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Climatological variations of total alkalinity and total inorganic carbon Climatological variations of total alkalinity and total 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 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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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).

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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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 $p\text{CO}_2$ 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

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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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$\pm 50 \mu\text{mol kg}^{-1}$ (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

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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).

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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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.

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5 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.

10 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.

20 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.

25 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.

30 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

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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.

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- 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

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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.

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- 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.
- 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.

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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.

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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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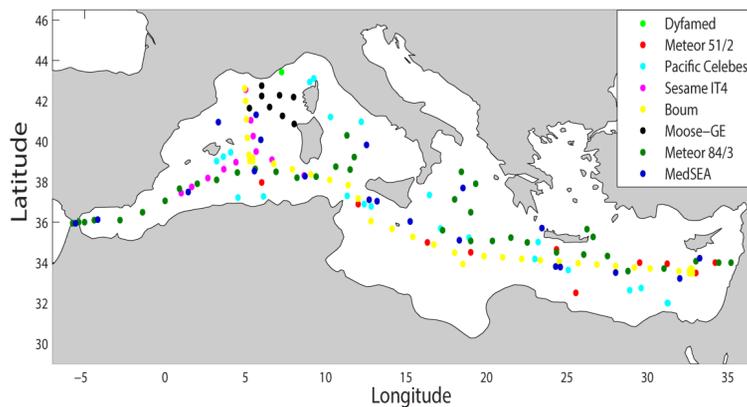


Table 4. Third order polynomial fit to derive C_T from salinity and temperature in the Mediterranean Sea surface waters.

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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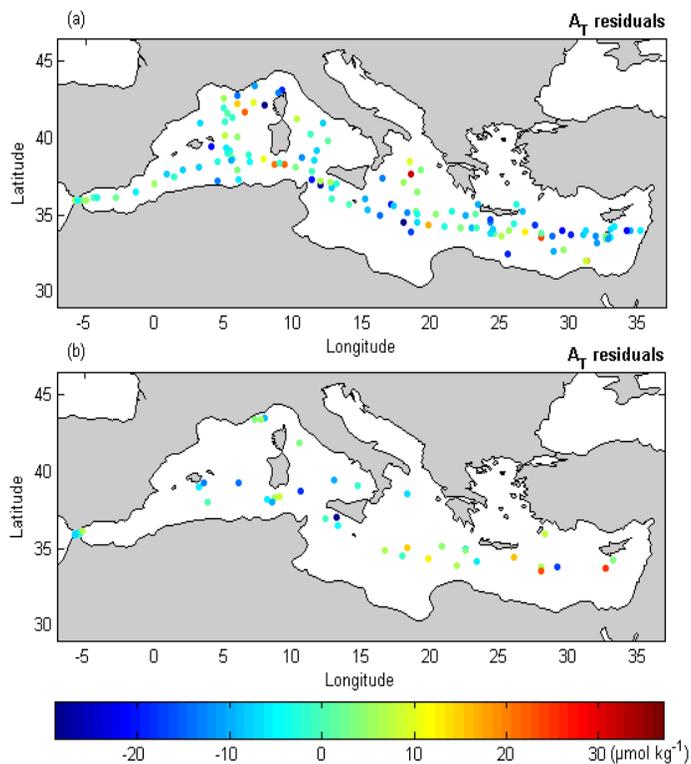


Figure 2. Map of the residuals of the A_T algorithm (Table 1; Eq. 1) applied the (a) training and (b) testing datasets.

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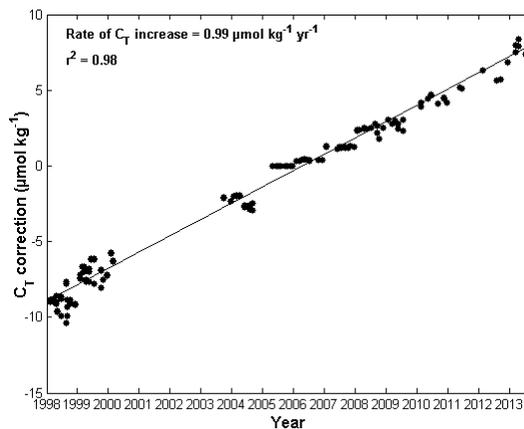


Figure 3. Rate of increase applied to correct the C_T measurements in reference to the year 2005.

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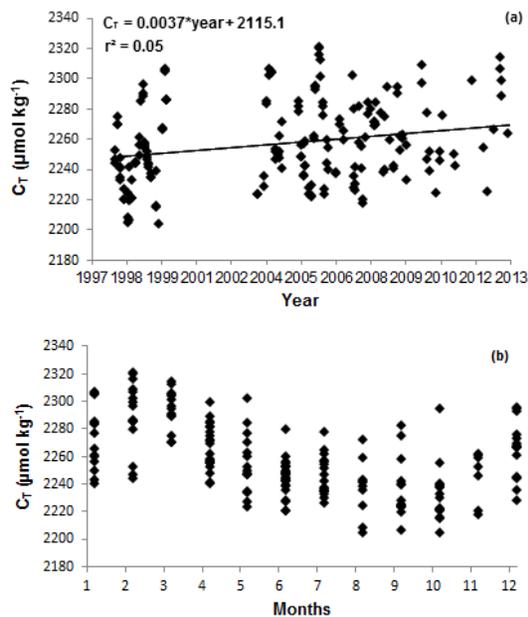


Figure 4. (a) Temporal and (b) seasonal variations of C_T measured at the Dyfamed time-series station between 1998 and 2013.

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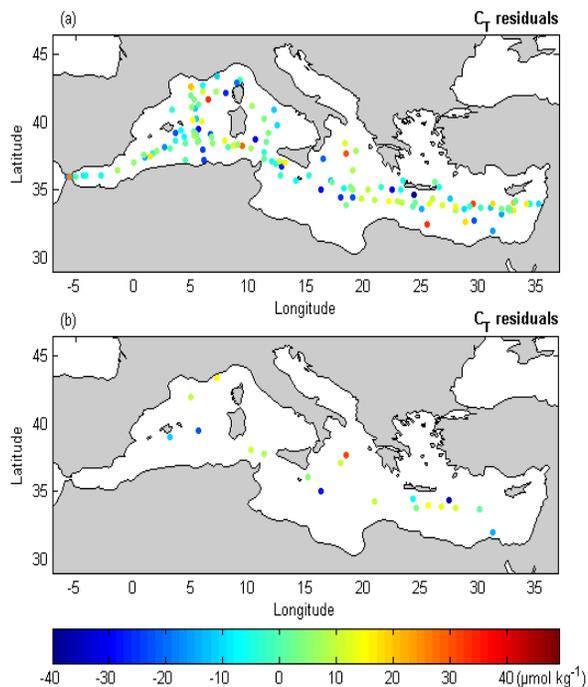


Figure 5. Comparison of the predicted C_T values from the C_T algorithm given in Table 1 – Eq. (2) with measurements which are (a) included or (b) excluded when deriving the fit.

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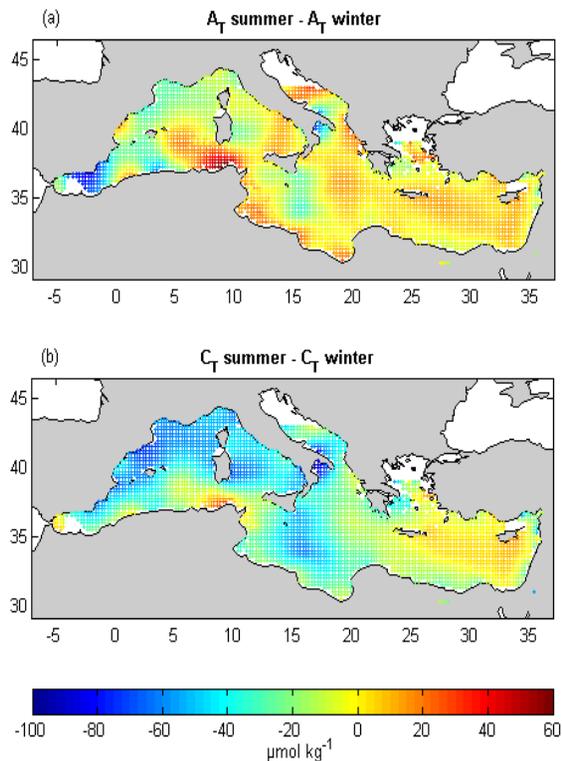


Figure 7. Distribution of the summer-winter differences of (a) surface A_T predicted from Eq. (1) and (b) surface C_T predicted from Eq. (2), applied to the 2005–2012 climatological fields of S and T from the WOA13.

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