



HAL
open science

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

Elissar Gemayel, Abed El Rahman Hassoun, Mohamed Benallal, Catherine Goyet, P Rivaro, M Abboud-Abi Saab, E Krasakopoulou, Franck Touratier, P Ziveri

► To cite this version:

Elissar Gemayel, Abed El Rahman Hassoun, Mohamed Benallal, Catherine Goyet, P Rivaro, et al.. Climatological variations of total alkalinity and total inorganic carbon Climatological variations of total alkalinity and total inorganic carbon in the Mediterranean Sea surface waters. *Earth System Dynamics*, 2015, 6, pp.1499-1533. 10.5194/esdd-6-1499-2015 . hal-01229908

HAL Id: hal-01229908

<https://univ-perp.hal.science/hal-01229908v1>

Submitted on 17 Nov 2015

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

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

E. Gemayel^{1,2,3}, A. E. R. Hassoun³, M. A. Benallal^{1,2}, C. Goyet^{1,2}, P. Rivaro⁴, M. Abboud-Abi Saab³, E. Krasakopoulou⁵, F. Touratier^{1,2}, and P. Ziveri^{6,7}

¹Université de Perpignan Via Domitia, IMAGES_ESPACE-DEV, 52 avenue Paul Alduy, 66860 Perpignan CEDEX 9, France

²ESPACE-DEV, UG UA UR UM IRD, Maison de la télédétection, 500 rue Jean-François Breton, 34093 Montpellier CEDEX 5, France

³National Council for Scientific Research, National Center for Marines Sciences, P.O. Box 534, Batroun, Lebanon

⁴University of Genova, Department of Chemistry and Industrial Chemistry, via Dodecaneso 31, 16146 Genova, Italy

⁵University of the Aegean, Department of Marine Sciences, University Hill, 81100 Mytilene, Greece

⁶Universitat Autònoma de Barcelona (UAB), Institute of Environmental Science and Technology (ICTA), Barcelona, Spain

⁷ICREA, Catalan Institution for Research and Advanced Studies, Barcelona, Spain

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Received: 28 June 2015 – Accepted: 4 August 2015 – Published: 24 August 2015

Correspondence to: E. Gemayel (elissargemayel@hotmail.com)

Published by Copernicus Publications on behalf of the European Geosciences Union.

ESDD

6, 1499–1533, 2015

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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.

ESDD

6, 1499–1533, 2015

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

ESDD

6, 1499–1533, 2015

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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-

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



waters 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 30° 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 downloaded 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 $13.9 \mu\text{mol kg}^{-1}$, which is not significantly different from the model trained using measurements without anthropogenic corrections (Eq. (2); $\text{RMSE} = 14.3 \mu\text{mol kg}^{-1}$).

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 $0.99 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ (Fig. 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 $0.99 \mu\text{mol kg}^{-1} \text{ yr}^{-1}$ as well as the RMSE difference of $\pm 0.4 \mu\text{mol kg}^{-1}$ between the two models (with or without anthropogenic corrections) are both smaller than the uncertainty of the C_T measurements of at least $\pm 2 \mu\text{mol kg}^{-1}$ (Millero, 2007). A recent study also showed that the uncertainty of the C_T measurements can be significantly higher than $\pm 2 \mu\text{mol kg}^{-1}$, as most laboratories

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



$\pm 50 \mu\text{mol kg}^{-1}$ (1σ). Applying the C_T algorithm to the testing dataset (Fig. 5b), yields a mean residual of $1.48 \pm 19.80 \mu\text{mol kg}^{-1}$ (1σ) 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 $\pm 20 \mu\text{mol kg}^{-1}$.

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 $\pm 14.3 \mu\text{mol kg}^{-1}$ (1σ) and a $r^2 = 0.90$ (Table 4, 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 to 23.57 °C 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 to 18.43 °C. The estimations of A_T and C_T in surface waters from Eqs. (1) and (2) respectively are only applicable in the appropriate ranges of $T > 13^\circ\text{C}$ 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 Eqs. (1) and (2) respectively (Tables 2 and 4). Excluding few near-shore areas and the influence of cold Atlantic Waters in winter, the ranges in which Eqs. (1) and (2) can be applied are within those of the climatological products of T and S of the WOA13.

The mapped climatologies for 2005–2012 at 5 m depth showed a strong increase in the eastward gradient for both A_T and C_T with the highest concentrations always found in the Eastern Mediterranean (Fig. 6). The minimum values of $2400 \mu\text{mol kg}^{-1}$ for A_T and $2100 \mu\text{mol kg}^{-1}$ for C_T are found near the Strait of Gibraltar and the maximum

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



As a consequence of uptake of atmospheric CO_2 , the eastward $p\text{CO}_2$ increase is parallel to that of C_T (D'Ortenzio et al., 2008). For example the Ionian and Levantine sub-basin are characterized by a $p\text{CO}_2$ as high as $470 \mu\text{atm}$ (Bégovic, 2001), whereas the Algerian sub-basin is characterized by a much lower $p\text{CO}_2$ of $310 \mu\text{atm}$ (Calleja et al., 2013). The high $p\text{CO}_2$ and C_T encountered in the eastern basin make it a permanent source of atmospheric CO_2 (D'Ortenzio et al., 2008; Taillandier et al., 2012). 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 Fig. 7. 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 (Fig. 7a). The largest magnitudes are marked in the Alboran sub-basin with differences reaching up to $-80 \mu\text{mol kg}^{-1}$; 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 ($\sim -30 \mu\text{mol kg}^{-1}$). For these three sub-basins, the C_T has a higher summer-winter magnitude than A_T ($\sim -70 \mu\text{mol kg}^{-1}$). 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).

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 ($\sim +20 \mu\text{mol kg}^{-1}$). 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 (Fig. 7b). 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.

4 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 ($\pm 10.4 \mu\text{mol kg}^{-1}$) 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.

University and Research, the Ministry of Economy and Finance, the Ministry of the Environment and Protection of Natural Resources and the Ministry of Agriculture and Forestry with an Integrated Special Fund for Research (FISR).

- The MedSEA 2013 cruise data were provided by the University of Perpignan Via Domitia: “Institut de Modélisation et d’Analyse en Géo-Environnements et Santé, ESPACE-DEV” (Goyet, C. and Hassoun, A. E. R.). This project was funded by the EC “Mediterranean Sea Acidification in a changing climate” project (MedSeA; grant agreement 265 103).

Authors are also grateful to the National Council for Scientific Research (CNRS) in Lebanon for the PhD thesis scholarship granted to Miss Gemayel Elissar.

References

- Álvarez, M., Sanleón-Bartolomé, H., Tanhua, T., Mintrop, L., Luchetta, A., Cantoni, C., Schroeder, K., and Civitarese, G.: The CO₂ system in the Mediterranean Sea: a basin wide perspective, *Ocean Sci.*, 10, 69–92, doi:10.5194/os-10-69-2014, 2014.
- Bakker, D. C. E., de Baar, H. J. W., and de Jong, E.: The dependence on temperature and salinity of dissolved inorganic carbon in East Atlantic surface waters, *Mar. Chem.*, 65, 263–280, 1999.
- Bakun, A. and Agostini, V. N.: Seasonal patterns of wind-induced upwelling/downwelling in the Mediterranean Sea, *Sci. Mar.*, 65, 243–257, 2001.
- Bates, N. R.: Interannual variability of the oceanic CO₂ sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades, *J Geophys. Res.*, 112, C09013, doi:10.1029/2006jc003759, 2007.
- Bates, N. R., Pequignet, A. C., and Sabine, C. L.: Ocean carbon cycling in the Indian Ocean: 1. Spatiotemporal variability of inorganic carbon and air-sea CO₂ gas exchange, *Global Biogeochem. Cy.*, 20, GB3020, doi:10.1029/2005gb002491, 2006.
- Bégovic, M.: Contribution à l’étude du système des carbonates en Méditerranée, Distribution et variation spatio-temporelle de la pression partielle de CO₂ dans les eaux superficielles du bassin Liguro-Provençal, 2001, Thèse, Université Paris, Paris, 303 pp., 2001.
- Bégovic, M. and Copin-Montégut, C.: Processes controlling annual variations in the partial pressure of CO₂ in surface waters of the central northwestern Mediterranean Sea (Dyfamed site), *Deep-Sea Res. Pt. II*, 49, 2031–2047, 2002.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Bégovic, M. and Copin, C.: Alkalinity and pH measurements on water bottle samples during THALASSA cruise PROSOPE, <http://doi.pangaea.de/10.1594/PANGAEA.805265> (last access: 20 August 2015), 2013.

Bockmon, E. E. and Dickson, A. G.: An inter-laboratory comparison assessing the quality of seawater carbon dioxide measurements, *Mar. Chem.*, 171, 36–43, 2015.

Breiman, L.: Stacked regressions, *Mach. Learn.*, 24, 49–64, 1996.

Calleja, M. L., Duarte, C. M., Álvarez, M., Vaquer-Sunyer, R., Agustí, S., and Herndl, G. J.: Prevalence of strong vertical CO₂ and O₂ variability in the top meters of the ocean, *Global Biogeochem. Cy.*, 27, 941–949, 2013.

Cantoni, C., Luchetta, A., Celio, M., Cozzi, S., Raicich, F., and Catalano, G.: Carbonate system variability in the Gulf of Trieste (North Adriatic Sea), *Estuar. Coast. Shelf S.*, 115, 51–62, 2012.

CIESM: Designing Med-SHIP: a Program for repeated oceanographic surveys, CIESM, Monaco, 164 pp., 2012.

Copin-Montégut, C.: Alkalinity and carbon budgets in the Mediterranean Sea, *Global Biogeochem. Cy.*, 7, 915–925, 1993.

Copin-Montégut, C. and Bégovic, M.: Distributions of carbonate properties and oxygen along the water column (0–2000 m) in the central part of the NW Mediterranean Sea (Dyfamed site): influence of winter vertical mixing on air–sea CO₂ and O₂ exchanges, *Deep-Sea Res. Pt. II*, 49, 2049–2066, 2002.

Cossarini, G., Lazzari, P., and Solidoro, C.: Spatiotemporal variability of alkalinity in the Mediterranean Sea, *Biogeosciences*, 12, 1647–1658, doi:10.5194/bg-12-1647-2015, 2015.

D’Ortenzio, F., Antoine, D., and Marullo, S.: Satellite-driven modeling of the upper ocean mixed layer and air–sea CO₂ flux in the Mediterranean Sea, *Deep-Sea Res. Pt. I*, 55, 405–434, 2008.

Goyet, C. and Davis, D.: Estimation of total CO₂ concentration throughout the water column, *Deep-Sea Res. Pt. I*, 44, 859–877, 1997.

Goyet, C., Hassoun, A. E. R., and Gemayel, E.: Carbonate system during the May 2013 Med-SeA cruise, <http://doi.pangaea.de/10.1594/PANGAEA.841933>, last access: 20 August 2015.

Hassoun, A. E. R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Guglielmi, V., Touratier, F., and Falco, C.: Acidification of the Mediterranean Sea from anthropogenic carbon penetration, *Deep-Sea Res. Pt. I*, 102, 1–15, 2015a.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Hassoun, A. E. R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Ziveri, P., Touratier, F., Guglielmi, V., and Falco, C.: Modeling of the total alkalinity and the total inorganic carbon in the Mediterranean Sea, *J. Water Resour. Ocean Sci.*, 4, 24–32, 2015b, <http://www.ocean-sci.net/4/24/2015/>.

Hood, E. M. and Merlivat, L.: Annual to interannual variations of $f\text{CO}_2$ in the northwestern Mediterranean Sea: results from hourly measurements made by CARIOCA buoys, 1995–1997, *J. Mar. Res.*, 59, 113–131, 2001.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-2, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618899, 2007a.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-3, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618898, 2007b.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-4, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618897, 2007c.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-5, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618896, 2007d.

Huertas, E.: Hydrochemistry measured on water bottle samples during Al Amir Moulay Abdallah cruise CARBOGIB-6, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618895, 2007e.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-1, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618816, 2007f.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-2, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618815, 2007g.

Huertas, E.: Hydrochemistry measured on water bottle samples during Garcia del Cid cruise GIFT-3, Unidad de Tecnología Marina – Consejo Superior de Investigaciones Científicas, doi:10.1594/PANGAEA.618814, 2007h.

Hydes, D., Jiang, Z., Hartman, M. C., Campbell, J. M., Hartman, S. E., Pagnani, M. R., and Kelly-Gerrey, B. A.: Surface DIC and TALK measurements along the M/V Pacific Celebes

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



VOS line during the 2007–2012 cruises, available at: http://cdiac.ornl.gov/ftp/oceans/VOS_Pacific_Celebes_line/, last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.VOS_PC_2007-2012, 2012.

- 5 Ishii, M., Saito, S., Tokieda, T., Kawano, T., Matsumoto, K., and Inoue, H. Y.: Variability of surface layer CO₂ parameters in the western and Central Equatorial Pacific, in: *Global Environmental Change in the Ocean and on Land*, edited by: Shiyomi, M. K. H., Koizumi, H., Tsuda, A., and Awaya, Y., TERRAPUB, Tokyo, 2004.
- Keeling, R. F., Najjar, R. P., Bender, M. L., and Tans, P. P.: What atmospheric oxygen measurements can tell us about the global carbon cycle, *Global Biogeochem. Cy.*, 7, 37–67, 1993.
- 10 Key, R. M., Kozyr, A., Sabine, C. L., Lee, K., Wanninkhof, R., Bullister, J. L., Feely, R. A., Millero, F. J., Mordy, C., and Peng, T. H.: A global ocean carbon climatology: results from global data analysis project (GLODAP), *Global Biogeochem. Cy.*, 18, GB4031, doi:10.1029/2004gb002247, 2004.
- 15 Koeve, W., Duteil, O., Oschlies, A., Kähler, P., and Segschneider, J.: Methods to evaluate CaCO₃ cycle modules in coupled global biogeochemical ocean models, *Geosci. Model Dev.*, 7, 2393–2408, doi:10.5194/gmd-7-2393-2014, 2014.
- Koffi, U., Lefèvre, N., Kouadio, G., and Boutin, J.: Surface CO₂ parameters and air-sea CO₂ flux distribution in the Eastern Equatorial Atlantic Ocean, *J. Marine Syst.*, 82, 135–144, 2010.
- 20 Krasakopoulou, E., Souvermezoglou, E., and Goyet, C.: Anthropogenic CO₂ fluxes in the Otranto Strait (E. Mediterranean) in February 1995, *Deep-Sea Res. Pt. I*, 58, 1103–1114, 2011.
- Lazzari, P., Solidoro, C., Ibello, V., Salon, S., Teruzzi, A., Béranger, K., Colella, S., and Crise, A.: Seasonal and inter-annual variability of plankton chlorophyll and primary production in the Mediterranean Sea: a modelling approach, *Biogeosciences*, 9, 217–233, doi:10.5194/bg-9-217-2012, 2012.
- 25 Lee, K., Wanninkhof, R., Feely, R. A., Millero, F. J., and Peng, T.-H.: Global relationships of total inorganic carbon with temperature and nitrate in surface seawater, *Global Biogeochem. Cy.*, 14, 979–994, 2000.
- 30 Lee, K., Tong, L. T., Millero, F. J., Sabine, C. L., Dickson, A. G., Goyet, C., Park, G.-H., Wanninkhof, R., Feely, R. A., and Key, R. M.: Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophys. Res. Lett.*, 33, L19605, doi:10.1029/2007gl027207, 2006.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Lee, K., Sabine, C. L., Tanhua, T., Kim, T.-W., Feely, R. A., and Kim, H.-C.: Roles of marginal seas in absorbing and storing fossil fuel CO₂, *Energ. Environ. Sci.*, 4, 1133–1146, 2011.
- Locarnini, R. A., Mishonov, A. V., Antonov, J. I., Boyer, T. P., Garcia, H. E., Baranova, O. K., Zweng, M. M., Paver, C. R., Reagan, J. R., Johnson, D. R., Hamilton, M., and Seidov, D.: World Ocean Atlas 2013, Volume 1: Temperature, NOAA Atlas NESDIS 73, Silver Spring, MD, 33 pp., 2013.
- Louanchi, F., Boudjakdji, M., and Nacef, L.: Decadal changes in surface carbon dioxide and related variables in the Mediterranean Sea as inferred from a coupled data-diagnostic model approach, *ICES J. Mar. Sci.*, 66, 1538–1546, 2009.
- Lovato, T. and Vichi, M.: An objective reconstruction of the Mediterranean sea carbonate system, *Deep-Sea Res. Pt. I*, 98, 21–30, 2015.
- Luchetta, A., Cantoni, C., and Catalano, G.: New observations of CO₂ induced acidification in the northern Adriatic Sea over the last quarter century, *Chem. Ecol.*, 26, 1–17, 2010.
- McNeil, B. I., Metzl, N., Key, R. M., Matear, R. J., and Corbiere, A.: An empirical estimate of the Southern Ocean air-sea CO₂ flux, *Global Biogeochem. Cy.*, 21, GB3011, doi:10.1029/2007gb002991, 2007.
- Medar-Group: MEDATLAS 2002, Mediterranean and Black Sea database of temperature, salinity and biochemical parameters, Climatological Atlas, IFREMER, Plouzane, France, 2002.
- Millero, F. J.: The Marine inorganic carbon cycle, *Chem. Rev.*, 107, 308–341, 2007.
- Millero, F. J., Lee, K., and Roche, M.: Distribution of alkalinity in the surface waters of the major oceans, *Mar. Chem.*, 60, 111–130, 1998.
- Moutin, T. and Raimbault, P.: Primary production, carbon export and nutrients availability in western and Eastern Mediterranean Sea in early summer 1996 (MINOS cruise), *J. Mar. Syst.*, 33, 273–288, 2002.
- Omta, A. W., Dutkiewicz, S., and Follows, M. J.: Dependence of the ocean–atmosphere partitioning of carbon on temperature and alkalinity, *Global Biogeochem. Cy.*, 25, GB1003, doi:10.102/2010gb003839, 2011.
- Perez, F. F., Rios, A. F., Pelegri, J. L., de la Paz, M., Alonso, F., Royo, E., Velo, A., Garcia-Ibanez, M., and Padin, X. A.: Carbon Data Obtained During the R/V Hesperides Cruise in the Atlantic Ocean on CLIVAR Repeat Hydrography Section A17, FICARAM XV, (20 March–2 May 2013), available at: http://cdiac.ornl.gov/ftp/oceans/CLIVAR/A17_FICARAM_XV_2013/, last access: 20 August 2015, Carbon Dioxide Information Analysis

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.CLIVAR_FICARAM_XV, 2013.

Poisson, A., Metzl, N., Brunet, C., Schauer, B., Bres, B., Ruiz-Pino, D., and Louanchi, F.: Variability of sources and sinks of CO₂ in the western Indian and southern oceans during the year 1991, *J. Geophys. Res.*, 98, 22759–22778, 1993.

Rivaro, P., Messa, R., Massolo, S., and Frache, R.: Distributions of carbonate properties along the water column in the Mediterranean Sea: spatial and temporal variations, *Mar. Chem.*, 121, 236–245, 2010.

Rödenbeck, C., Keeling, R. F., Bakker, D. C. E., Metzl, N., Olsen, A., Sabine, C., and Heimann, M.: Global surface-ocean pCO₂ and sea–air CO₂ flux variability from an observation-driven ocean mixed-layer scheme, *Ocean Sci.*, 9, 193–216, doi:10.5194/os-9-193-2013, 2013.

Rohling, E. J., Abu-Zied, R. H., Casford, J. S. L., Hayes, A., and Hoogakker, B. A. A.: The marine environment: present and past, in: *The Physical Geography of the Mediterranean*, edited by: Woodward, J. C., Oxford University Press, 2009.

Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T.-H., Kozyr, A., Ono, T., and Rios, A. F.: The oceanic sink for anthropogenic CO₂, *Science*, 305, 367–371, 2004.

Santana-Casiano, J. M., Gonzalez-Davila, M., and Laglera, L. M.: The carbon dioxide system in the Strait of Gibraltar, *Deep-Sea Res. Pt. II*, 49, 4145–4161, 2002.

Sasse, T. P., McNeil, B. I., and Abramowitz, G.: A novel method for diagnosing seasonal to inter-annual surface ocean carbon dynamics from bottle data using neural networks, *Biogeosciences*, 10, 4319–4340, doi:10.5194/bg-10-4319-2013, 2013.

Schneider, A., Wallace, D. W. R., and Körtzinger, A.: Alkalinity of the Mediterranean Sea, *Geophys. Res. Lett.*, 34, L15608, doi:10.1029/2006gl028842, 2007.

Schneider, A., Tanhua, T., Körtzinger, A., and Wallace, D. W. R.: High anthropogenic carbon content in the Eastern Mediterranean, *J. Geophys. Res.*, 115, C12050, doi:10.1029/2010jc006171, 2010.

Schneider, B. and Roether, W.: Meteor 06MT20011018 cruise data from the 2001 cruises, CARINA Data Set, available at: <http://cdiac.ornl.gov/ftp/oceans/CARINA/Meteor/06MT512/>, last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/otg.CARINA_06MT20011018, 2007.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Souvermezoglou, E., Krasakopoulou, E., and Goyet, C.: Total Inorganic Carbon and Total Alkalinity Distribution in the Aegean Sea, CIESM, Venice, Italy, 312 pp., 2010.
- Stone, M.: Cross validatory choice and assessment of statistical predictions, *J. Roy. Stat. Soc. B.*, 36, 111–147, 1974.
- 5 Taillandier, V., D'Ortenzio, F., and Antoine, D.: Carbon fluxes in the mixed layer of the Mediterranean Sea in the 1980s and the 2000s, *Deep-Sea Res. Pt. I*, 65, 73–84, 2012.
- Takahashi, T., Olafsson, J., Goddard, J. G., Chipman, D. W., and Sutherland, S. C.: Seasonal variation of CO₂ and nutrients in the high-latitude surface oceans: a comparative study, *Global Biogeochem. Cy.*, 7, 843–878, 1993.
- 10 Takahashi, T., Sutherland, S. C., Wanninkhof, R., Sweeney, C., Feely, R. A., Chipman, D. W., Hales, B., Friederich, G., Chavez, F., Sabine, C., Watson, A., Bakker, D. C. E., Schuster, U., Metzl, N., Yoshikawa-Inoue, H., Ishii, M., Midorikawa, T., Nojiri, Y., Körtzinger, A., Steinhoff, T., Hoppema, M., Olafsson, J., Arnarson, T. S., Tilbrook, B., Johannessen, T., Olsen, A., Bellerby, R., Wong, C. S., Delille, B., Bates, N. R., and de Baar, H. J. W.: Climatological mean and decadal change in surface ocean pCO₂, and net sea-air CO₂ flux over the global oceans, *Deep-Sea Res. Pt. II*, 56, 554–577, 2009.
- 15 Takahashi, T., Sutherland, S. C., Chipman, D. W., Goddard, J. G., Ho, C., Newberger, T., Sweeney, C., and Munro, D. R.: Climatological distributions of pH, pCO₂, total CO₂, alkalinity, and CaCO₃ saturation in the global surface ocean, and temporal changes at selected locations, *Mar. Chem.*, 164, 95–125, 2014.
- 20 Tanhua, T., Alvarez, M., and Mintrop, L.: Carbon dioxide, hydrographic, and chemical data obtained during the R/V Meteor MT84_3 Mediterranean Sea cruise (5 April–28 April 2011), available at: http://cdiac.ornl.gov/ftp/oceans/CLIVAR/Met_84_3_Med_Sea/, last access: 20 August 2015, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge, Tennessee, doi:10.3334/CDIAC/OTG.CLIVAR_06MT20110405, 2012.
- 25 Touratier, F. and Goyet, C.: Decadal evolution of anthropogenic CO₂ in the northwestern Mediterranean Sea from the mid-1990s to the mid-2000s, *Deep-Sea Res. Pt. I*, 56, 1708–1716, 2009.
- 30 Touratier, F. and Goyet, C.: Impact of the Eastern Mediterranean transient on the distribution of anthropogenic CO₂ and first estimate of acidification for the Mediterranean Sea, *Deep-Sea Res. Pt. I*, 58, 1–15, 2011.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Touratier, F., Guglielmi, V., Goyet, C., Prieur, L., Pujo-Pay, M., Conan, P., and Falco, C.: Distributions of the carbonate system properties, anthropogenic CO₂, and acidification during the 2008 BOUM cruise (Mediterranean Sea), *Biogeosciences Discuss.*, 9, 2709–2753, doi:10.5194/bgd-9-2709-2012, 2012.

5 Wanninkhof, R., Park, G. -H., Takahashi, T., Sweeney, C., Feely, R., Nojiri, Y., Gruber, N., Doney, S. C., McKinley, G. A., Lenton, A., Le Quéré, C., Heinze, C., Schwinger, J., Graven, H., and Khatiwala, S.: Global ocean carbon uptake: magnitude, variability and trends, *Biogeosciences*, 10, 1983–2000, doi:10.5194/bg-10-1983-2013, 2013.

10 Watson, A. and Orr, J.: Carbon dioxide fluxes in the Global Ocean, in: *Ocean Biogeochemistry, Global Change – The IGBP Series (closed)*, edited by: Fasham, M. R., Springer, Berlin, Heidelberg, 2003.

15 Zweng, M. M., Reagan, J. R., Antonov, J. I., Locarnini, R. A., Mishonov, A. V., Boyer, T. P., Garcia, H. E., Baranova, O. K., Johnson, D. R., Seidov, D., and Biddle, M. M.: *World Ocean Atlas 2013, Volume 2: Salinity*, edited by: Levitus, S. and Mishonov, A., Technical Edn., NOAA Atlas Nesdis 74, Silver Spring, MD, 39 pp., 2013.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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

Dataset	Period	Carbonate system parameters	Reference
Prosopé	Sep–Oct 1999	A_T and pH	Bégovic and Copin (2013)
Meteor 51/2	Oct–Nov 2001	A_T and C_T	Schneider and Roether (2007)
Meteor 84/3	Apr 2004	A_T , C_T and pH	Tanhua et al. (2012)
Carbogib 2–6	2005–2006	A_T and pH	Huertas (2007a–e)
Gift 1–3	2005–2006	A_T and pH	Huertas (2007f–h)
Transmed	Jun 2007	A_T and pH	Rivaro et al. (2010)
Sesame IT-4	Mar–Apr 2008	A_T and C_T	SeaDataNet
Boum	Jun–Jul 2008	A_T and C_T	Touratier et al. (2012)
Pacific–Celebes	2007–2009	A_T and C_T	Hydes et al. (2012)
Moose-GE	May 2010	A_T and C_T	SeaDataNet
Hesperides	May 2013	A_T	Perez et al. (2013)
MedSEA	May 2013	A_T and C_T	Goyet et al. (2015)
Dyfamed time-series	1998–2013	A_T and C_T	Oceanological Observatory of Villefranche-sur-Mer

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

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 ($\mu\text{mol kg}^{-1}$)	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	$A_T = 1/(6.57 \times 10^{-5} + 1.77 \times 10^{-2})/S - (5.93 - 10^{-4}(\ln \theta)/\theta^2)$	± 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)

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

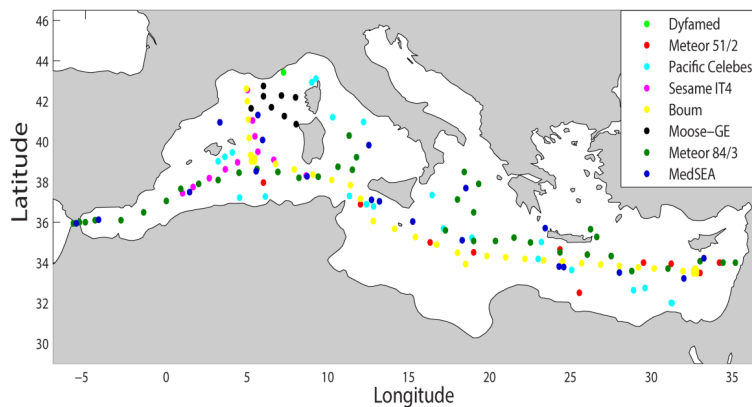


Table 4. Third order polynomial fit to derive C_T from salinity and temperature in the Mediterranean Sea surface waters.

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

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

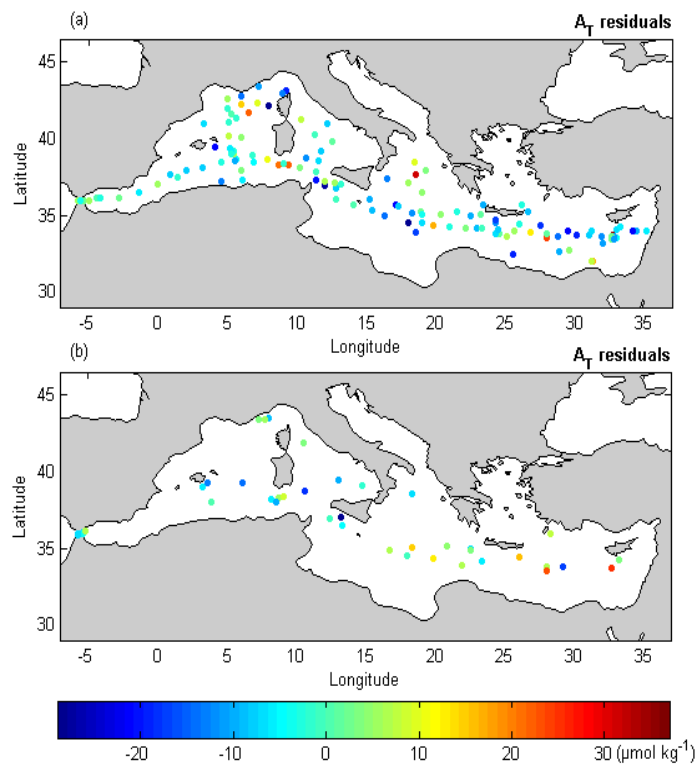


Figure 2. Map of the residuals of the A_T algorithm (Table 1; Eq. 1) applied the (a) training and (b) testing datasets.

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

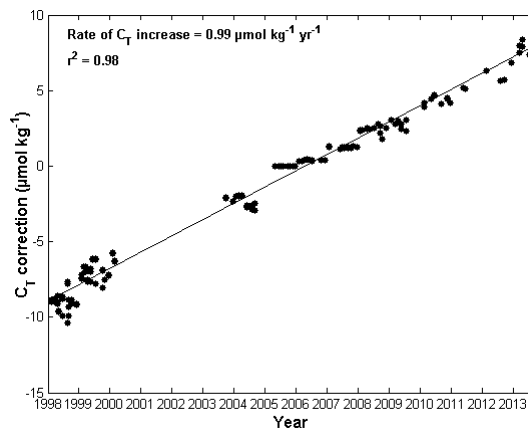


Figure 3. Rate of increase applied to correct the C_T measurements in reference to the year 2005.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

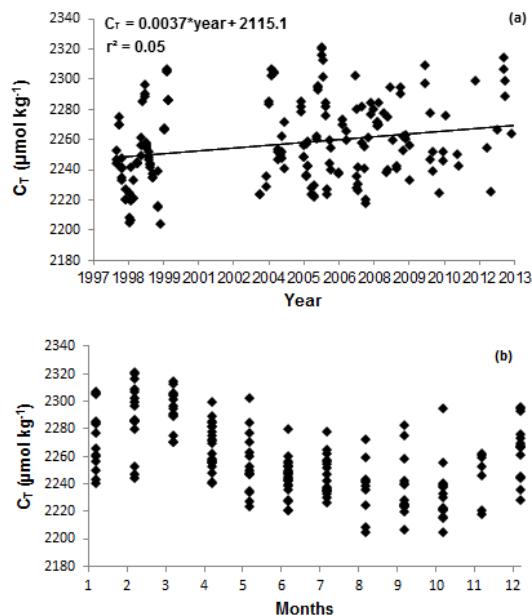


Figure 4. (a) Temporal and (b) seasonal variations of C_T measured at the Dyfamed time-series station between 1998 and 2013.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

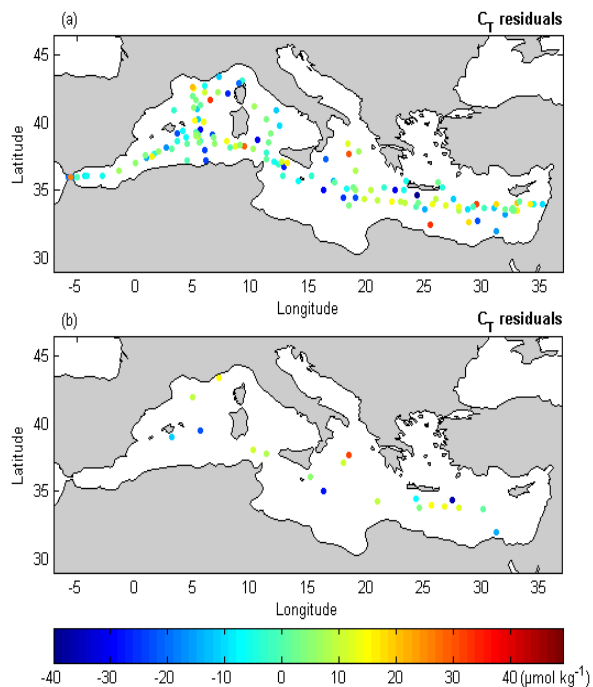


Figure 5. Comparison of the predicted C_T values from the C_T algorithm given in Table 1 – Eq. (2) with measurements which are **(a)** included or **(b)** excluded when deriving the fit.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

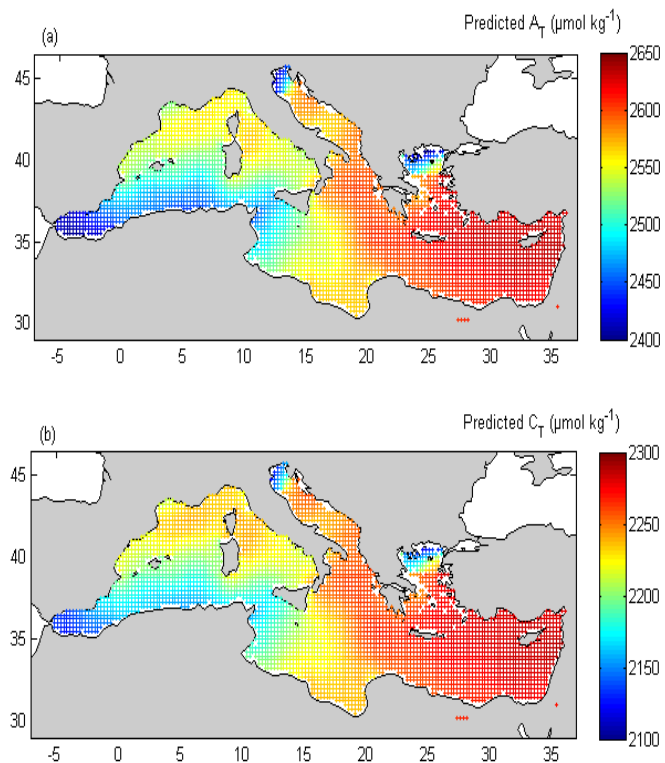


Figure 6. The seven years averages spatial variability of **(a)** surface A_T predicted from Eq. (1) and **(b)** surface C_T predicted from Eq. (2), applied to the 2005–2012 climatological fields of S and T from the WOA13.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Climatological variations of total alkalinity and total inorganic carbon

E. Gemayel et al.

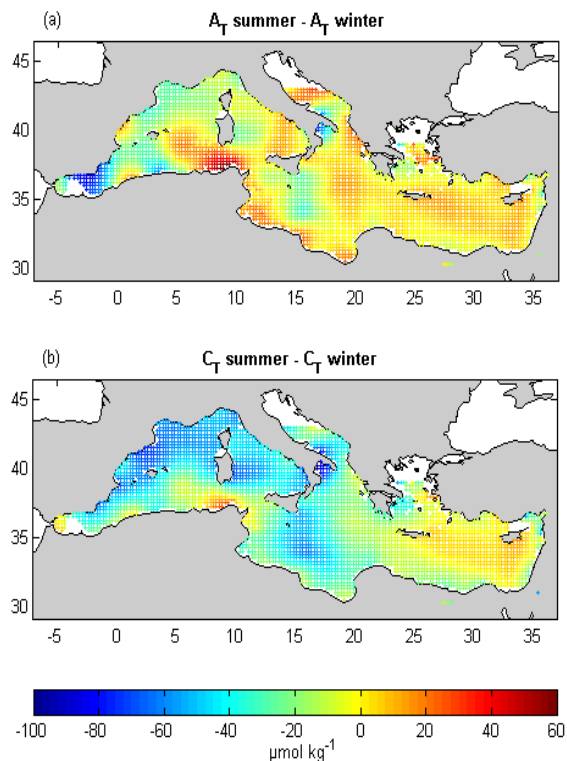


Figure 7. Distribution of the summer-winter differences of (a) surface A_T predicted from Eq. (1) and (b) surface C_T predicted from Eq. (2), applied to the 2005–2012 climatological fields of S and T from the WOA13.