure 4**). This might be the result of the mixing of water masses with different  $A_T$ - $S$  relationships during winter mixing.

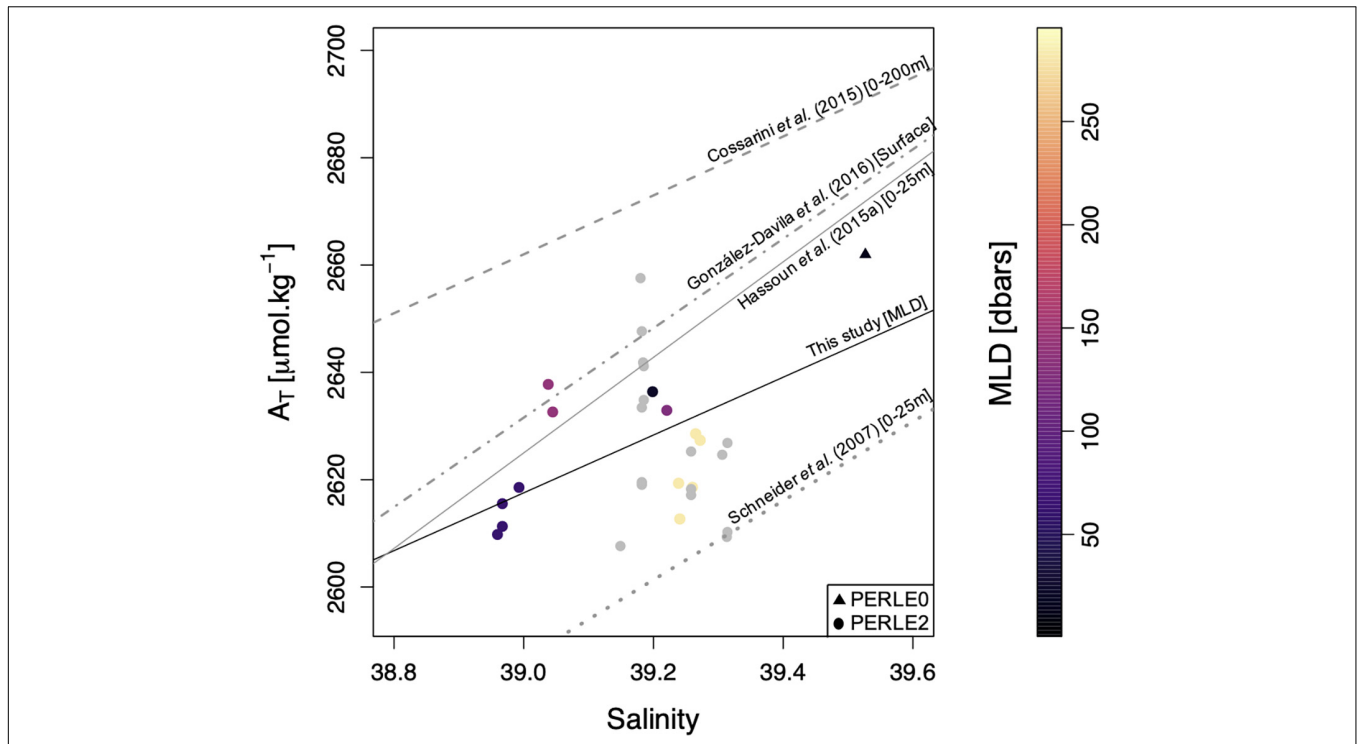
As  $A_T$  values were available only for PERLE0 and PERLE2 cruises, the  $A_T$ - $S$  relationship derived for the PERLE cruises in the mixed layer (and in the NWLB) have been based on a very limited number of data. The PERLE  $A_T$ - $S$  linear relationship was tested against the Hassoun  $A_T$ - $S$  linear model (Hassoun et al., 2015a). No significant differences were found on either the slope ( $t$ -test = 1.86,  $n = 14$ ,  $p < 0.05$ ) or the intercept ( $t$ -test = 0.27,  $n = 14$ ,  $p < 0.05$ ). Therefore, the annual time-series were reconstructed based on the  $A_T$ - $S$  linear relationship measured by Hassoun et al. (2015a) in the surface waters (0–25 m) of the eastern Mediterranean sub-basin, and  $A_T$  has been estimated based on this relationship.

## ATYPICAL DRIVERS OF THE SEASONAL DYNAMICS OF THE CARBONATE CHEMISTRY WITHIN THE MIXED LAYER OF THE NORTH WESTERN LEVANTINE BASIN

### Seasonal Variations in Total Alkalinity and Total Inorganic Carbon

During the PERLE cruises, the NWLB exhibited a greater range in  $A_T$  than  $C_T$  values within the mixed layer (see section “Total alkalinity control on the seasonal air-sea  $\text{CO}_2$  exchanges”).  $A_T$  ranged between 2,610 and 2,693  $\mu\text{mol.kg}^{-1}$  whereas  $C_T$  ranged between 2,292 and 2,332  $\mu\text{mol.kg}^{-1}$ . Over an annual scale, the ratio of the range in  $A_T$  variations to the range in  $C_T$  variations ( $\Delta A_T/\Delta C_T$ ) can be used to infer the sensitivity to  $A_T$  and  $C_T$  changes in the upper ocean. Over the period studied, in the NWLB, the ratio  $\Delta A_T/\Delta C_T$  is equal to 2.1. In the global ocean, long-term time-series  $\Delta A_T/\Delta C_T$  ratios are lower than 1.0 (**Table 2**).

The reasons for these apparent and rather unique ranges of  $A_T$  and  $C_T$  over the year in the NWLB can be attributed to several factors: (1) The main drivers of the  $C_T$  gradient in the water column are, primary production transforming the  $C_T$  into organic carbon in the photic layer, and respiration transforming the organic carbon into  $C_T$ . As the EMed is an area of low productivity (Moutin and Raimbault, 2002), the vertical  $C_T$  gradient is lower than in other oceanic areas. Consequently, the  $C_T$  range in surface waters, driven by  $C_T$  consumption during the stratified period and replenishment via vertical mixing with subsurface waters enriched in  $C_T$ , is greatly reduced. (2) The high levels of evaporation that affect the MAW in the EMed during the summer season increases salinity by nearly  $1 \text{ g.kg}^{-1}$  (**Figure 2**) between the end of winter (PERLE2) and the end of summer (PERLE1). The  $A_T$  and  $C_T$  parameters should be equally affected by evaporation in a closed system. However, when reported on a  $A_T/C_T$  diagram (with normalised axes—see **Figure 5**), a higher range of  $A_T$  variation compared to  $C_T$  is observed. This indicates that when salinity increases in surface waters, a concomitant consumption of  $C_T$  must occur to compensate for the  $C_T$  increase due to evaporation to maintain an apparent stability in  $C_T$  concentrations. The biological consumption of  $C_T$



**FIGURE 4 |**  $A_T$  vs. Salinity during PERLE0 and PERLE2 cruises within the mixed layer for all stations situated in the North Western Levantine Basin. The colour scale corresponds to the mixed layer depth (MLD—dbars). The black line corresponds to the significant linear regression (in the NWLB). The different grey lines correspond to the linear regressions between  $A_T$  and salinity in the surface EMed reported by Schneider et al. (2007), Cossarini et al. (2015), Hassoun et al. (2015a), and González-Davila et al. (2016). The grey dots correspond to data in the Cretan Sea (not used in the linear regression).

**TABLE 2 |** Ratios ( $\Delta A_T / \Delta C_T$ ) of the range in  $A_T$  variations (maximum value minus minimum value) to the range in  $C_T$  variations (maximum value minus minimum value) in the upper ocean for the different time-series.

	NWLB	ANTARES Time-series	DYFAMED Time-series	BATS (Bermuda Atlantic Time-series Study)	HOT (Hawaii Ocean Time-series)	ESTOC (European station for Time-series in the ocean Canary islands)	Iceland sea
Localisation	EMed	WMed	WMed	North western Atlantic	North Pacific	North eastern Atlantic	Iceland sea
Depth	MLD	0–30 dbars	0–30 dbars	0–30 dbars	0–30 dbars	Surface	0–30 dbars
Period	2018–2019	2009–2019	1994–2018	1988–2019	1988–2018	1996–2004	2014–2019
$\Delta A_T / \Delta C_T$	2.1	0.6	0.9	0.2	0.9	0.8	0.5
References	This study	Lefèvre, 2010	Coppola et al., 2020	Bates et al., 1996	Dore et al., 2009	Santana-Casiano and González-Dávila, 2010	Olafsson et al., 2009

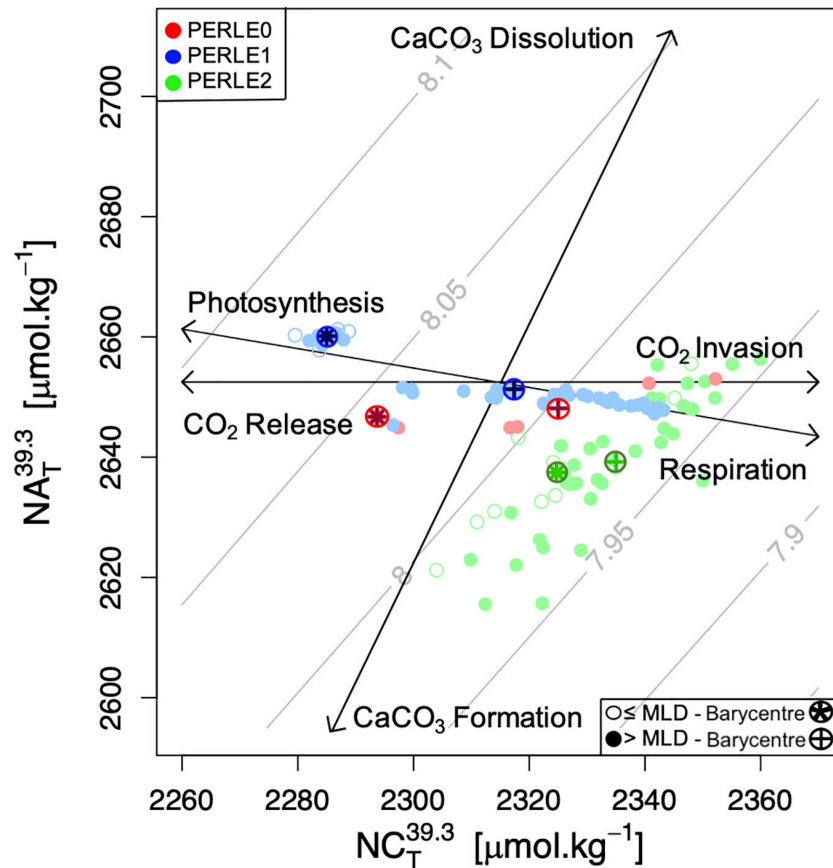
will be discussed in the next section as a possible mechanism to explain this low  $C_T$  variability.

### Impact of Biological Processes on Variations in Seasonal Carbonate Parameters

To understand the overall impact of biological processes on the seasonal variations in the carbonate system in the NWLB, changes in  $A_T$  and  $C_T$  need to be considered independently from the changes induced by dilution and evaporation. For this purpose, salinity-normalised changes of  $A_T$  and  $C_T$  in the upper 200 dbars are plotted in Figure 5. To differentiate waters affected by air-sea exchanges from sub-surface waters, the upper

200 dbars of water column has been divided into two layers: within and below the mixed layer (0 dbars—MLD and MLD—200 dbars). The barycentre of all observational points, defined as the coordinate of the mean  $A_T$  and  $C_T$  values during each cruise, is reported and considered to be representative of the “season” sampled.

The barycentres are spread along the photosynthesis-respiration line between the three cruises, reflecting the effects of biological processes on the carbonate system over the year. From the early summer period (PERLE0—red dots on Figure 5) to the end of the summer period (PERLE1—blue dots on Figure 5), for both layers, the barycentre shift was a signature for increased photosynthetic processes compared



**FIGURE 5** | Salinity-normalised  $A_T$  ( $NA_T^{39.3}$ ) vs. salinity-normalised  $C_T$  ( $NC_T^{39.3}$ ) during the three PERLE cruise in the upper 200 dbars for all stations situated in the North Western Levantine Basin. The layer of 0–200 dbars has been chosen as having the highest AOU variability because of the biological signal. Salinity-normalised values have been calculated with the mean PERLE salinity above 200 dbars (*i.e.*, 39.3). Empty and full dots represent data within and below the mixed layer, respectively. Circled crosses and circled stars represent the barycentre of data below and within the mixed layer, respectively. Black vectors reflect theoretical impacts of various processes (photosynthesis/respiration, carbonate dissolution/formation and  $CO_2$  release/invasion) on  $A_T$  and  $C_T$ . Grey isolines indicate levels of constant  $pH_T^{25}$  as a function of  $A_T$  and  $C_T$ .

to respiration processes. The deepening of the DCM observed between the PERLE0 and PERLE1 cruises and the negative AOU values recorded during these cruises supported this observation. The deepening of the DCM is a signature to the downward displacement of primary producers related to surface nutrient depletion (Sigman and Hain, 2012), and negative AOU values reflect oxygen production. All these elements indicate that autotrophic processes dominate the upper water column between early and late summer. Based on these assumptions, between the end of the summer period (PERLE1) and the end of the winter period (PERLE2—green dots on **Figure 5**), the barycentre shift indicates that heterotrophic processes were dominant in the upper water column. Whilst observations cannot be time related, it can be assumed that between the late winter period of PERLE2 and the early summer period of PERLE0, the “theoretical” shift of the barycentre indicates a balance in favor of autotrophic processes during this period. When considered together, these seasonal changes in normalised  $A_T$  and  $C_T$  confirm that during periods of high evaporation, autotrophic processes are consuming  $C_T$  and increasing  $A_T$ . This can explain

the apparent  $C_T$  stability and the important change in  $A_T$  over an annual cycle.

Based on the assumption that, below the mixed layer, the PERLE sampling area is a closed system (unimpacted by air-sea  $CO_2$  fluxes), the temporal evolution in  $NA_T^{39.3}$  and  $NC_T^{39.3}$  was used to calculate NEP and NEC fluxes. From the end of the bloom period (PERLE0) to the end of the summer period (PERLE1), daily NEP and NEC values of 0.53 and 0.01  $\mu\text{molC.kg}^{-1}.\text{d}^{-1}$ , respectively, were estimated whereas from the end of the summer period (PERLE1) to the start of the bloom period (PERLE2), negative daily NEP and NEC values of  $-1.02$  and  $-0.04$   $\mu\text{molC.kg}^{-1}.\text{d}^{-1}$ , respectively, were estimated. In the MedSea, the MLD seasonal variability is characterised by a deepening from November to February–March (D’Ortenzio et al., 2005). Therefore, it can be assumed that the water masses below the mixed layer remain isolated from surface  $CO_2$  inputs between the PERLE0 and PERLE1 cruises. However, due to the late winter deepening of the MLD (**Figure 3**), between the end of the summer period (PERLE1) and the late winter period (PERLE2), NEC and NEP could be biased by air-sea exchanges.

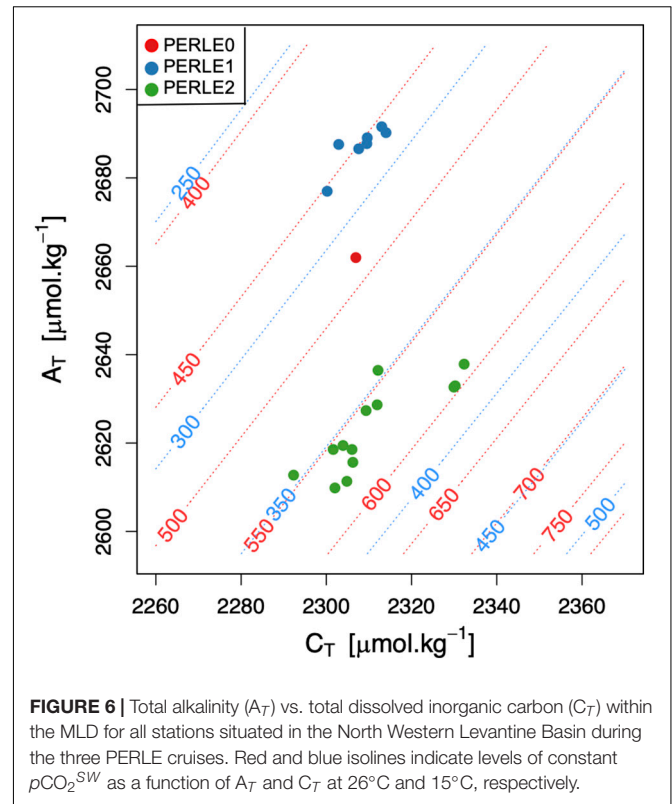
The seasonal NEP values estimated in this study confirm previous estimations based on oxygen concentration changes monitored with short-time incubations during the stratified period. In June 2006, Regaudie-de-Gioux et al. (2009) reported a positive NEP value of  $0.22 \pm 1.30 \text{ mmol O}_2 \cdot \text{m}^{-3} \cdot \text{d}^{-1}$  in waters above 100 meters in the EMed and in summer 2008, Christaki et al. (2011) reported positive NEP values of  $4 \pm 14 \text{ mmol O}_2 \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ . As previously observed by Schneider et al. (2007), the contribution of calcification and dissolution processes to variations in the carbonate system could be assumed to have a minor role in the MedSea. The NEC values calculated in the NWLB confirm this. The spreading of PERLE2 data points along the  $\text{CaCO}_3$  formation/dissolution line in **Figure 5** (green dots) might be associated to the spatial changes in alkalinity content across the geographical distribution of sampling sites during this cruise rather than to calcification and dissolution processes.

### Total Alkalinity Control on the Seasonal Air-Sea $\text{CO}_2$ Exchanges

To address the question of the control of  $A_T$  and  $C_T$  changes on the “source” ( $p\text{CO}_2^{\text{SW}} > p\text{CO}_2^{\text{ATM}}$ ) or “sink” ( $p\text{CO}_2^{\text{SW}} < p\text{CO}_2^{\text{ATM}}$ ) of  $\text{CO}_2$  in the NWLB, PERLE’s  $A_T$  and  $C_T$  values are reported in **Figure 6**. The temperature range in the area has been used to draw the red and blue “iso  $p\text{CO}_2^{\text{SW}}$ -lines” as representative of the  $p\text{CO}_2^{\text{SW}}$  values encountered during the winter and summer PERLE cruises. Considering a mean atmospheric partial pressure ( $p\text{CO}_2^{\text{ATM}}$ ) value of  $403 \mu\text{atm}$  (recorded at Lampedusa site from October 2018 to December 2019; Dlugokencky et al., 2021), the upper seawaters encountered at the warm end of summer with high alkalinity (PERLE1) were a “source” of  $\text{CO}_2$ . In contrast, the cold and low alkalinity end of winter (PERLE2) surface waters were a “sink” of  $\text{CO}_2$  with  $p\text{CO}_2^{\text{SW}}$ .

Although the  $C_T$  content remained almost stable between the PERLE cruises, the  $A_T$  variability was noticeable with the lowest  $A_T$  values measured at the end of the winter period (PERLE2) and the highest  $A_T$  values estimated during PERLE1, at the end of the summer period. When considering the large  $p\text{CO}_2^{\text{SW}}$  variations due to the temperature variability represented by the shift between the red and blue isolines, the high alkalinity seawater at the end of summer (PERLE1–blue dots on **Figure 6**) induces low  $p\text{CO}_2^{\text{SW}}$  values when seawater starts to cool and therefore highlights the potential for surface waters to absorb atmospheric  $\text{CO}_2$ . In the NWLB, the variability of the  $A_T$  content of the surface waters over an annual cycle impacts the air-sea  $\text{CO}_2$  exchanges. The “classical” vision that the  $p\text{CO}_2^{\text{SW}}$  variability is not driven by temperature change but by the biological control on  $C_T$ , must be largely revisited in light of the important effect that variations in  $A_T$  have on the  $p\text{CO}_2^{\text{SW}}$  regulation capability in the EMed.

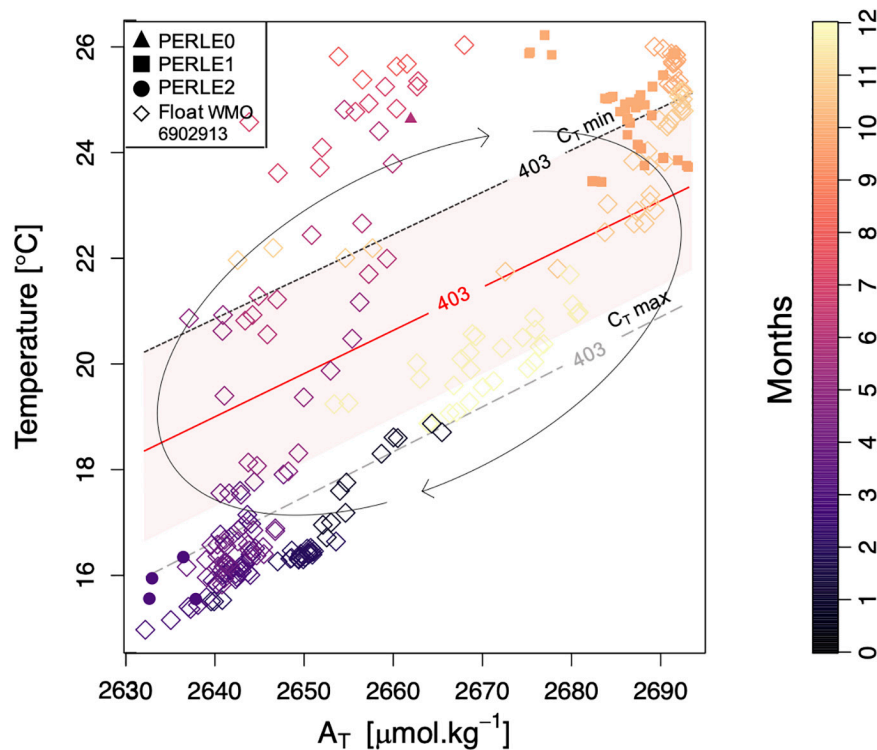
In order to estimate the effect of the  $A_T$  variability on the  $p\text{CO}_2^{\text{SW}}$  over an annual cycle, alkalinity was derived from salinity data from an Argo float that cycled in the



**FIGURE 6** | Total alkalinity ( $A_T$ ) vs. total dissolved inorganic carbon ( $C_T$ ) within the MLD for all stations situated in the North Western Levantine Basin during the three PERLE cruises. Red and blue isolines indicate levels of constant  $p\text{CO}_2^{\text{SW}}$  as a function of  $A_T$  and  $C_T$  at  $26^\circ\text{C}$  and  $15^\circ\text{C}$ , respectively.

NWLB for over a year. The temperature and total alkalinity (derived from salinity) values recorded by the float in the upper 20 dbars of the water column representative of the surface mixed layer affected by air-sea exchanges are presented in **Figure 7**. The cruise data within the mixed layer are also reported. In **Figure 7**, the red “iso  $p\text{CO}_2^{\text{SW}}$ -line” indicates the  $p\text{CO}_2$  equilibrium between the ocean and the atmosphere. This isoline was derived at constant  $C_T$ , based on the assumption that the  $p\text{CO}_2^{\text{SW}}$  is, apart from temperature, controlled by  $A_T$  rather than by  $C_T$  in the NWLB. The distribution of data above and below this line highlights the “source” or “sink” status of the NWLB for atmospheric  $\text{CO}_2$ , respectively.

The float derived data agreed with data measured during the PERLE cruises and indicate a penetration of atmospheric  $\text{CO}_2$  into the EMed from December to April, and a release of  $\text{CO}_2$  into the atmosphere from May to November. It must be noted that these estimates are sensitive to the  $C_T$  value used. Indeed, by considering a high  $C_T$  content (grey isoline labelled “ $C_T$  max” in **Figure 7**), the period of  $\text{CO}_2$  “sink” for the atmosphere will be shorter (from February to April). Conversely, if the lowest  $C_T$  mean value is considered (black isoline labelled “ $C_T$  min” in **Figure 7**), the area will act as a “sink” from December to May. The observed “iso  $p\text{CO}_2^{\text{SW}}$ -lines” shift (grey and black isolines in **Figure 7**) from the “iso  $p\text{CO}_2^{\text{SW}}$ -line” at mean  $C_T$  (red isoline in **Figure 7**) due to the  $C_T$  variability over a year induces a temporal change in the status of “source” or “sink” of the upper water masses.



**FIGURE 7 |** Total alkalinity ( $A_T$ ) vs. temperature in the upper 20 dbars during the three PERLE cruises and for the WMO 6902913 float data from October 2018 to July 2020 [ $A_T$  values have been estimated from the float salinity following the  $A_T$ -S sub-surface relationship proposed by Hassoun et al. (2015a)]. The colour bar corresponds to the “month of the year.” The red “iso  $pCO_2^{SW}$ -line” corresponds to the mean  $pCO_2^{ATM}$  value at Lampedusa site (estimated from the mean mole fraction of  $CO_2$  in ppm) calculated with the mean  $C_T$  values for all PERLE cruises ( $= 403 \mu\text{atm}$ ). The two others grey isolines correspond to the same constant  $pCO_2^{SW}$  with the minimum and maximum  $C_T$  values (from PERLE cruises) (2,292 and 2,332  $\mu\text{mol.kg}^{-1}$ , respectively). Arrows reflect the theoretical changes in  $A_T$  and temperature throughout the year. The coloured area represents the error associated to the red “iso  $pCO_2^{SW}$ -line” deduced by combining the uncertainty associated to the  $A_T$  values (*i.e.*,  $\pm 19 \mu\text{mol.kg}^{-1}$ ) with the default standard uncertainties from the constants (Orr et al., 2018).

Moreover, by considering the accuracy of  $\pm 19 \mu\text{mol.kg}^{-1}$  associated to the  $A_T$  estimation (according to Hassoun et al., 2015a), the uncertainty of the estimated  $pCO_2^{SW}$  has been calculated (Orr et al., 2018) and ranged between the two “iso  $pCO_2^{SW}$ -lines” deduced from the maximum and minimum  $C_T$  values (red area on Figure 7). Although the displacement of the air-sea  $pCO_2$  equilibrium might shift considering the  $A_T$  uncertainty, the temporal succession of the “sink” or “source” status for atmospheric  $CO_2$  throughout a year in the NWLB is evidenced. It confirms that the  $A_T$  content of the surface waters is a significant driver of the air-sea  $CO_2$  fluxes in the NWLB.

These are, to the best of our knowledge, the first estimates of the succession of the “sink” and “source” status in the NWLB based on *in situ* data. Previous estimates based on satellite observations of sea surface properties, and on a model characterising the evolution of the mixed layer  $pCO_2^{SW}$  (D’Ortenzio et al., 2008; Taillandier et al., 2012) are confirmed by this study. Moreover, coastal observations in the South eastern Levantine basin close to the Israeli shelf have also reported a  $CO_2$  source for the atmosphere in summer (from May to December) and a sink of atmospheric  $CO_2$  in winter (from January to April) (Sisma-Ventura et al., 2017).

## LONG TERM TEMPORAL CHANGES IN CARBONATE CHEMISTRY IN THE NORTH WESTERN LEVANTINE BASIN

### Decadal Carbonate Chemistry Trends in Surface Waters in the NWLB

Based on historical observations from the CARIMED dataset and observations from the PERLE cruises, temporal changes in carbonate chemistry between 2001 and 2019 in the surface NWLB have been assessed to study the mechanisms that could explain the carbonate system changes over the last twenty years (Figure 8). The surface layer has been defined to a depth of 50 dbars to include sufficient data. Due to the seasonal changes in surface salinity in the EMED (Grotsky et al., 2019), salinity-normalised  $A_T$  ( $NA_T^{39.3}$ ) and  $C_T$  ( $NC_T^{39.3}$ ) were used to facilitate the comparison between the different datasets across space and time. Indeed, due to the strong salinity dependency of alkalinity, by normalising by salinity, a significant part of the seasonal signal for alkalinity is removed.

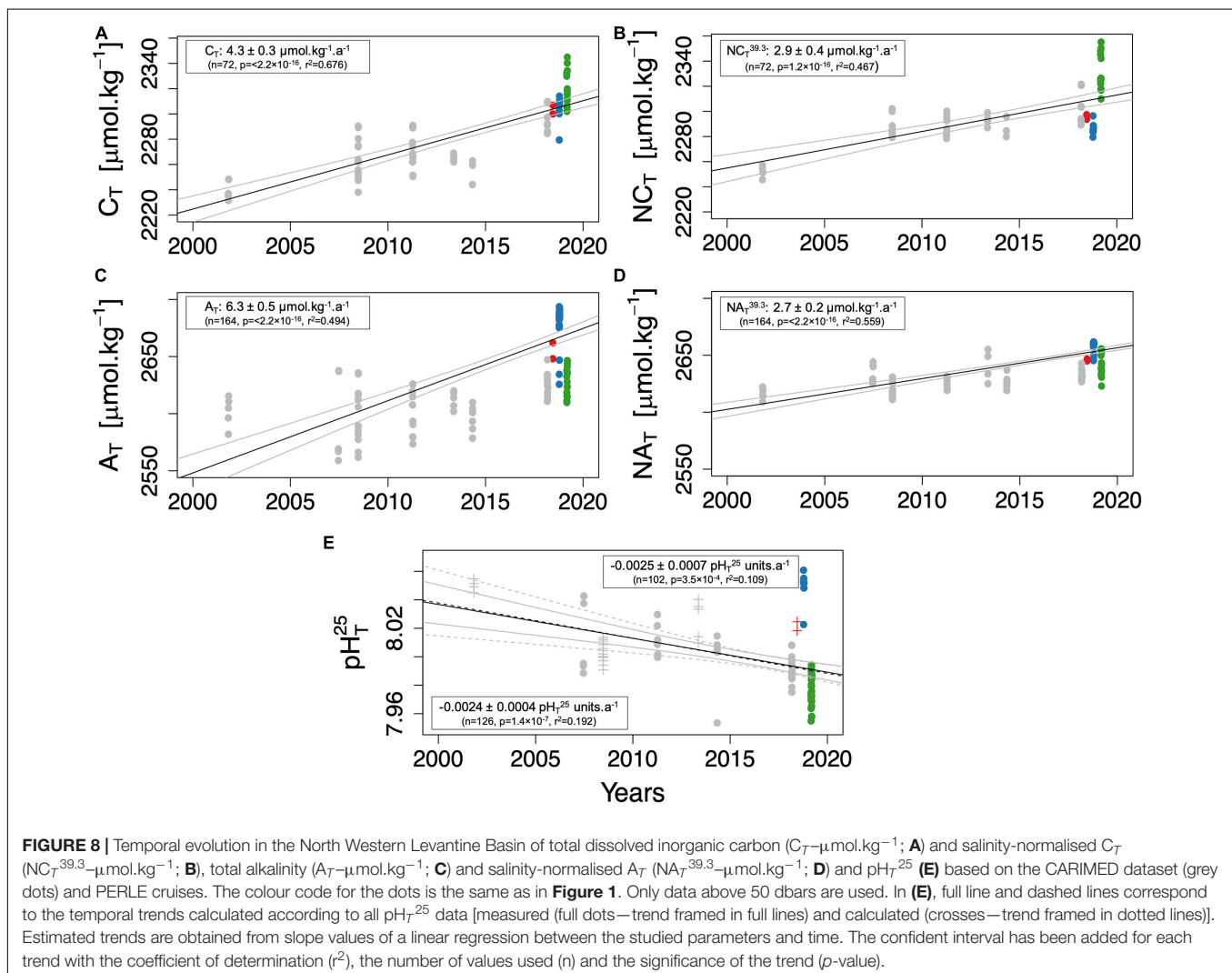
While being higher (even when salinity-normalised) than the trends observed in the North Western MedSea (*i.e.*,  $1.40 \pm 0.15 \mu\text{mol.kg}^{-1}.\text{a}^{-1}$ ; Merlivat et al., 2018), the temporal  $C_T$  increase

in the NWLB surface waters (**Figure 8A**) is consistent with other trends measured in the eastern Levantine basin (*i.e.*,  $5 \pm 2 \mu\text{mol.kg}^{-1}.\text{a}^{-1}$ ; Hassoun et al., 2019). However, when compared to other time-series over the global ocean, the trends measured in the surface NWLB waters are 3.7–1.5 times higher (if the  $\text{NC}_T^{39.3}$  trend is considered) than the global ocean range which lies between  $0.78 \mu\text{mol.kg}^{-1}.\text{a}^{-1}$  (Munida South Pacific time-series) and  $1.89 \mu\text{mol.kg}^{-1}.\text{a}^{-1}$  (CARIOCA time-series; Bates et al., 2014). This suggests that distinct mechanisms explaining the increasing  $C_T$  trend exist in the NWLB.

While  $A_T$  is considered insensitive to atmospheric  $\text{CO}_2$  penetration (Zeebe, 2012), positive trends in  $C_T$  and negative trends in  $\text{pH}_T^{25}$  (**Figures 8A,E**) can be explained, at least partially, by the increase in atmospheric  $\text{CO}_2$ . Indeed, between 2006 and 2018, a mean annual increase of  $2.2 \pm 0.08 \text{ ppm.a}^{-1}$  in  $x\text{CO}_2^{\text{ATM}}$  (mole fraction of  $\text{CO}_2$ ) was recorded at the Lampedusa site (equivalent to the trend recorded on a global scale; Dlugokencky et al., 2021). To estimate the sensitivity of the estimated trends to the increase in atmospheric  $\text{CO}_2$ , the increase in  $x\text{CO}_2^{\text{ATM}}$  was assumed to be equivalent to a

surface ocean increase in  $\text{pCO}_2^{\text{SW}}$ . Based on the estimated trends in  $\text{pCO}_2^{\text{SW}}$ ,  $\text{NA}_T^{39.3}$ , and  $\text{NC}_T^{39.3}$ , annual changes in carbonate chemistry  $\text{pCO}_2^{\text{SW}}$  have been calculated by solving thermodynamic equations (**Table 3**). The observed annual decrease in  $\text{pH}_T^{25}$  (**Figure 8E**) and increase in  $C_T$  (**Figure 8A**) lies between the values estimated with and without an  $A_T$  increase. This suggests that an  $A_T$  increase must exist to compensate for the decrease in pH and the increase in  $C_T$  or, in other words, that the high observed  $C_T$  trend is the consequence of the observed  $A_T$  increase. Although a positive  $A_T$  trend has been observed elsewhere in a coastal site of the MedSea (Kapsenberg et al., 2017), it remains unexplained. These changes could be related to changes in riverine inputs or changes in Black Sea water inputs (Schneider et al., 2007).

It is worth noting that the CARIMED database, by merging data measured over the past 20 years, has a large over-representation of the spring season (**Supplementary Figure 1** and **Supplementary Table 2**). Moreover, the spatial distribution of the sampled stations was different for each cruise. The



**TABLE 3** | Projection of annual changes on the carbonate parameters. Considering the temporal trends calculated in section “Decadal carbonate chemistry Trends in Surface Waters in the NWLB,” changes were calculated by adding the trend values to the mean values estimated for the surface layer (0–50 dbars) of the PERLE area.

	Trends presented in this study	Projection of annual changes			
		$p\text{CO}_2^{\text{SW}}$ increase ( $A_T$ constant)	$\text{NC}_T^{39.3}$ increase ( $A_T$ constant)	$\text{NC}_T^{39.3}$ and $\text{NA}_T^{39.3}$ increases	$\text{NA}_T^{39.3}$ and $p\text{CO}_2^{\text{SW}}$ increases
*Annual $p\text{CO}_2^{\text{SW}}$ changes ( $\mu\text{atm}\cdot\text{a}^{-1}$ )	+2.2	+2.2	+ 4.7	+1.2	+2.2
Annual $\text{pH}_T^{25}$ changes ( $\text{pH}_T^{25}$ units. $\text{a}^{-1}$ )	−0.0024	−0.0020	−0.0042	−0.0007	−0.0016
Annual $\text{NC}_T^{39.3}$ changes ( $\mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{a}^{-1}$ )	+2.9	+1.4	+ 2.9	+2.9	+3.6
Annual $\text{NA}_T^{39.3}$ changes ( $\mu\text{mol}\cdot\text{kg}^{-1}\cdot\text{a}^{-1}$ )	+2.7	/	/	+2.7	+2.7

\*Assuming that the increase in  $p\text{CO}_2^{\text{SW}}$  in the surface ocean is equal to the increase in  $x\text{CO}_2^{\text{ATM}}$ .

scarcity of observations in the NWLB precludes the estimation of the seasonal variability on the observed trends. Due to the observed influence of seasonal conditions on the carbonate parameters during the PERLE cruises, time-series that would include observations of the peculiar conditions observed in the late summer (high surface  $\text{pH}_T^{25}$  associated with high  $A_T$  values during PERLE1—**Figure 2C**) or winter could modulate the observed temporal trends. Nonetheless, when data collected during “not spring” cruises are not considered to estimate the trends, despite shifting the temporal trend values, tendencies remain significant for each parameter. Thus, the conclusion that a decadal  $A_T$  increase must exist to counterbalance the pH decrease associated to the  $C_T$  increase remains coherent and valid.

## Perspectives on the Future Functioning of the Eastern Mediterranean Carbonate System

In the projected warmer MedSea (Nykjaer, 2009), increased stratification but also reduced nutrient inputs from river discharge caused by more frequent drought periods could increase the oligotrophy of the MedSea (e.g., Moon et al., 2016; Pagès et al., 2019, 2020). As this study suggests that the magnitude of the annual  $C_T$  variation in surface waters is reduced in the EMed due to the low  $C_T$  vertical gradients, all processes that could decrease primary production in the future could reduce the  $C_T$  contribution to the air-sea exchanges.

Even if internal thermohaline oscillation needs to be considered to draw solid conclusions about salinity trends, over the past 30 years, a positive long-term trend in salinity for the LSW and LIW has been recorded (Ozer et al., 2017). Because of the salinity impact on alkalinity concentrations (**Figure 4**) and of the  $A_T$  impact on the air-sea  $\text{CO}_2$  fluxes (**Figure 7**), if the PERLE1 conditions are exacerbated in the future with marine heatwaves extending over longer periods of the year, even more

alkaline waters can be expected at the end of the summer. An even greater potential  $p\text{CO}_2^{\text{ATM}}$  sink will result when surface seawaters cool. The gyres (such as the IE), which have a higher  $A_T$  content due to their saltier waters, might be even more efficient at catching atmospheric  $\text{CO}_2$  when seawater cools. The control of air-sea  $\text{CO}_2$  exchange by alkalinity that is suggested in this study could be enhanced in a future warmer and less productive EMed. However, as  $C_T$  and  $A_T$  are equally affected by evaporation and as, in the future less productive EMed, the  $C_T$  biological consumption will be less efficient, the mechanisms leading to stable inorganic carbon content described in this study might be altered.

In an attempt to quantify the sensitivity of the carbonate system to future  $C_T$  and  $A_T$  changes, estimated buffer factors within the MLD for each PERLE cruise are presented in **Table 4**. At a comparable period of the year (March–April for PERLE2 cruise), the estimated buffer factors are in good agreement with former estimates (Álvarez et al., 2014) whereas the estimated buffer factors for PERLE0 and PERLE1 cruises during summer are significantly higher. Higher absolute buffer values imply higher buffering capacity and lower changes in  $[\text{CO}_2]$ , pH or  $\Omega$  for a given change in  $A_T$  or  $C_T$ . Assuming that the PERLE1 conditions will be exacerbated in the future (Darmaraki et al., 2019), the EMed surface water is moving toward an overall increase in its buffering capacity (relative to changes in  $A_T$  and  $C_T$ ).

It is worth noting that, when atmospheric  $\text{CO}_2$  dissolves in seawater, the  $\text{CO}_2$  concentration in solution changes due to the carbonate ion buffering effect. The future effects of the decadal trends measured in the NWLB on the buffering capacities of the carbonate ion can be discussed using three different perspectives: (1) By considering the observed decrease in  $\text{pH}_T^{25}$ , the carbonate ion availability will decrease accordingly, reducing the atmospheric  $\text{CO}_2$  uptake by the MedSea. (2) The greater increase in  $C_T$  in comparison to the increase in  $A_T$  will reduce the carbonate ion availability, but, nevertheless, will compensate

**TABLE 4** | Mean values and standard deviations of buffer factors (in  $\text{mmol}\cdot\text{kg}^{-1}$ ) during PERLE cruises.

Cruise	Season	$\gamma_{CT}$	$\beta_{CT}$	$\omega_{CT}$	$\gamma_{AT}$	$\beta_{AT}$	$\omega_{AT}$
PERLE0	Early summer period	$0.26 \pm \text{NA}$	$0.33 \pm \text{NA}$	$-0.44 \pm \text{NA}$	$-0.33 \pm \text{NA}$	$-0.36 \pm \text{NA}$	$0.41 \pm \text{NA}$
PERLE1	End of summer period	$0.27 \pm 0.00$	$0.34 \pm 0.00$	$-0.46 \pm 0.00$	$-0.34 \pm 0.00$	$-0.38 \pm 0.00$	$0.43 \pm 0.00$
PERLE2	End of winter period	$0.24 \pm 0.00$	$0.30 \pm 0.00$	$-0.38 \pm 0.00$	$-0.30 \pm 0.00$	$-0.32 \pm 0.01$	$0.35 \pm 0.01$

for the impact of a pH decrease on the carbonate ion content, so allowing the CO<sub>2</sub> uptake into the atmosphere. (3) The positive trend in  $A_T$ , and its impact on the CO<sub>2</sub> atmospheric uptake and on mitigating the decreasing pH trend, may indirectly increase the  $C_T$ .

## CONCLUSION

Based on data collected in the EMed over three different seasons of the year, this study provides for the first time, an annual overview of the seasonal dynamics of the carbonate chemistry in the NWLB. In this area, an atypical seasonal range in  $A_T$  variations compared to the range in  $C_T$  variations results from the combination of high rates of evaporation and biological processes.

The high  $A_T$  content at the “end of summer” period has a strong impact on the air-sea exchanges of CO<sub>2</sub>. In the NWLB, the status of “source” or “sink” for atmospheric CO<sub>2</sub> is adjusted by the  $A_T$  variability more than the  $C_T$  variability. Over longer time scales, and by compiling historical data, the reported increasing trends in  $A_T$  and  $C_T$  impact with divergent effects the observed acidification. These “end of summer” conditions will occur more frequently and lasting longer in the future. This ocean warming up will result in an increased buffer capacity that could mitigate the ocean acidification of the EMed.

## DATA AVAILABILITY STATEMENT

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession number(s) can be found below: <https://mistrals.sedoo.fr/MERMeX/> and <http://www.coriolis.eu.org>.

## AUTHOR CONTRIBUTIONS

CW-R, TW, and DL initiated and design the study. MÁ provided the CARIMED database and contributed to carbonate chemistry interpretation. PR helped supervising the study. MP-P and PC provided the nutrients database. MF, LC, TM, LN-C, CW-R, and TW performed on board carbonate parameters and oxygen analytical measurements. VT and FD'O provided CTD and ARGO dataset. FD'O, XD, and PC planned and designed the

PERLE Research cruises. CW-R, TW, and DL wrote the first draft of the manuscript. All authors contributed to manuscript revision, read, and approved the submitted version.

## FUNDING

This study takes part of the PERLE (Pelagic Ecosystem Response to the Levantine Experiment) of the MISTRALS-MERMEX project. The project leading to this publication has received funding from European FEDER Fund under project 1166-39417. The SNAPO-CO<sub>2</sub> service at LOCEAN was supported by the CNRS-INSU and OSU Ecce-Terra.

## ACKNOWLEDGMENTS

We wish to thank the crew members of the R/V “Téthys II” operated by the DT-INSU, for making the PERLE0 (BIO-ARGO-MED2018) cruise possible. We gratefully acknowledge the Délégation Générale de l'Armement which funded the program Protevs II into which the PROTEVS-PERLE1 campaign was scheduled, the French Naval Hydrologic and Oceanographic Service (SHOM) and the crew of the R/V “L'Atalante” (IFREMER) for their contribution to the PROTEVS-PERLE1 campaign. We acknowledge “Flotte Oceanographique Française”, FOF, and the crew of the R/V “Pourquoi Pas?” (IFREMER) for their help in the PERLE2 sampling. The many researchers responsible for the collection of data and quality control are thanked for their contribution. For seawater sample analyses, we also thank the SNAPO-CO<sub>2</sub> at LOCEAN, Paris, and in particular J. Fin and N. Metzl. Argo data were collected and made freely available by the Coriolis project and contributing programmes (<http://www.coriolis.eu.org>). The Argo Program is part of the Global Ocean Observing System. We thank Tracy Lynne Bentley for language editing. The two referees are thanked for helping improve this work.

## SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fmars.2021.649246/full#supplementary-material>

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