Climatological variations of total alkalinity and total dissolved inorganic carbon in the Mediterranean Sea surface waters

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Abstract

A compilation of several cruises data from 1998 to 2013 was used to derive polynomial fits that estimate total alkalinity (A_T) and total dissolved inorganic carbon (C_T) from measurements of salinity and temperature in the Mediterranean Sea surface waters. The optimal equations were chosen based on the 10-fold cross validation results and revealed that a second and third order polynomials fit the A_T and C_T data respectively. The A_T surface fit yielded a root mean square error (RMSE) of ± 10.6 µmol.kg^{-1}, and salinity and temperature contribute to 96% of the variability. Furthermore we present the first annual mean C_T parameterization for the Mediterranean Sea surface waters with a RMSE of ± 14.3 µmol.kg^{-1}. Excluding the marginal seas of the Adriatic and the Aegean, these equations can be used to estimate A_T and C_T in case of the lack of measurements. The identified empirical equations were applied on the quarter degree climatologies of temperature and salinity, available from the World Ocean Atlas 2013. The seven years averages (2005-2012) showed that A_T and C_T have similar patterns with an increasing Eastward gradient. The variability is influenced by the inflow of cold Atlantic waters through the Strait of Gibraltar and by the oligotrophic and thermohaline gradient that characterize the Mediterranean Sea. The summer-winter seasonality was also mapped and showed different patterns for A_T and C_T. During the winter, the A_T and C_T concentrations were higher in the Western than in the Eastern basin. The opposite was observed in the summer where the Eastern basin was marked by higher A_T and C_T concentrations than in winter**.** The strong evaporation that takes place in this season along with the ultra-oligotrophy of the Eastern basin determines the increase of both A_T and C_T concentrations.

Keywords: Mediterranean Sea; Carbonate System; Surface Waters; Empirical Modeling; Seasonal Variations

1. Introduction

The role of the ocean in mitigating climate change is well known as it absorbs about 2 Pg C yr^{-1} of anthropogenic CO_2 (Wanninkhof et al., 2013). Worldwide measurements of surface seawater CO_2 properties are being conducted as they are important for advancing our understanding of the carbon cycle and the underlying processes controlling it. For instance, the buffer capacity of the CO_2 system varies with temperature, the distribution of total inorganic carbon and total alkalinity (Omta et al., 2011).

Our understanding of the open-ocean CO_2 dynamics has drastically improved over the years (Rödenbeck et al., 2013; Sabine et al., 2004; Takahashi et al., 2009; Watson and Orr, 2003). However our understanding of marginal seas such as the Mediterranean remains poor due to the limited measurements combined with the enhanced complexity of the land-ocean interactions. In the Mediterranean Sea, available measurements of the carbonate system are still scarce and only available in specific regions such as the Alboran sea (Copin-Montégut, 1993), the Gibraltar Strait (Santana-Casiano et al., 2002), the Dyfamed time-series in the Ligurian Sea (Bégovic and Copin-Montégut, 2002; Copin-Montégut and Bégovic, 2002; Touratier and Goyet, 2009) and the Otranto Strait (Krasakopoulou et al., 2011). Large geographical distribution of CO_2 data are often confined to cruises with a short sampling period (Álvarez et al., 2014; Goyet et al., 2015; Rivaro et al., 2010; Schneider et al., 2007; Touratier et al., 2012). Numerical models have provided some insights of the carbon dynamics in the Mediterranean Sea (Cossarini et al., 2015; D'Ortenzio et al., 2008; Louanchi et al., 2009), but it remains important to constrain the system from in situ measurements to validate their output.

The scarcity of the CO_2 system measurements in the Mediterranean Sea make it difficult to constrain the CO_2 uptake in this landlocked area and also limits our understanding of the magnitude and mechanisms driving the natural variability on the ocean carbon system (Touratier and Goyet, 2009). Empirical modeling has been successfully used to study the marine carbon biogeochemical processes such as the estimation of biologically produced O_2 in the mixed layer (Keeling et al., 1993), estimation of global inventories of anthropogenic CO_2 (Sabine et al., 2004) and estimation of the $CaCO_3$ cycle (Koeve et al., 2014). Empirical algorithms were also used to relate limited A_T and C_T measurements to more widely available physical parameters such as salinity and temperature (Bakker et al., 1999; Ishii et al., 2004; Lee et al., 2006). The A_T and C_T fields can then be used to calculate pCO_2 fields and thus predict the CO_2 flux across the air-sea interface (McNeil et al., 2007).

Previous empirical approaches to constrain A_T in the Mediterranean Sea have only covered selected cruises (Schneider et al., 2007; Touratier and Goyet, 2009) or local areas such as the Dyfamed time-series station or the Strait of Gibraltar (Copin-Montégut, 1993; Santana-Casiano et al., 2002). As for C_T, empirical models have only been applied to data below the mixed layer depth (MLD) following the equation of Goyet and Davis (1997) at the Dyfamed time series station (Touratier and Goyet, 2009) or using the composite dataset from Meteor 51/2 and Dyfamed (Touratier and Goyet, 2011). Also Lovato and Vichi (2015) proposed an optimal multiple linear model for C_T using the Meteor 84/3 full water colum data. To the best of our knowledge the reconstruction of C_T in surface waters has not been yet performed in the Mediterranean Sea. This is probably due to the lack of measurements available for previous studies to capture the more complex interplay of biological, physical and solubility processes that drive C_T variability in the surface waters.

In this study we have compiled CO_2 system measurements from 14 cruises between 1995 and 2013, that allowed us to constrain an improved and new empirical algorithms for A_T and C_T in the Mediterranean Sea surface waters. We also evaluated the spatial and seasonal variability of the carbon system in the Mediterranean Sea surface waters, by mapping the 2005-2012 annual and seasonal averages of surface A_T and C_T using the quarter degree climatologies of salinity and temperature from the World Ocean Atlas 2013 (WOA13).

2. Methods

2.1. Surface A_T and C_T data in the Mediterranean Sea

Between 1998 and 2013, there have been multiple research cruises sampling the seawater properties throughout the Mediterranean Sea. This includes parameters of the carbonate system more specifically A_T, pH and C_T and physico-chemical properties of in situ salinity, and temperature. In this study we have compiled surface water samples between 0 and 10 m depth, totaling 490 and 426 measurements for A_T and C_T respectively (Table 1).

2.2. Polynomial model for fitting A_T and C_T data

Two polynomial equations for fitting A_T or C_T from salinity (S) alone or combined with sea surface temperature (T) in the surface waters (0 – 10 m) of the Mediterranean Sea were chosen from the results of the 10-fold cross validation method (Breiman, 1996; Stone, 1974). This type of analysis was previously performed by Lee et al. (2006) for general relationships of A_T with salinity and temperature. This model validation technique is performed by randomly portioning the dataset into 10 equal subsamples. One subsample is used as the validation data, and the 9 remaining subsamples are used as training data. The cross validation process is then repeated 10 times, with each of the 10 subsamples used exactly once as the validation data. In this manner, all observations are used both for training and validation, and each observation is used for validation only once. The best fit is chosen by computing the residuals from each regression model, and computing independently the performance of the selected optimal polynomial on the remaining subsets.

The analysis was applied for polynomials of order 1 to 3, and the optimal equation was chosen based on the lowest Root Mean Square Error (RMSE) and the highest coefficient of determination (r^2). High-order polynomials (4 and above) were discarded because they can be oscillatory between the data points, leading to a poorer fit to the data.

The dataset consists of 490 and 400 data points for A_T and C_T, respectively (Table 1). To ensure the same spatial and temporal coverage of the polynomial fits, the same training dataset was retained for both A_T and C_T. This was performed by selecting stations were both parameters were simultaneously measured; yielding 360 data points (Figure 1). To validate the general use of the proposed parameterizations we tested the algorithms with measurements which are not included in the fits (Validation dataset). For A_T, the validation dataset consists of 130 data points which are formed from the testing subset of the 10th fold (40 data points), and from cruises where A_T was measured without accompanying C_T (90 data points). For C_T, the validation dataset is the same as the testing subset of the 10th fold (40 data points).

2.3. Climatological and seasonal mapping of A_T and C_T

The climatological and seasonal averages of salinity (Zweng et al., 2013) and temperature (Locarnini et al., 2013) in 1/4*1/4 degree grid cells were downloaded from the World Ocean Atlas 2013 (WOA13). The seven years averages (2005-2012) and the summer-winter seasonality of A_T and C_T fields were mapped at 5 m depth by applying the respective derived algorithms in their appropriate ranges of S and T. The summer seasonality is defined as the average of the months of July, August and September. The winter seasonality is defined as the average of the months of January, February, and March.

3. Results and Discussion

3.1. Fitting A_T in the Mediterranean Sea surface waters

In the surface ocean the A_T variability is controlled by freshwater addition or the effect of evaporation, and salinity contributes to more than 80% of the A_T variability (Millero et al., 1998). In the Mediterranean Sea, several studies have shown that the relationship between A_T and S is linear (Copin-Montégut, 1993; Copin-Montégut and Bégovic, 2002; Hassoun et al., 2015b; Rivaro et al., 2010; Schneider et al., 2007). In other studies, the sea surface temperature (T) has been included as an additional proxy for changes in surface water A_T related to convective mixing (Lee et al., 2006; Touratier and Goyet, 2011).

The results of the 10-fold cross validation analysis revealed that the optimal model for A_T is a second order polynomial in which A_T is fitted to both S and T (Eq 1).

$$A_T = 2558.4 + 49.83(S - 38.2) - 3.89(T - 18) - 3.12(S - 38.2)^2 - 1.06(T - 18)^2 \quad (1)$$

Valid for T > 13 ºC and 36.30 < S < 39.65

n = 375; r^2 = 0.96; RMSE = 10.6 µmol.kg^{-1}

A linear relationship between A_T and S yields a higher RMSE (14.5 µmol.kg^{-1}) and a lower r^2 (0.91) than Eq (1). In a semi-enclosed basin such as the Mediterranean Sea, the insulation and high evaporation as well as the input of rivers and little precipitation leads to a negative freshwater balance (Rohling et al., 2009). The resulting anti-estuarine thermohaline circulation could explain the contribution of temperature to the A_T variability (Touratier and Goyet, 2011).

The residuals of training dataset used to generate the second order polynomial fit for A_T are presented in Figure 2a. Most of the A_T residuals (340 over 375) were within a range of ± 15 µmol.kg^{-1} (1 σ). However 35 residuals over were high up to ± 30 µmol.kg^{-1} (1 σ). Applying the A_T algorithm to the testing dataset (Figure 2b), yields a mean residual of 0.91 ± 10.30 µmol.kg^{-1} (1 σ), and only 6 data points have residuals higher than ± 15 µmol.kg^{-1} (1 σ). Furthermore, to make sure that the A_T algorithm does not overfit the data, we tested the difference in means between the RMSE and residuals between the training set compared to the testing set. The results show that for both RMSE and mean residual, we cannot reject the null hypothesis (that assumes equals means) between the training and validation datasets (Table 2).

The comparison of the RMSE as reported by other studies with that of Eq (1) does not indicate if the parameterization developed here has advanced or not on previous attempts in the Mediterranean Sea. In that order, we independently applied each of the previous equations on the same training dataset used to develop Eq (1) and then computed the RMSE and r^2 for every one (Table 3). The results show that Eq (1) has a lower RMSE and a higher r^2 than all of the parameterizations presented in Table 3. For instance, the general relationship of Lee et al. (2006) applied to the dataset of this study yields an RMSE as high as ± 40.50 µmol.kg^{-1}. The RMSE of other studies developed strictly in the Mediterranean Sea varied from ± 13.81 to ± 26.11 µmol.kg^{-1} using the equations of Touratier and Goyet (2011) and Schneider et al. (2007) respectively.

By applying directly the previous parameterizations to our training dataset, the calculated RMSE are significantly higher than the ones reported in their respective studies. For instance the reported RMSE in Lee et al. (2006) for sub-tropical oceanic regions is ± 8 µmol.kg^{-1} and that of Schneider et al. (2007) for the Meteor 51/2 cruise is ± 4.2 µmol.kg^{-1}. This shows that previous models were constrained by their spatial coverage, time span and used datasets. In fact the previous equations were calculated in local areas such as the Alboran Sea (Copin-Montégut, 1993), the Strait of Gibraltar (Santana-Casiano et al., 2002) or the Dyfamed Site (Copin-Montégut and Bégovic, 2002; Touratier and Goyet, 2009). On a large scale, equations were applied using limited datasets such as the Meteor 51/2 cruise in October-November 2001 (Schneider et al., 2007), the Transmed cruise in May-June 2007 (Rivaro et al., 2010) or the Meteor 51/2 and the Dyfamed time series station (Touratier and Goyet, 2011).

The proposed algorithm including surface data from multiple cruises, and on a large time span, presents a more representative relationship to estimate A_T from S and T than the previously presented equations (Table 3). In Equation 1, T and S contribute to 96% of the A_T

variability and the RMSE of ± 10.6 μmol.kg^{-1} presents a significant improvement of the spatial and temporal estimations of A_T in the Mediterranean Sea surface waters (Mean difference t-test, H = 1; p = 0.04).

3.2. Fitting C_T in the Mediterranean Sea surface waters

The surface C_T concentrations are influenced by lateral and vertical mixing, photosynthesis, oxidation of organic matter and changes in temperature and salinity (Poisson et al., 1993; Takahashi et al., 1993). All these processes are directly or indirectly correlated with sea-surface temperature (Lee et al., 2000). Hence, the parameterization of C_T includes both physical (S and T) and/or biological parameters (Bakker et al., 1999; Bates et al., 2006; Koffi et al., 2010; Lee et al., 2000; Sasse et al., 2013).

The results of the 10-fold cross validation analysis showed that a first order polynome fits C_T to S and T with an RMSE of 16.25 μmol.kg^{-1} and r^2 = 0.87. These values are comparable to the RMSE and r^2 found by previous empirical approaches applied in the Eastern Atlantic (Bakker et al., 1999; Koffi et al., 2010). However we found that a third order polynome improved the RMSE and r^2 of the equation compared to the first order fit (Eq 2). Hence we will retain the large dataset used to develop Eq (2), where temperature and salinity explain 90% of the C_T variability encountered in the Mediterranean Sea surface waters. The remaining 10% could be attributed to the biological and air-sea exchange contributions to the C_T variability.

$$C_T = 2234 + 38.15(S-38.2) - 14.38(T-17.7) - 4.48(S-38.2)^2 - 1.43(S-38.2)(T-17.7) + 9.62(T-17.7)^2 - 1.10(S-38.2)^3 + 3.53(T-17.7)(S-38.2)^2 + 1.47(S-38.2)(T-17.7)^2 - 4.61(T-17.7)^3 \quad (2)$$

Valid for T > 13 ºC and 36.30 < S < 39.65

n = 375, r^2 = 0.90; RMSE = 14.3 μmol.kg^{-1}

The C_T parameterization developed in this study (Eq 2) showed a higher uncertainty than that of A_T regarding both RMSE and r^2. The estimation of C_T in the mixed layer adds a high uncertainty due to the seasonal variability (Sabine et al., 2004). Also in the C_T are directly affected by air-sea exchange, and their concentrations will increase in response to the oceanic uptake of anthropogenic CO_2.

Previous models accounted for the anthropogenic biases in the C_T measurements by calculating the C_T rate of increase (Bates, 2007; Lee et al., 2000; Sasse et al., 2013; Takahashi et al., 2014). However in a study, Lee et al. (2000) also did not correct the C_T concentrations for regions above 30º latitude such as the Mediterranean Sea. In the following we will assess the importance of accounting or not for anthropogenic biases in the C_T measurements. In that order we dowloaded the monthly atmospheric pCO_2 concentrations measured from 1999 to 2013 at the Lampedusa Island Station (Italy) from the World Data Center for Green House Gases (http://ds.data.jma.go.jp/gmd/wdcgg/). Following the method described by Sasse et al. (2013), we corrected the C_T measurements to the nominal year of

2005 and applied the same 10-fold cross validation analysis using data with and without anthropogenic C_T corrections. We found that the RMSE of the C_T model trained using measurements with anthropogenic corrections is 13.9 $\mu mol.kg^{-1}$, which is not significantly different from the model trained using measurements without anthropogenic corrections (Eq 2; RMSE = 14.3 $\mu mol.kg^{-1}$).

The yearly increase of C_T concentrations is difficult to assess due to the wide spatial distribution of the training dataset used to generate Eq (2). Hence we will refer to the monthly C_T concentrations measured between 1998 and 2013 at the Dyfamed time-series station. We found that the rate of increase in C_T concentrations at the Dyfamed site was 0.99 $\mu mol.kg^{-1}.yr^{-1}$ (Figure 3), which is consistent with the anthropogenic C_T correction rate used in the previous studies of Lee et al. (2000), Bates (2007) and Sasse et al. (2013).

The rate of increase in C_T concentrations of 0.99 $\mu mol.kg^{-1}.yr^{-1}$ as well as the RMSE difference of ± 0.4 $\mu mol.kg^{-1}$ between the two models (with or without anthropogenic corrections) are both smaller than the uncertainty of the C_T measurements of at least ± 2 $\mu mol.kg^{-1}$ (Millero, 2007). A recent study also showed that the uncertainty of the C_T measurements can be significantly higher than ± 2 $\mu mol.kg^{-1}$, as most laboratories reported values of C_T for the measures that were within a range of ± 10 $\mu mol.kg^{-1}$ of the stated value (Bockmon and Dickson, 2015).

Between 1998 and 2013, the C_T concentrations measured at the Dyfamed time-series station showed a slightly increasing trend (r^2 = 0.05). The increase in C_T concentrations in response to elevated atmospheric CO_2, was masked by the high seasonal variations. For example, during the year 1999 the variation in C_T concentrations reached as high as 100 $\mu mol.kg^{-1}$ (Figure 4a). Also there is a clear seasonal cycle of C_T in the Dyfamed station (Figure 4b). In the summer, the C_T starts to increase gradually to reach a maximum of 2320 $\mu mol.kg^{-1}$ during the winter season, after which a gradual decrease is observed to reach a minimum of 2200 $\mu mol.kg^{-1}$ by the end of spring. The seasonal cycle can be explained by the counter effect of temperature and biology on the C_T variations. During the spring, the increasing effect of warming of pCO_2 is counteracted by the photosynthetic activity that lowers the C_T. During the winter, the decreasing effect of cooling on pCO_2 is counteracted by the upwelling of deep waters rich in C_T (Hood and Merlivat, 2001; Takahashi et al., 1993). This shows that the C_T concentrations were more affected by the seasonal variations than by anthropogenic forcing.

Considering the small differences in the RMSE obtained by the two models, the uncertainties in the C_T measurements and the clear signal of the seasonal variations; no corrections were made to account for the rising atmospheric CO_2 concentrations. Also the dynamic overturning circulation in the Mediterranean Sea plays an effective role in absorbing the anthropogenic CO_2 and transports it from the surface to the interior of the basins (Hassoun et al., 2015a; Lee et al., 2011).

The residuals of the dataset used to generate the third order polynomial fit for C_T are presented in Figure 5a. Most of the C_T residuals (330 over 360) were within a range of ± 18

$\mu mol.kg^{-1}$ (1 σ). In contrast only few residuals (12 over 360) reached up to ± 50 $\mu mol.kg^{-1}$ (1 σ). Applying the C_T algorithm to the testing dataset (Figure 5b), yields a mean residual of 4.5 ± 17 $\mu mol.kg^{-1}$ (1 σ) which is close to the uncertainties of our C_T relationship. The high residuals observed in this study are consistent with the results of the optimal multiple linear regression performed by Lovato and Vichi (2015), where the largest discrepancies between observations and reconstructed data were detected at the surface layer with RMSE higher than ± 20 $\mu mol.kg^{-1}$. To make sure that the C_T algorithm does not overfit the data, we conducted the same analysis performed on the A_T datasets. The results show that for both RMSE and mean residual, we cannot reject the null hypothesis (that assumes equals means) between the training and validation datasets (Table 4).

Considering the high uncertainties of the C_T measurements, the seasonal variations and the anthropogenic forcing; Eq (2) presents the first parametrization for C_T in the Mediterranean Sea surface waters, with an RMSE of ± 14.3 $\mu mol.kg^{-1}$ (1 σ) and a $r^2 = 0.90$ (Eq 2).

3.3. Spatial and seasonal variability of A_T and C_T in surface waters

The ranges of the 2005-2012 average annual climatologies of the World Ocean Atlas 2013 (WOA13) are from 35.91 to 39.50 for S and from 16.50 ºC to 23.57 ºC for T (Locarnini et al., 2013; Zweng et al., 2013). However a wider range is observed for the seasonal climatologies, especially during the winter season where T ranges from 9.05 ºC to 18.43 ºC. The estimations of A_T and C_T in surface waters from Eq (1) and (2) respectively are only applicable in the appropriate ranges of T > 13 ºC and 36.3 < S < 39.65. Hence the surface waters A_T and C_T concentrations were mapped only where T and S were within the validity range of Eq (1) and (2) respectively. Excluding few near-shore areas and the influence of cold Atlantic Waters in winter, the ranges in which Eq (1) and Eq (2) can be applied are within those of the climatological products of T and S of the WOA13 (Figure 6).

The mapped climatologies for 2005-2012 at 5m depth show a strong increase in the Eastward gradient for both A_T and C_T with the highest concentrations always found in the Eastern Mediterranean (Figure 7). The minimum values of 2400 $\mu mol.kg^{-1}$ for A_T and 2100 $\mu mol.kg^{-1}$ for C_T are found near the Strait of Gibraltar and the maximum values of 2650 $\mu mol.kg^{-1}$ and 2300 $\mu mol.kg^{-1}$ are found in the Levantine and Aegean sub-basin for A_T and C_T respectively.

The A_T parameterization of this study detects a clear signature of the alkaline waters entering through the Strait of Gibraltar that remains traceable to the Strait of Sicily as also shown by Cossarini et al. (2015). In the Eastern basin the positive balance between evaporation and precipitation contributes to the increasing surface A_T. Local effects from some coastal areas such as the Gulf of Gabes and riverine inputs from the Rhone and Po River are also detected.

Our results for surface A_T have a similar spatial pattern and range as the annual climatology of Cossarini et al. (2015) which simulates surface A_T values from 2400 to 2700 $\mu mol.kg^{-1}$. The main difference is marked in the upper ends of the Adriatic and Aegean sub-basins where our algorithm predicts A_T values around 2400-2500 $\mu mol.kg^{-1}$, whereas the analysis of

Cossarini et al. (2015) yields a maximum of 2700 µmol.kg^{-1} in these regions. Regressions in regions of river input indicate a negative correlation between alkalinity and salinity (Luchetta et al., 2010). Hence, Eastern marginal seas such as the Adriatic and Aegean sub-basins have high A_T concentrations due to the freshwater inputs (Cantoni et al., 2012; Souvermezoglou et al., 2010). This shows the sensitivity of our algorithms to temperature and salinity especially in areas that are more influenced by continental inputs such as the Po River and inputs of the Dardanelle in the northern Adriatic and northern Aegean respectively (Figure 7a).

At the surface, the basin wide distributions of C_T are affected by physical processes and their gradient is similar to that of A_T (Figure 7b). The lowest C_T concentrations are found in the zone of the inflowing Atlantic water and increases toward the East in part due to evaporation as also shown by Schneider et al. (2010). Our results for surface C_T have a similar range as the optimal linear regression performed by Lovato and Vichi (2015) which estimates surface C_T values from 2180 to 2260 µmol.kg^{-1}. Moreover, the results show that the Mediterranean Sea is characterized by C_T values that are much higher (100–200 µmol.kg^{-1} higher) than those observed in the Atlantic Ocean at the same latitude (Key et al., 2004).

Overall the Western basin has a lower surface C_T content than the Eastern basin which could be explained by the Eastward decrease of the Mediterranean Sea trophic gradient (Lazzari et al., 2012). The higher rate of inorganic carbon consumption by photosynthesis in the Western basin can lead to the depletion of C_T in the surface waters, whereas the ultra-oligotrophic state in the Eastern basin can lead to a high remineralization rate that consumes oxygen and enriches surface waters with C_T (Moutin and Raimbault, 2002).

The magnitude of the seasonal variability between summer and winter for A_T and C_T is shown in Figure 8. Unlike the seven years averages, the seasonal climatological variations (2005-2012) of A_T have different spatial patterns than those of C_T. Overall the summer-winter time differences for A_T have an increasing Eastward gradient (Figure 8a). The largest magnitudes are marked in the Alboran Sea with differences reaching up to - 80 µmol.kg^{-1}; the negative difference implies that during the winter inflowing surface Atlantic water has higher A_T concentrations than in summer. Higher winter than summer time A_T concentrations are also observed in the Balearic, Ligurian and the South-Western Ionian sub-basins but with a less pronounced seasonality (~ -30 µmol.kg^{-1}). For these three sub-basins, the C_T has a higher summer-winter magnitude than A_T (~ -70 µmol.kg^{-1}). The winter cooling of surface waters increases their density and promotes a mixing with deeper water. Thus, the enrichment in winter time likely reflects the upwelling of deep waters that have accumulated A_T and C_T from the remineralization of organic matter, respiration and the dissolution of $CaCO_3$. The seasonality is more pronounced for C_T, which likely reflects the stronger response of C_T to biological processes than A_T (Takahashi et al., 1993).

In the Algerian sub-basin and along the coasts of Tunisia and Libya, the seasonality is inversed with higher A_T and C_T concentrations prevailing in the summer. The African coast is an area of coastal downwelling during the winter season. However, during summer the coastal upwelling appears in response to turning of the wind near the coast toward the West

(Bakun and Agostini, 2001). In general, the magnitude of the A_T seasonal variability is higher in summer than in winter for the Eastern basin and more particularly in the Ionian and Levantine sub-basins. During this season strong evaporation takes place and induce an increase of A_T concentrations (Schneider et al., 2007). In the Eastern basin, the high evaporation during the summer has a smaller effect on the C_T, and magnitudes reach their maxima in the Levantine sub-basin (~ + 20 µmol.kg^{-1}). During winter time the Western basin and South East of Sicily appear to be dominated by higher C_T concentrations than the rest of the Eastern basin, where the summer C_T concentrations are prevailing (Figure 8b). During winter the high C_T concentrations that coincide with low SST in the Western basin, could result from the deepening of the mixed layer and could be enhanced by the upwelling associated with the Tramontane-Mistral winds that blow from the southern of France and reach the Balearic Islands and the Spanish coast.

Summary

The A_T and C_T algorithms are derived from a compilation of 490 and 426 quality controlled surface measurements respectively, collected between 1999 and 2013 in the Mediterranean Sea. A second order polynomial relating A_T to both S and T yielded a lower RMSE (± 10.4 µmol.kg^{-1}) and a higher r^2 (0.96) than a linear fit deriving A_T from S alone. This confirmed the important contribution of temperature to the A_T variability. Hence, temperature should be included in future algorithms to help better constrain the surface A_T variations. The proposed second order polynomial had a lower RMSE than other studies when we applied their respective algorithms to the same training dataset. In this study we propose an improved and more global relationship to estimate the A_T spatial and temporal variations in the Mediterranean Sea surface waters.

The C_T parameterization is a first attempt to estimate the surface variations in the Mediterranean Sea. A third order polynomial is suggested to fit the C_T to T and S with a RMSE of ± 14.3 µmol.kg^{-1}. The biological contributions to the C_T variations were less pronounced than the physical processes. The contributions of to the physical processes and biology to the C_T variability were 90 and 10 % respectively. In terms of anthropogenic forcing, the C_T rate of increase of 0.99 µmol.kg^{-1}.yr^{-1} was significantly lower than the uncertainty of the measurements than can reach ± 10 µmol.kg^{-1} between different laboratories. Moreover the C_T concentrations were more affected by the seasonal variations than the increase of atmospheric CO_2.

We propose to use Equations (1) and (2) for the estimation of surface A_T and C_T in the Mediterranean Sea when salinity and temperature of the area are available and are in the appropriate ranges of the equations. However in the Eastern marginal seas especially the northern Adriatic and northern Aegean there is a need to develop a more specific equation that minimizes the errors in these areas. Hence, it is important to enrich the existing dataset by an extensive sampling program such as the Med-SHIP initiative (CIESM, 2012) in order to improve the modeling of the carbonate system over the whole Mediterranean Sea.

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Table 1. List of available carbonate system datasets for the Mediterranean Sea

Dataset	Period	Area	Carbonate system parameters	Data points	Reference
Prosope	Sep-Oct 1999	Mediterranean Sea	A_T and pH	20	Bégovic and Copin (2013)
Meteor 51/2	Oct-Nov 2001	Eastern Mediterranean	A_T and C_T	16	Schneider and Roether (2007)
Meteor 84/3	Apr 2004	Southern Mediterranean	A_T, C_T and pH	16	Tanhua et al. (2012)
Carbogib 2-6	2005-2006	Gibraltar Strait	A_T and pH	28	(Huertas, 2007a, b, c, d, e)
Gift 1-3	2005-2006	Gibraltar Strait	A_T and pH	12	(Huertas, 2007f, g, h)
Transmed	Jun 2007	Eastern Mediterranean	A_T and pH	20	Rivaro et al. (2010)
Sesame IT-4	Mar - Apr 2008	Northern Mediterranean	A_T and C_T	16	SeaDataNet
Boum	Jun-Jul 2008	Mediterranean Sea	A_T and C_T	75	Touratier et al. (2012)
Pacific-Celebes	2007-2009	Mediterranean Sea	A_T and C_T	22	Hydes et al. (2012)
Moose-GE	May 2010	Ligurian Sea	A_T and C_T	44	SeaDataNet
Hesperides	May 2013	Gibraltar Strait	A_T	10	Perez et al. (2013)
MedSeA	May 2013	Southern Mediterranean	A_T and C_T	59	Goyet et al. (2015)
Dyfamed time-series	1998-2013	Ligurian Sea	A_T and C_T	152	Oceanological Observatory of Villefranche-sur-Mer

Table 2. Mean difference t-test for the A_T algorithm between the training and validation datasets

	Training dataset	Validation dataset	
RMSE ($\mu mol.kg^{-1}$)	10.60	10.34	Mean difference t-test: H = 0; p = 0.83
Mean residual ($\mu mol.kg^{-1}$)	2.64e-13 ± 10.57	0.91 ± 10.30	Mean difference t-test: H = 0; p = 0.42

Table 3. Performance of the different parameterizations for the estimation of A_T applied independently to the training dataset of this study

Region	**Parameterization**	**RMSE (μmol.kg^{-1})**	**r^2**	**Reference**
Alboran Sea	$A_T = 94.85(S) - 1072.6$	± 16.61	0.92	Copin-Montégut (1993)
Dyfamed site	$A_T = 93.99(S) - 1038.1$	± 16.31	0.92	Copin-Montégut and Bégovic (2002)
Strait of Gibraltar	$A_T = 92.28(S) - 968.7$	± 16.48	0.92	Santana-Casiano et al. (2002)
Mediterranean Sea	$A_T = 73.7(S) - 285.7$	± 26.11	0.68	Schneider et al. (2007)
Dyfamed site	$A_T = 99.26(S) - 1238.4$	± 18.53	0.91	Touratier and Goyet (2009)
Western Mediterranean	$A_T = 95.25(S) - 1089.3$	± 16.97	0.92	Rivaro et al. (2010)
Eastern Mediterranean	$A_T = 80.04(S) - 499.8$	± 14.58	0.91	
Mediterranean Sea	$A_T = 1/(6.57*10^{-5}+1.77\text{-}10^{-2})/S - (5.93 - 10^{-4}(\ln\theta))/\theta^2)$	± 13.81	0.92	Touratier and Goyet (2011)
Global relationship (Sub-tropics)	$A_T = 2305 + 58.66 (S - 35) + 2.32 (S - 35)^2 + 1.41 (T - 20) + 0.04 (T - 20)^2$	± 40.50	0.26	Lee et al. (2006)

Table 4. Mean difference t-test for the C_T algorithm between the training and validation datasets

	Training dataset	Validation dataset	
RMSE ($\mu mol.kg^{-1}$)	14.3	16.2	Mean difference t-test: H = 0; p = 0.04
Mean residual ($\mu mol.kg^{-1}$)	-1.5e-12 ± 14.2	4.5 ± 17	Mean difference t-test: H = 0; p = 0.06

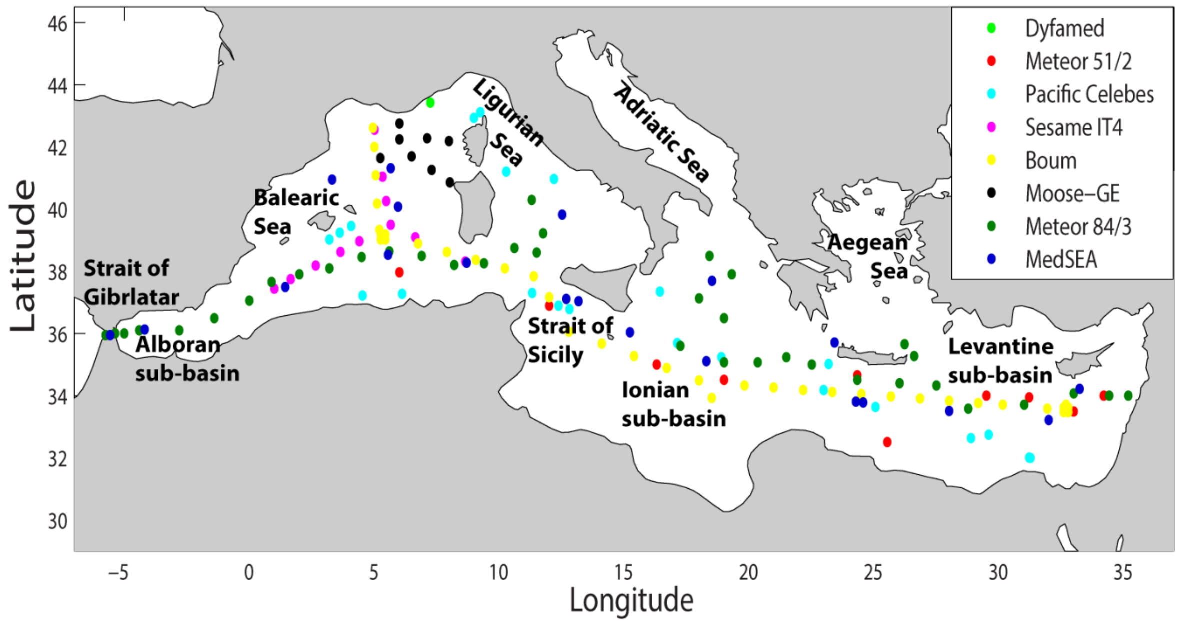

Figure 1. Spatial distribution of data points used to initiate the fits of A_T and C_T

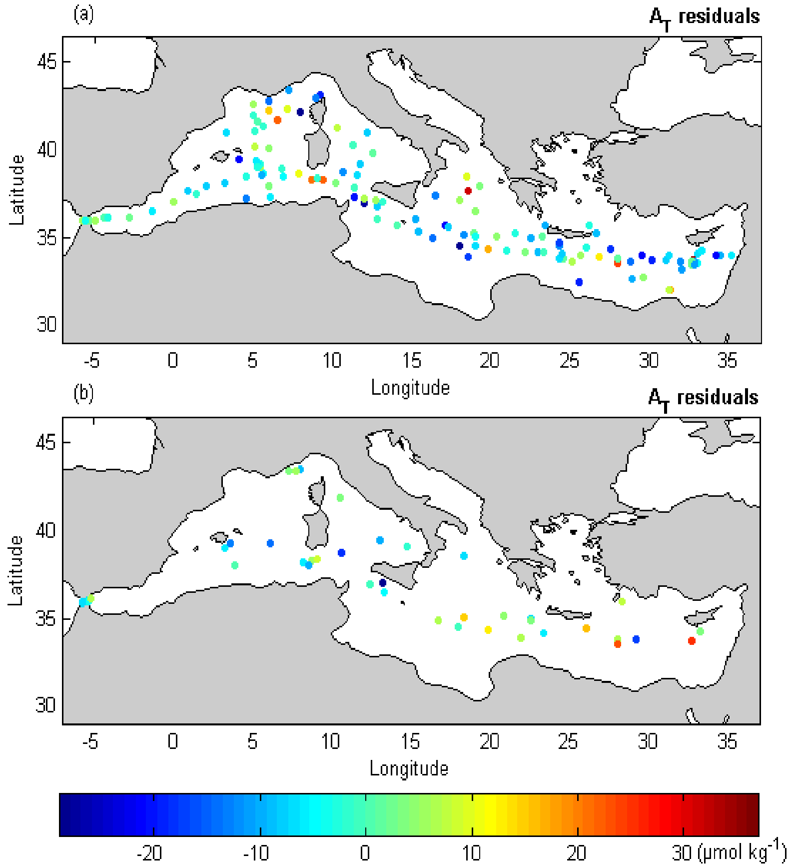

Figure 2. Map of the residuals of the A_T algorithm (Eq 1) applied the (a) training and (b) testing datasets

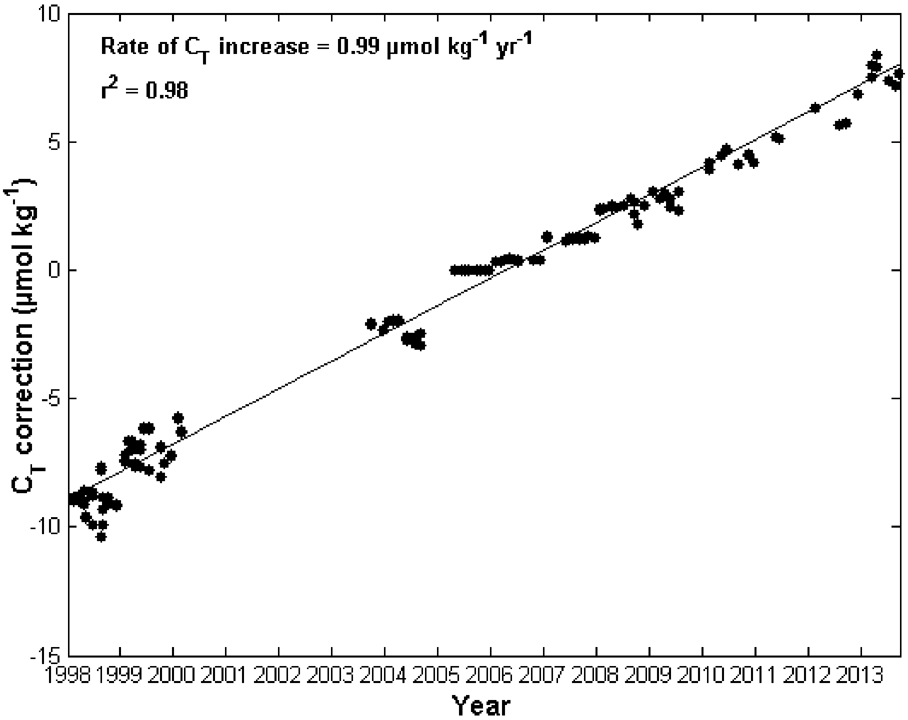

Figure 3. Rate of increase applied to correct the C_T measurements in reference to the year 2005

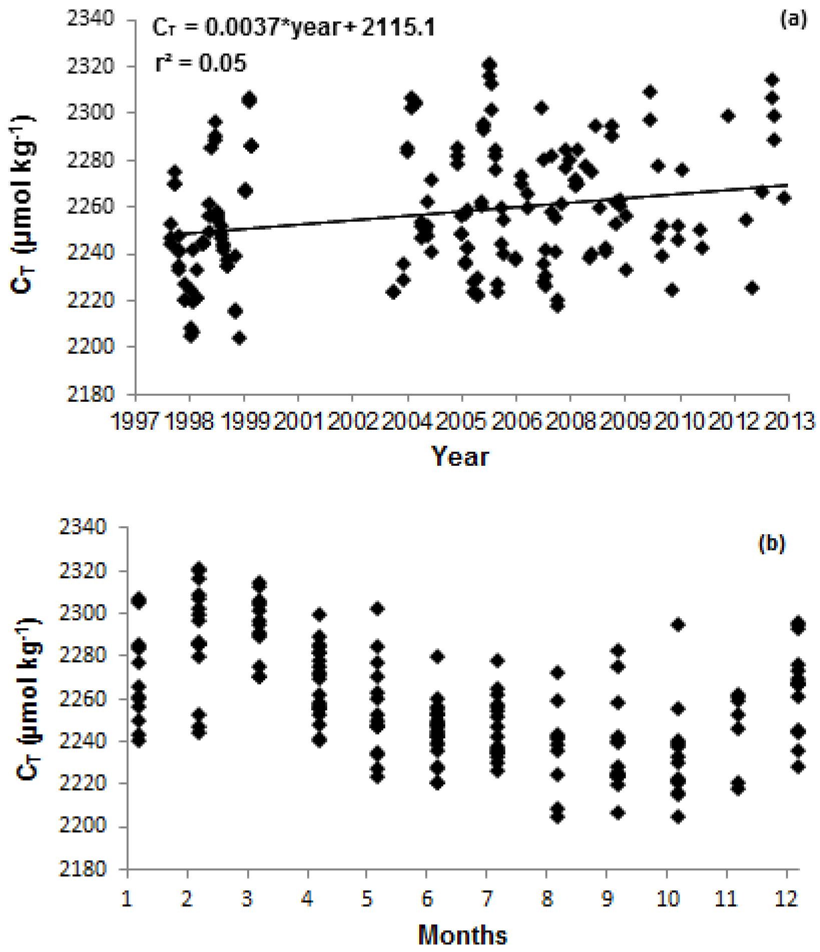

Figure 4. (a) Temporal and (b) seasonal variations of C_T measured at the Dyfamed time-series station between 1998 and 2013

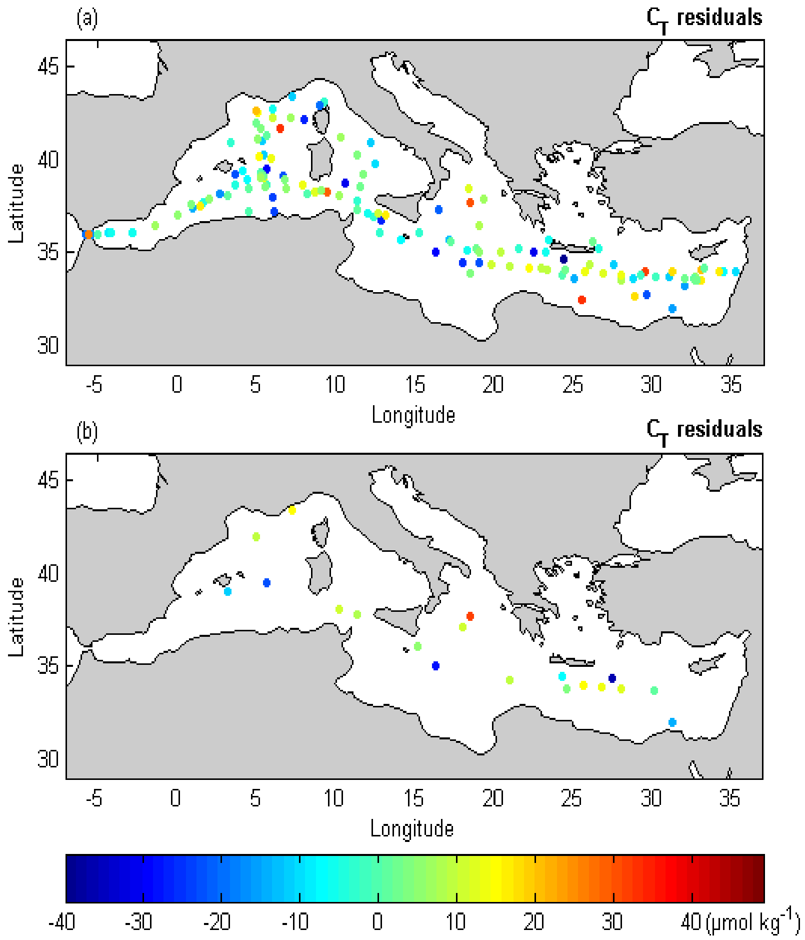

Figure 5. Comparison of the predicted C_T values from the C_T algorithm given in Eq (2) with measurements which are (a) included or (b) excluded when deriving the fit

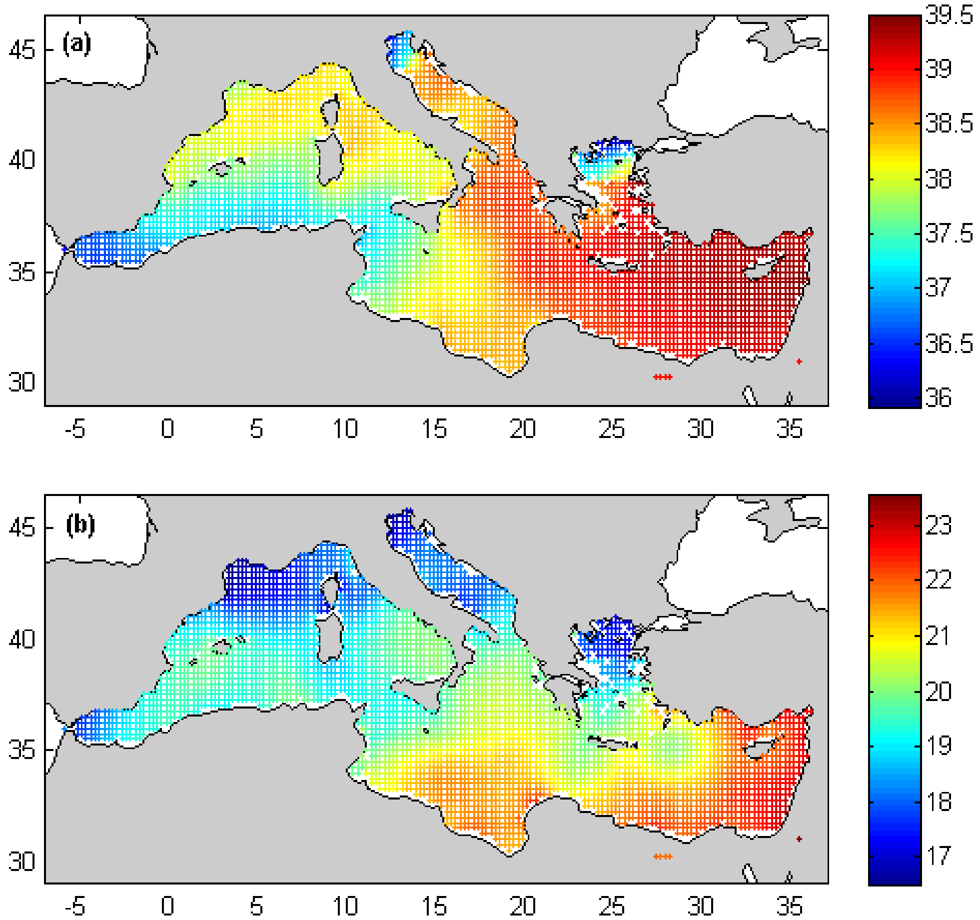

Figure 6. The seven years averages (2005-2012) of (a) SSS and (b) SST climatological fields of the WOA13 (Locarnini et al., 2013; Zweng et al., 2013)

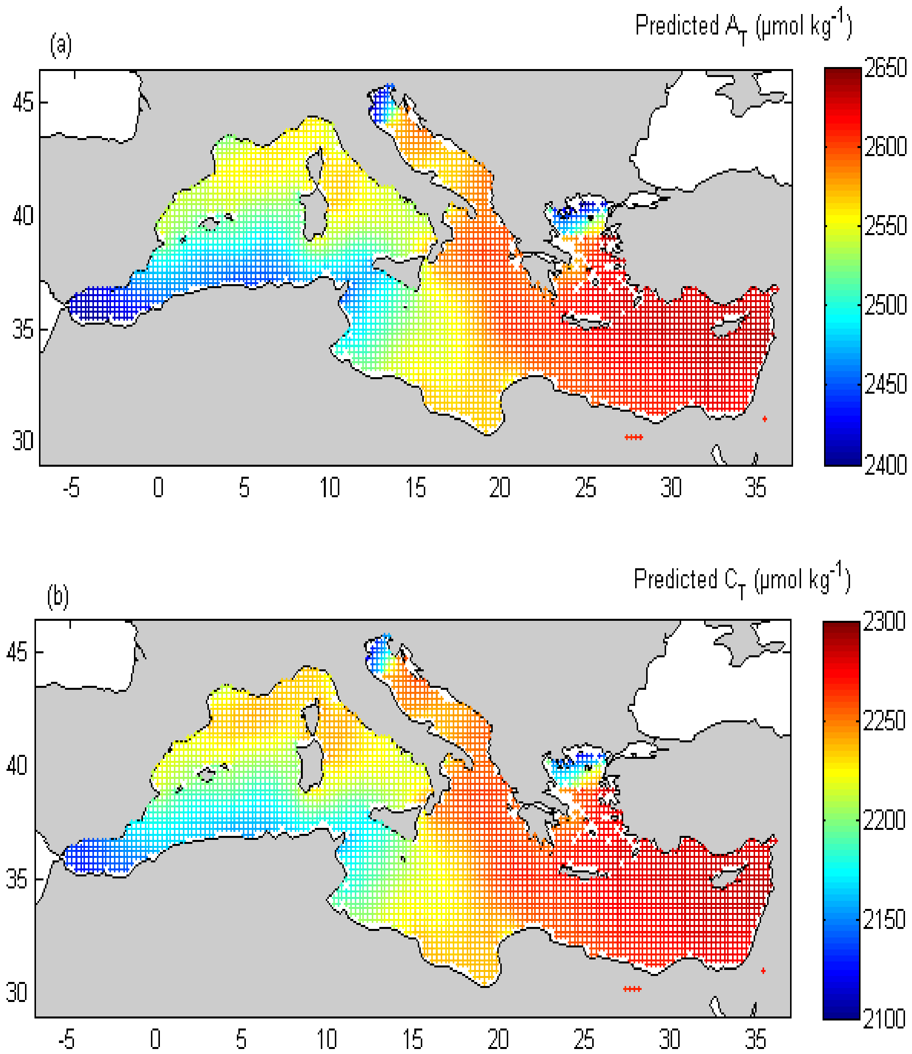

Figure 7. The seven years averages spatial variability of (a) surface A_T predicted from Eq (1) and (b) surface C_T predicted from Eq (2), applied to the 2005-2012 climatological fields of S and T from the WOA13

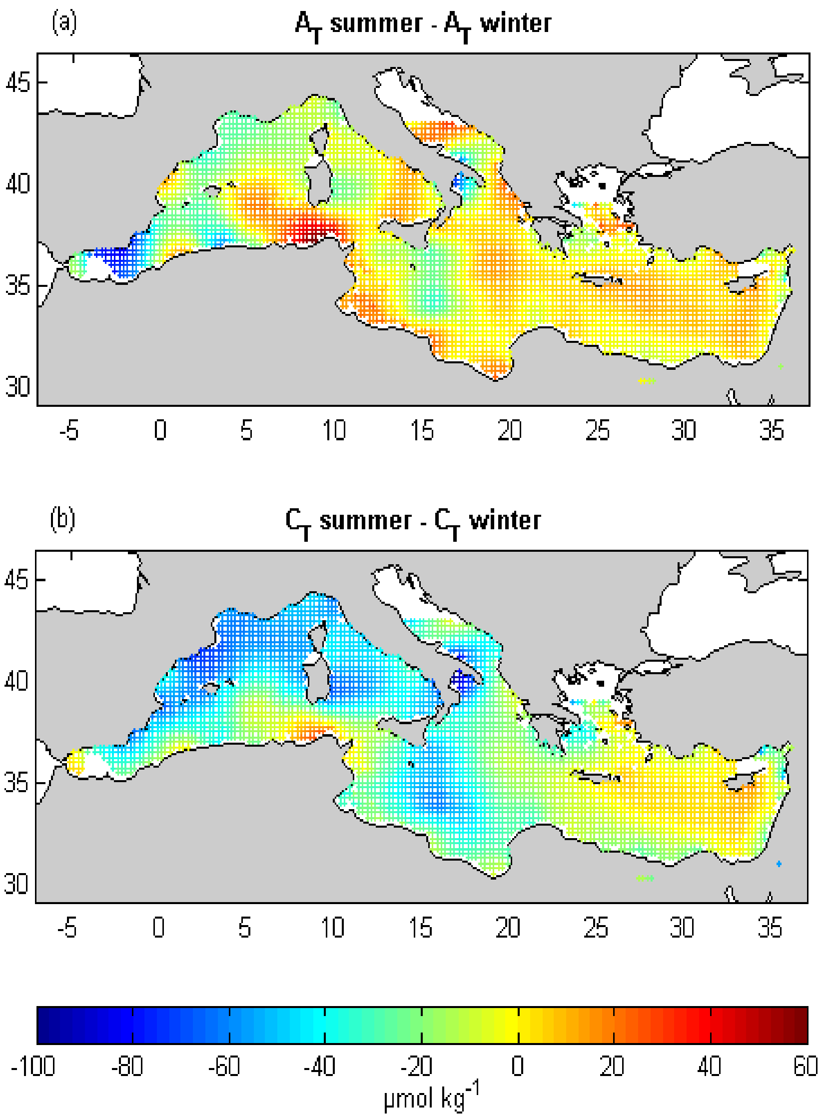

Figure 8. Distribution of the summer-winter differences of (a) surface A_T predicted from Eq (1) and (b) surface C_T predicted from Eq (2), applied to the 2005-2012 climatological fields of S and T from the WOA13