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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 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 showed an improved root mean square error (RMSE) of $\pm 10.6 \mu\text{mol kg}^{-1}$. Furthermore we present the first annual mean C_T parameterization for the Mediterranean Sea surface waters with a RMSE of $\pm 14.3 \mu\text{mol kg}^{-1}$. 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 seven years averages (2005–2012) mapped using the quarter degree climatologies of the World Ocean Atlas 2013 showed that in surface waters A_T and C_T have similar patterns with an increasing eastward gradient. The surface 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, primarily due to the deepening of the mixed layer and upwelling of dense waters. 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.

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1 Introduction

The role of the ocean in mitigating climate change is well known as it absorbs about 2 PgCyr^{-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 repartition 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

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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 fluxes 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 column 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 the C_T variability in 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 sea-water 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. However, the number of the nutrients concentrations was very limited. 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 global relationships of A_T with salinity and temperature. This model validation technique is performed by retaining a single subsample used for testing and training the algorithm on the 9 remaining subsamples. The cross validation process is then repeated 10 times. 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).

To ensure the same spatial and temporal distribution of A_T and C_T polynomial fits we only selected stations where A_T and C_T were simultaneously measured (Table 1; Fig. 1). To validate the general use of the proposed parameterizations we tested the algorithms with measurements which are not included in the fits (Testing dataset). Hence for the A_T , 375 and 115 data points are used for the training and testing datasets re-

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spectively. For the C_T the training dataset is formed from 381 data points and the validation dataset is the same as the testing subset of the 10th fold (45 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 $1/4 \times 1/4^\circ$ 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 .

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 (Table 2, Eq. 1). A linear relationship between A_T and S yields a higher RMSE ($14.5 \mu\text{mol kg}^{-1}$) 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

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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 global relationship to estimate A_T from S and T than the previously presented equations (Table 3). In Eq. (1), T and S contribute to 96 % of the A_T variability and the RMSE of $\pm 10.6 \mu\text{mol kg}^{-1}$ presents a significant improvement of the spatial and temporal estimations of A_T in the Mediterranean Sea surface waters.

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 in surface waters 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 $16.25 \mu\text{mol kg}^{-1}$ 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 (Table 4, Eq. 2). Hence we will retain the large dataset used to develop Eq. (2), where temperature and salinity contribute to 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.

The C_T parameterization developed in this study (Table 4; Eq. 2) showed a higher uncertainty than that of A_T regarding both RMSE and r^2 . In fact, the interpolation of C_T in the mixed layer adds a high uncertainty due to the seasonal variability. Also in surface

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reported values of C_T for the measures that were within a range of $\pm 10 \mu\text{mol kg}^{-1}$ 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 $100 \mu\text{mol kg}^{-1}$ (Fig. 4a). Also there is a clear seasonal cycle of surface waters C_T in the Dyfamed station (Fig. 4b). In the summer, the C_T starts to increase gradually to reach a maximum of $2320 \mu\text{mol kg}^{-1}$ during the winter season, after which a gradual decrease is observed to reach a minimum of $2200 \mu\text{mol kg}^{-1}$ 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 $p\text{CO}_2$ is counteracted by the photosynthetic activity that lowers the C_T . During the winter, the decreasing effect of cooling on $p\text{CO}_2$ 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 in surface waters were more affected by the seasonal variations than by anthropogenic forcing.

Considering the small differences in 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. In regions above 30° latitude such as the Mediterranean Sea, the corrections of C_T are small considering that the outcropping of deep isopycnal surfaces dilutes the anthropogenic CO_2 throughout the water column (Lee et al., 2000). 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 Fig. 5a. Most of the C_T residuals (330 over 381) were within a range of $\pm 18 \mu\text{mol kg}^{-1}$ (1σ). In contrast only few residuals (12 over 381) reached up to

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In this study we propose an improved and 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 $\pm 14.3 \mu\text{mol kg}^{-1}$. 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 $0.99 \mu\text{mol kg}^{-1} \text{yr}^{-1}$ was significantly lower than the uncertainty of the measurements than can reach $\pm 10 \mu\text{mol kg}^{-1}$ 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 Eqs. (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 2. Second order polynomial fit to derive A_T from salinity and temperature in the Mediterranean Sea surface waters.

Polynomial fit	N	r^2	RMSE ($\mu\text{mol kg}^{-1}$)
Eq. (1): $A_T = 2558.4 + 49.83(S - 38.2) - 3.89(T - 18) - 3.12(S - 38.2)^2 - 1.06(T - 18)^2$ $T > 13^\circ\text{C}$ and $36.30 < S < 39.65$	375	0.96	10.6

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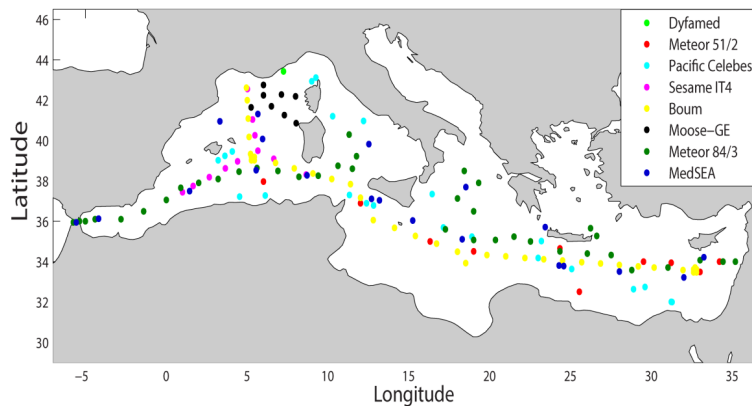


Table 4. Third order polynomial fit to derive C_T from salinity and temperature in the Mediterranean Sea surface waters.

Polynomial fit	N	r^2	RMSE ($\mu\text{mol kg}^{-1}$)
Eq. (2): $C_T = 2234 + 38.15(S - 38.2) - 14.38(T - 17.7) - 4.48(S - 38.2)^2 - 1.43(S - 38.2)(T - 17.7) + 9.62(T - 17.7)^2 - 1.10(S - 38.2)^3 + 3.53(T - 17.7)(S - 38.2)^2 + 1.47(S - 38.2)(T - 17.7)^2 - 4.61(T - 17.7)^3$ $T > 13^\circ\text{C}$ and $36.30 < S < 39.65$	381	0.90	14.3

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

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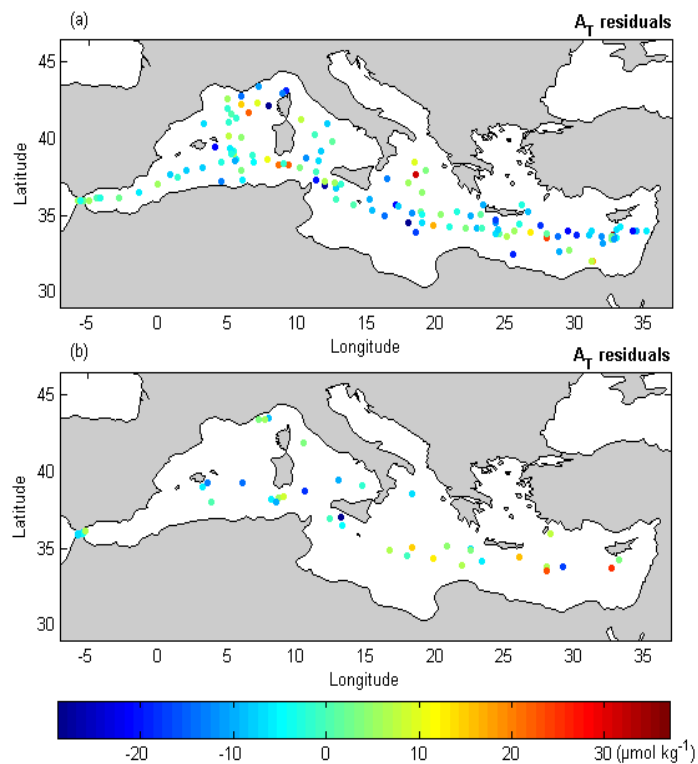


Figure 2. Map of the residuals of the A_T algorithm (Table 1; Eq. 1) applied the (a) training and (b) testing datasets.

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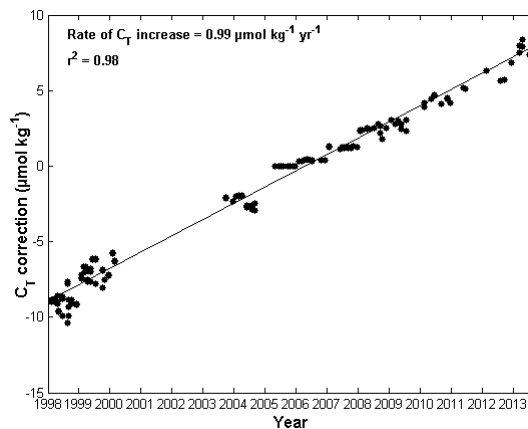


Figure 3. Rate of increase applied to correct the C_T measurements in reference to the year 2005.

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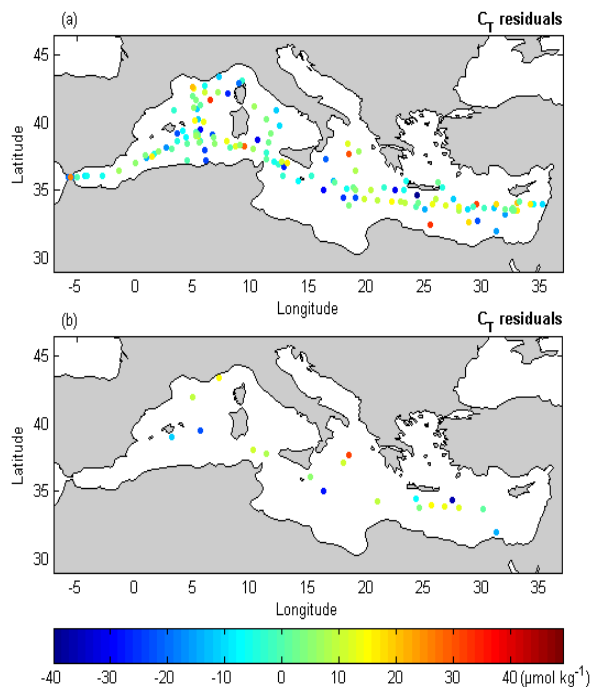


Figure 5. Comparison of the predicted C_T values from the C_T algorithm given in Table 1 – Eq. (2) with measurements which are (a) included or (b) excluded when deriving the fit.

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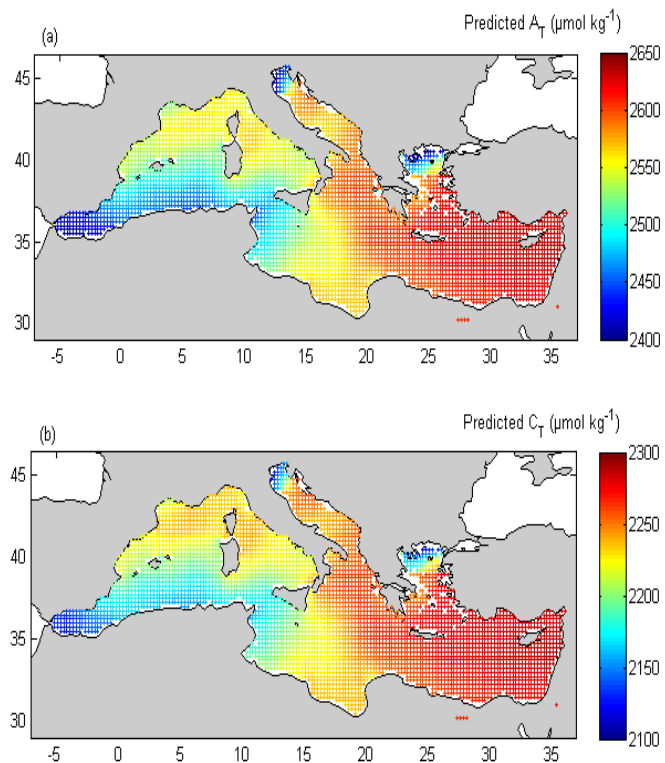


Figure 6. The seven years averages spatial variability of **(a)** surface A_T predicted from Eq. (1) and **(b)** surface C_T predicted from Eq. (2), applied to the 2005–2012 climatological fields of S and T from the WOA13.

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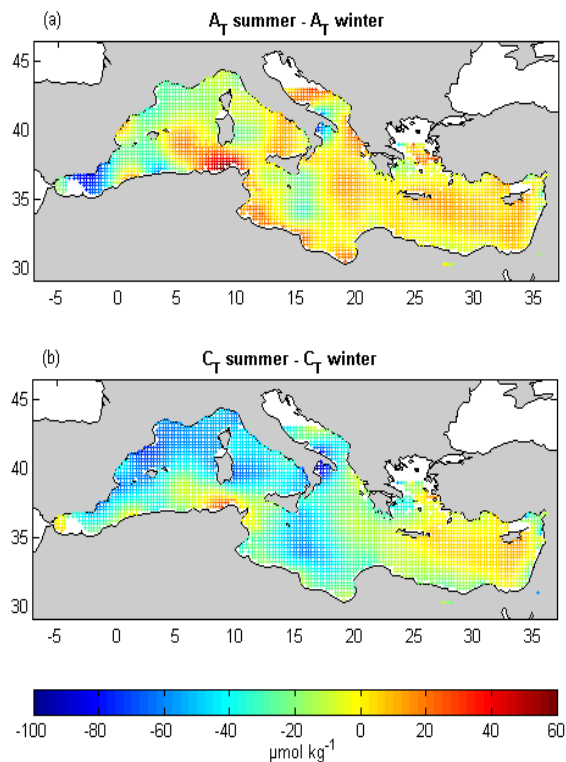


Figure 7. Distribution of the summer-winter differences of **(a)** surface A_T predicted from Eq. (1) and **(b)** surface C_T predicted from Eq. (2), applied to the 2005–2012 climatological fields of S and T from the WOA13.