Role of deep convection on anthropogenic CO2 sequestration in the Gulf of Lions (northwestern Mediterranean Sea)

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Abstract :

The most active deep convection area in the western Mediterranean Sea is located in the Gulf of Lions. Recent studies in this area provides some insights on the complexity of the physical dynamics of convective regions, but very little is known about their impacts on the biogeochemical properties. The CASCADE (CAscading, Surge, Convection, Advection and Downwelling Events) cruise, planed in winter 2011, give us the opportunity to compare vertical profiles of properties sampled either during stratified conditions or after/during a convection event. In the present study, we focus on the distributions of the carbonate system properties (mainly total alkalinity, A(T); and total dissolved inorganic carbon, C-T) because, in the context of the climate change, deep convection areas are suspected to significantly increase the sequestration of anthropogenic CO2 (C-ANT). Given its limited size, the impact of the Mediterranean Sea on the global carbon budget is probably minor but this marginal sea can be used as a laboratory to better understand carbon sequestration and its transfer to the basin interior by deep convection processes. Distributions of A(T) and C-T, both measured from bottle samples, and that of C-ANT (estimated with the TrOCA approach) are first analyzed in the light of other key properties (salinity, temperature, and dissolved oxygen). An objective interpolation procedure is then applied to estimate C-T and A(T) from CTD measured properties. With this procedure, the vertical resolution goes from a maximum of 32 samples per station to one property estimate every meter (more detailed distributions are obtained). Results provide arguments to conclude that C-ANT is rapidly transferred to the deepest layer due to deep convection events. During deep convection events, the increase of C-ANT in the water column is positively correlated to that of potential density and oxygen content. The challenge of quantifying the amount of sequestered carbon is however not resolved due to the complexity and the highly dynamical nature of the convective regions. Deep convection in the Gulf of Lions, in parallel with cascading along the continental slope, could thus potentially explain the very high levels of both C-ANT and acidification estimated in the deep layers of the western Mediterranean Sea.

Introduction

CO₂ sequestration capacity of the Mediterranean Sea is still poorly quantified. Up to the end of the 90's, the DYFAMED time-series station (northwestern Mediterranean Sea) represented the sole valuable database by providing very accurate profiles of key properties on a monthly basis (the carbonate system properties were among the core parameters; Copin-Montégut and Begovic 2002; Begovic and Copin-Montégut 2002; Touratier and Goyet 2009). However, the response of the Mediterranean Sea to anthropogenic perturbations cannot be fully understood using data from a single geographical location. The Mediterranean Sea was simply out of the scope of most world ocean programs like WOCE (World Ocean Circulation Experiment; http://www.nodc.noaa.gov/woce/wdiu/) or EPOCA (European Project on OCean Acidification; http://www.epoca-project.eu/). The issue of atmospheric CO₂ accumulation and its consequences (global warming, mitigation effect induced by the CO_2 sequestration in the ocean, and seawater acidification) stimulated the emergence of new research programs, some of them being specifically developed to understand the role played by coastal areas and marginal seas like the Mediterranean Sea (i.e. very important places for the local economy, the ecology, and the population health). Since the multidisciplinary German METEOR 51 cruise (2001), that crossed the whole Mediterranean Sea from West to East, several European and national programs [e.g. PROSOPE (productivity of oceanic pelagic systems), SESAME

(southern European seas: assessing and modelling ecosystems), MedSEa (mediterranean sea acidification in a changing climate), MERMEX (marine ecosystems response in the Mediterranean experiment), MOOSE (mediterranean ocean observing system on environment), BOUSOLE (buoy for the acquisition of the long term time series), BOUM (biogeochemistry from the oligotrophic to the ultra-oligotrophic Mediterranean)] have both significantly increased the amount of high quality carbonate system data, and our global understanding on the Mediterranean carbon chemistry. At least two of the four properties that describe the carbonate system (total dissolved inorganic carbon, C_T; total alkalinity, A_T; CO₂ partial pressure, pCO₂; and pH) were usually measured from seawater samples in order to draw their distributions in the Western and the Eastern basins (e.g. Schneider et al. 2007; Rivaro et al. 2010). Several authors have then estimated the distribution of anthropogenic CO₂ (C_{ANT}) using various approaches (Touratier and Goyet, 2009; Schneider et al., 2010; Touratier and Goyet, 2011), from which it was possible to estimate the level of acidification since the preindustrial era (Touratier and Goyet 2011; Touratier et al., 2012). According to these authors, pH decrease ranges from 0.06 to 0.14 pH unit (whatever the depth or the location) which clearly supports one of the recommendations of CIESM (2008) that the Mediterranean Sea acidification issue clearly becomes a priority.

A large proportion of the CO₂ sequestration in the ocean is clearly linked to its capacity to form new dense waters that sink to depths. Particular conditions of wind and temperature in the atmosphere must prevail during adequate period of time in order to significantly increase the evaporation and the cooling of the surface seawater (both processes increase the density). For the western Mediterranean Sea, several papers (e.g. Durrieu de Madron et al. 2005, Canals et al. 2006) have pointed out the importance and the complexity of the dense water formation processes in the Gulf of Lions. Dense water may be formed either offshore (deep convection process) or on the continental shelf before they cascade down along the continental slope. The canyon of Cap de Creus (see Fig. 1) is an important place where export of dense water occurs by cascading, a process enhanced by the East and Southeast storms, and the hydrology of the continental shelf waters which is influenced by the freshwater inputs in the region (main rivers are the Tech, the Têt, the Rhone, the Agly, the Orb, the Aude, and the Herault).

The first experiment [MEDOC Group, 1970], which pioneers the study of open-ocean convection in the Gulf of Lions, identified three different phases. During the 'pre-conditioning' phase, the mean cyclonic circulation of the northwestern Mediterranean Sea

and topographic effects (Hogg 1973; Madec et al., 1996) produce a dome of density (centered around 42°N, 5°E) which exposes for a longer period of time (Madec et al., 1991) an important volume of seawater, poorly stratified, to the atmospheric forcing. In winter, this dome of density is reinforced (uplift of isopycnals) due to the prevailing north and northwestern winds (the Mistral and the Tramontane are both dry and cold winds). During the second phase called 'vertical mixing', the stability of the water column in these preconditioned areas is further lowered by efficient evaporation and cooling. During this phase, regions of convection that might occupy the whole water column (up to 2500 m) appear and in which the vertical speed may reach 10 cm.s⁻¹ (Schott and Leaman, 1991). The third phase corresponds to a period of re-stratification and 'spreading' of the new dense water, with about half of the newly-formed deep waters incorporated into the northern current and the other half transported throughout the whole western Mediterranean Sea in the core of long-lived eddies (>1year) (Send et al., 1996; Testor and Gascard, 2003, 2006; Damien, 2015).

The impact of such meso-scale physical processes on the CO_2 sequestration is very difficult to evaluate since specific measurements must be done at the right place and during the right period of time. Results of the French BOUM 2008 cruise (Touratier et al., 2012) already pointed out the potentially important role played by the Algero-Provencal gyre (western Mediterranean Sea) in the CO_2 sequestration. However, the low spatial resolution of samples during the BOUM cruise prevented to visualize the impacts of the gyre on the distribution of the carbonate system properties.

The new measurements available for the Gulf of Lions from the CASCADE cruise are used in the present study to reach several objectives. The distributions of the main carbonate system properties (C_T and A_T) will be first drawn using bottle data and then interpreted in the light of the physical properties distributions. In order to increase the spatial resolution of the previous distributions, our second objective is to develop interpolation procedures to calculate C_T and A_T from the high frequency CTD measurements available for S, θ , and O₂. Using the TrOCA approach developed by Touratier et al. (2007), our third objective is to estimate the distribution of anthropogenic (C_{ANT}) and the resulting levels of acidification reached at the time of the CASCADE cruise since the preindustrial era. Finally, using all previous results, our final objective is to assess and to quantify the impact of deep convection observed in the Gulf of Lions on the sequestration of carbon.

1. Study area and sampling of CO₂ properties

The CASCADE cruise occurred from 1 to 23 March 2011, on board the R/V L'Atalante. This oceanographic campaign was supported by the European HERMIONE (Hotspot Ecosystem Research and Man's Impact on European Seas) project and by the French MERMEX (Marine Ecosystems in the Mediterranean Experiments) research program. This cruise aimed to determine the characteristics of deep convection on the formation of deep waters in the Gulf of Lions, and to analyze their impacts on the hydrology, the hydrodynamics, and the biogeochemistry (see the paper of Severin et al. 2014 for these aspects) of shelf and open-sea water. The Gulf of Lions and its continental shelf area are covered by a network of stations which is organized according to 7 sections (see Fig. 1). Section L (stations CL01 to CL012; 4-7th March) and section M (stations CM01 to CM12; 7-11th March) are open-sea transects while sections A (20th March), B (19th March), C(18th March), D(17th March), and E (14th March) are continental shelf transects. Sections L and M crosses at a specific station called CS2400 (42.03°N, 4.69°E), which is located close to the Lion long-term mooring (from 150 m to the bottom) installed since 2007 in the center of the Gulf of Lions deep convection area. During the CASCADE cruise, station CS2400 were thus visited several times since periods of time for sections L and M are different. Due to the low number of C_T and A_T measurements available on the shelf, sections A to E are not considered in the present study.

For this paper, we use the following properties: potential temperature (θ ; °C), salinity (S), dissolved oxygen (O₂; µmol.kg⁻¹), total alkalinity (A_T; µmol.kg⁻¹), and total dissolved inorganic carbon (C_T; µmol.kg⁻¹). A total of 179 profiles for θ , S (conductivity) were obtained using a Sea-Bird Electronics 911 PLUS CTD (Conductivity Temperature Depth) system (see details of measurements in the CASCADE cruise Technical Report; Durrieu de Madron 2011). A carousel of 24 Niskin bottles was used to collect seawater samples to perform the analysis of the other chemical and biological properties.

Seawater was collected in 125 cm³ borosilicate glass bottles for dissolved O₂ measurements. Samples were fixed immediately according to the Winkler methodology (Winkler 1988, Dickson 1996). Dissolved O₂ concentration was measured using an automated high-precision Winkler titration system linked to a photometric end-point detector (Williams and Jenkinson, 1982). Dissolved O₂ concentrations were also determined using an automated sensor (SBE43 Seabird®) mounted on the CTD. The sensor was calibrated using discrete sampling following

the procedure described in their specific application note of the manufacturer (http://www.seabird.com/application_notes/AN64-2.htm).

For A_T and C_T measurements, seawater samples were collected into washed 500 ml borosilicate glass bottles, and poisoned with a saturated solution of HgCl₂. At the end of the cruise, the samples were sent to the SNAPO (Service National d'Analyse des Paramètres Océaniques du CO₂; http://soon.ipsl.jussieu.fr/SNAPOCO2/) for analysis. The measurements of A_T and C_T were performed by potentiometric titration using a closed cell, as described in details in the handbook of methods for the analysis of the various parameters of the CO₂ system in seawater (DOE, 1994). The precisions obtained for these measurements are 2.7 µmol.kg⁻¹ and 2.2 µmol.kg⁻¹ for A_T and C_T , respectively.

2. Distributions of physical and chemical properties

The physical conditions prevailing during the CASCADE cruise are described using the distributions of θ , S, and σ_{θ} (potential density) obtained along the two sections L and M (Figs. 2 and 3, respectively).

These distributions cannot be fully understood by considering only the physics that occurred during the CASCADE cruise. These also result from the physics prevailing during the previous autumn and winter. Time-series data from the Lion mooring line (42.04°N, 4.68°E; 2350 m), which is located next to the crossroads of the two sections L and M (station CS2400), will help to appreciate the temporal evolution of the water column. This line, which span from 150 m deep to the bottom at 2350 m, provided temperature at 21 levels using temperature recorders (RBR TR-1050) and conductivity-temperature-depth recorders (SeaBird 39 SMP CTD) (Durrieu de Madron et al., 2013; Houpert 2013). A nearby Meteo-France weather buoy LION (5 miles north of the mooring line) provided temperature data from the upper layer (2-200 m) at 10 levels using temperature recorders (NKE SP2T). Dailyaveraged data from both the buoy and the mooring line were used to calculate the mixed layer depth (MLD). Because of the different accuracy of the different sensors and the variable depths of deep instruments, a double criterion able to estimate the mixed layer depth on the vertical profiles needed to be adopted. The MLD was first estimated a temperature difference $< 0.1^{\circ}$ C with respect to the uppermost sensor at 10 m depth (Houpert et al., 2015). When the MLD was at depths greater than 300 m, the estimation was based on the mooring line sensors

and considered a temperature difference of 0.01°C with respect to the temperature at 310 m depth corresponding to the depth of the first SBE37 CTD of the deep LION mooring located below the weather buoy oceanographic sensors (Houpert 2013). The ERA-Interim atmospheric forcing and the water column temperature from the LION mooring line and the buoy oceanographic line (Fig. 4) showed a typical seasonal cycle with (i) strong heat loss events and a deepening of the mixed layer depth between November 2010 and late January 2011 with the progressive mixing of surface Atlantic Water (AW) / Western Intermediate Water (WIW; a mode water formed in winter in the Western Mediterranean) and warmer and saltier Levantine Intermediate water (LIW), (ii) a sustained heat loss period and an homogenization of the entire water column from late-January to early-February 2011, and (iii) declining heat losses and even heat gains leading to a re-stratification interrupted by a short episode of heat loss and mixing down to 1500 m deep in early March 2011. Thus, it is worth noting that the main event of bottom-reaching convection occurred about one month before the CASCADE cruise in March 2011. The period of the cruise was characterized by a secondary mixing episode during the first days (2-5 March 2011), yielding an homogeneous layer of 1500 m depth, and subsequently a long-lasting re-stratification associated with the reappearance of AW and LIW in the upper 800 m of the water column.

Section L (4-7th March) is characterized by a convective region between stations CL02 and CL08 (in the present study, stations that belong to the convective are those for which the σ_{θ} value within the surface layer is > 29.09). The distance of this region along section L is approximately 100 km (Fig. 2). All properties (θ , S, σ_{θ} distributions shown in Figs. 2A-C) within the convective region are clearly homogenized from surface to ~1500 m. Typical values for these properties within the convective region are $\theta = 12.92$ °C, S=38.48, and $\sigma_{\theta} =$ 29.1. This trend is also clearly visible from the O_2 distribution (Fig. 2D) with a typical value close to $\sim 200 \,\mu\text{mol.kg}^{-1}$. Both the western and the eastern portion of section L (station CL01) and stations CL09 to CL12, respectively) are characterized by stratified conditions with the presence, from surface to bottom, of three water masses: AW/WIW are found in the first 100-200 meters, LIW is usually found in the depth range 100-700 m, and the Western Mediterranean Deep Water (WMDW) is found below LIW and up to the bottom. The positions of these water masses on the θ /S diagram of the CASCADE cruise are approximately reported on Fig. 5A: AW/WIW is characterized by an extreme variability of both S and θ due to interactions with the atmosphere (heat loss or gain, water precipitation or evaporation, etc.) and with the continent (coastal waters); waters characterized by the highest

temperature and salinity clearly belong to LIW while those with $\theta = ~12.9^{\circ}$ C and S = ~38.47 are part of the WMDW (σ_{θ} is maximal for this water mass). All stations from section M (7-11th March) are representative of stratified conditions (Fig. 3). LIW can be easily identified at almost all stations between 100 and 500m.

Horizontal velocity records combined to salinity and temperature data from the Lion mooring line indicated that horizontal advection play an important role in the re-stratification of AW and LIW after a convection event (Houpert, 2013). This highly dynamic system helps to understand why stratification may re-appear so quickly (less than one week) after the end of a convection period. Results from the Lion mooring line (Fig. 4) during the period of section L (4-7th March) also suggest that stratification observed at stations CL9 to CL12 probably resulted from a rapid (few days) invasion of AW and LIW from outside the convective area. This points out that despite short periods of time to get data from sections L and M (~4 days each), Figs. 2 and 3 do not provide instantaneous picture for the property distributions.

The distribution of O₂, C_T, and A_T concentrations determined from seawater samples (Niskin bottles) are drawn for sections L and M in Figs. 6 and 7, respectively. These bottle data were used to calibrate the O₂ CTD sensors which provide a much higher vertical resolution (every meter for all stations). When comparing the O₂ CTD distributions (Figs. 2D and 3D) to those obtained from seawater samples (Figs. 6A and 7A), the gain of information is very significant (the additional O_2 minima and maxima which appears on the distributions are all coherent with the θ , S, and σ_{θ} corresponding distributions). The convective region in section L is characterized by O₂ concentrations in the range 195-205 µmol.kg⁻¹. Since water from the convective region results from the mixing of several water masses usually found during stratified conditions, the range for O₂ concentration is intermediate between those determined for AW/WIW (> 210 μmol.kg⁻¹), WMDW (180-190 μmol.kg⁻¹), and LIW (< 180 μmol.kg⁻¹). The O₂ minimum associated to the presence of LIW is a known characteristics for the whole Mediterranean Sea (Kress et al. 2003; Klein et al. 2003). The O₂ maxima found in AW/WIW result from the exchange with the atmosphere while the intermediate O₂ level found in the bottom WMDW points out that deep waters get fresh O₂ supplies during winter convection events.

Previous studies describing the distribution of the carbonate properties in the Mediterranean Sea have shown that C_T is significantly higher in the western basin (> 2315 µmol.kg⁻¹) when compared to the values usually found in the eastern Mediterranean Sea (< 2315 µmol.kg⁻¹;

see Touratier and Goyet, 2011; and Touratier et al., 2012). The C_T distributions obtained during the CASCADE cruise (Figs. 6B and 7B) follow this trend since most C_T values are well above 2320 µmol.kg⁻¹. The lowest C_T concentrations are generally observed in the surface layer of the whole Mediterranean Sea (this also holds for stations of the CASCADE cruise, except those located in the convective region due to the water column homogenization). This vertical gradient for C_T mainly results from sedimentation of organic material that progressively releases CO_2 in seawater as the consequence of the respiration and the decomposition processes. The highest C_T concentrations during the CASCADE cruise are essentially observed in waters that belongs to LIW. The high content of C_T within LIW was first mentioned by Touratier and Goyet (2009) using data from the DYFAMED time-series station (central part of the Ligurian Sea).

The A_T distributions recorded during CASCADE (sections L and M, see Figs. 6C and 7C, respectively) also correspond to the picture described elsewhere in the literature for the Mediterranean Sea. The A_T concentration is usually lower in the western basin (< 2600 µmol.kg⁻¹) than in the eastern Mediterranean Sea (> 2600 µmol.kg⁻¹). These levels are the consequence of the major inputs (the rivers and the Black Sea) and outputs (sedimentation of calcium carbonate and exchange with the Atlantic Ocean) of A_T to the system (Schneider et al., 2007; Touratier and Goyet, 2011). As observed for C_T (see above) during the CASCADE cruise, the minima and the maxima of A_T are associated to AW/WIW and LIW, respectively.

3. Estimation of the anthropogenic CO₂ concentration (C_{ANT}; in µmol.kg⁻¹)

Since C_{ANT} cannot be measured, several approaches have been proposed in the literature to estimate this property in different regions of the world ocean. Vázquez-Rodríguez et al. (2009) give an overview of several approaches available from the literature to estimate C_{ANT} . Five of the most recent models (ΔC^* , Gruber et al., 1996; C_{IPSL}^0 , Lo Monaco et al., 2005; TTD, Waugh et al., 2006; TrOCA, Touratier et al., 2007; and the φC_T^o , Vázquez-Rodríguez et al. 2009) were used to perform an inter-comparison exercise of their C_{ANT} estimates using a common and a high quality dataset available for the Atlantic, the Antarctic, and the Arctic Oceans in order to feed the models with the required observations. One of the conclusions is that all methods give similar spatial distributions and magnitude of C_{ANT} between latitude 60°N-40°S, and that some differences are found among the methods in the Southern Ocean and the Nordic Seas. The C_{ANT} total inventories computed with the TrOCA approach for the whole Atlantic Ocean was 51 Pg C; this clearly shows that this

approach does not over- or underestimate C_{ANT} since it is well in the range of the inventories computed by the four other methods (from 47 to 67 Pg C).

Several studies have shown that the TrOCA approach is easily and successfully applied to a large variety of marine systems; Touratier and Goyet (2004), Touratier et al. (2005), and Vázquez-Rodriguez et al. (2009) used datasets from the Atlantic Ocean; Lo Monaco et al. (2005) and Sandrini et al. (2007) give results of the TrOCA approach for the southern Ocean and Antarctic Ocean; Goyet et al. (2009) computed C_{ANT} using the TrOCA approach in the southern Ocean (Touratier et al., 2007; Goyet and Touratier, 2009; Alvarez et al. 2009). On the other hand, the papers of Huertas et al. (2009), Yool et al. (2010), and Ríos et al. (2010) suggest that the TrOCA approach may provide overestimated estimates of C_{ANT} . However, as debated by Touratier et al. (2012; pages 2728-2731), most of the previous studies used the TrOCA approach in inappropriate conditions (in the surface layer where biological activity can be significant or using unrealistic outputs of a 3D model to test the validity of the TrOCA approach).

Regarding specifically at the Mediterranean Sea, Touratier and Goyet (2009, 2011) were the first to estimate C_{ANT} and to compute the resulting acidification for the Mediterranean Sea. Using data from the DYFAMED site, Touratier and Goyet (2009) showed the decadal evolution of C_{ANT} in the Northwestern Mediterranean Sea from the mid-1990s to the mid-2000s. During the year 2001, the German cruise 51/2 of the R/V Meteor provided high quality data of the carbonate system properties along a longitudinal section throughout the whole Mediterranean Sea, from which Touratier and Goyet (2011) were able to estimate the distribution of CANT. Using the latter database, Schneider et al. (2010) also computed the distribution of C_{ANT} but using the TTD approach that uses the CFC-12 transient tracer. Although similar patterns are generally obtained for the CANT distributions computed from TrOCA and TTD, it appears that the C_{ANT} minimum found in the oldest water mass (the depth range is $\sim 1000-1500$ m) of the Eastern basin is significantly higher with the TrOCA approach (37.5 µmol.kg-1) than with the TTD approach (20.5 µmol.kg-1). Such difference is surprising since the inter-comparison exercise performed for the Atlantic Ocean (Vázquez-Rodríguez et al. 2009) give similar values for the CANT total inventories with 48 Pg C and 51 Pg C for the TTD and the TrOCA approach, respectively.

Recently, using results of the 2008 BOUM cruise throughout the entire Mediterranean Sea, Touratier et al. (2012) compared the values of C_{ANT} estimated with the TrOCA approach to those provided with another approach, the MIX method, developed initially by Goyet et al. (1999) to study the Indian Ocean. Their conclusion is that the distribution of C_{ANT} calculated with the TrOCA approach is quantitatively very similar to the one computed using the MIX approach.

Given the simplicity, the worldwide applicability, the robustness, the precision, and the expertise of the TrOCA approach to estimate C_{ANT} within the Mediterranean waters, we choose to apply this method to the CASCADE dataset. The TrOCA approach is explained in details in Touratier et al. (2007); this simple approach requires only the knowledge of four properties (O₂, A_T, C_T, and θ) in order to provide an estimate of C_{ANT} :

$$C_{ANT} = \frac{TrOCA - TrOCA^{\circ}}{a} \tag{1}$$

with :

a = 1.279

$$TrOCA = O_{2} + a \left[C_{T} - \frac{1}{2} A_{T} \right]$$

$$TrOCA^{0} = e^{\left(7.511 - \left(1.087 \times 10^{-2} \right) \theta - \frac{7.81 \times 10^{5}}{A_{T}^{2}} \right)}$$
(2)
(3)

The uncertainty of the TrOCA approach is estimated to be 6.25 μ mol.kg⁻¹ (Touratier et al. 2007).

(4)

Previous studies (Touratier and Goyet 2009, 2011; Touratier et al. 2012) report that the minimum of C_{ANT} for the western Mediterranean Sea is close to 60 µmol.kg⁻¹, a value significantly higher than the minimum estimated for the eastern basin (only 37 µmol.kg⁻¹). This is mainly the result of efficient ventilations of deep waters in the western basin that lower the mean age of water masses and increase their mean O₂ and C_{ANT} levels. C_{ANT} estimates derived from bottle samples during the CASCADE cruise are presented in Figs. 6D and 7D for sections L and M, respectively. As expected, minima of C_{ANT} observed in the Gulf of Lions are effectively not less than 60 µmol.kg⁻¹. These minima (~68 µmol.kg⁻¹) are

clearly associated to the LIW cores when stratified conditions are prevailing, while maxima $(C_{ANT} > 90 \ \mu mol.kg^{-1})$ are observed in the surface layer. Like many other physical and chemical properties measured during the CASCADE cruise, vertical profiles of C_{ANT} are well homogenized within the convective region of section L with concentrations in the range 77-85 μ mol.kg⁻¹.

4. Interpolation of the CO₂ properties using the CTD records

As explained previously, Figs. 6 and 7 show the distribution of the CO₂ system properties $(C_T, A_T, and C_{ANT})$ measured from bottle samples, all spatially interpolated using the DIVA procedure (available in the Ocean Data View software). In this section, our aim is to improve the quality of these distributions using objective interpolation procedures derived from relationships between the C_T and A_T properties, and θ , S, and O₂. We also take advantage of the high frequency of vertical sampling (each meter) provided by the CTD for the input variables (θ , S, and O₂).

4.1 Estimation of calculated C_T (C_{Tc}):

The two studies of Touratier and Goyet (2009, 2011) dealing with the carbonate system properties in the Mediterranean Sea have shown that the property C_T can be estimated from the three properties S, θ , and O_2 using the approach developed by Goyet and Davis (1997). The latter authors have demonstrated that, for waters below the mixed layer, C_T can be parameterized using the following relationship:

 $C_{\rm T} = a + b\theta + cAOU + dS, \tag{5}$

where AOU (μ mol.kg⁻¹) is the Apparent Oxygen Utilization, which is usually calculated from S, O₂, and θ . The four coefficients *a* to *d* are then determined by multiple linear regression using measurements (C_T, θ , O₂, and S) from the CASCADE cruise. After selecting all data from below a depth of 200 m (we use the hypothesis that most of the biological activity –if significant- is within the surface layer) we estimate the following coefficient values specific for the Gulf of Lions:

$$\begin{cases} a = -151.22 \\ b = -23.51 \\ c = 0.38 \\ d = 71.75 \end{cases}$$
(6)

Using the above coefficients in Eq. (5), the calculated C_T values (C_{Tc}) are computed. The goodness of fit between C_T and C_{Tc} values is then assessed by examining the mean ($\overline{X}_R = 0$ µmol.kg⁻¹) and the standard deviation ($SD_R = 2.4 \mu mol.kg^{-1}$) of the residuals R (i.e. the difference $C_T - C_{Tc}$). These results show that it is possible to estimate C_T accurately in the Gulf of Lions (below 200 m) from the three properties θ , O_2 , and S, with a precision of 2.4 µmol.kg⁻¹. Note that the precision obtained here for the Gulf of Lions is significantly better than those obtained for CT_C using the DYFAMED dataset (precision of 4.7 µmol.kg⁻¹; Touratier and Goyet, 2009) or data from the METEOR 51 trans-mediterranean cruise (precision of 6.1 µmol.kg⁻¹, Touratier and Goyet, 2011). We estimate that a precision of 2.4 µmol.kg⁻¹ (i.e. 0.1 % of the averaged C_T property from the CASCADE dataset) is good enough to apply the above interpolation procedure (Eqs. 5 and 6) to the Gulf of Lions.

4.2 Estimation of calculated A_T (A_{Tc}):

Like in many other oceanic regions, several studies have shown that A_T is linearly correlated to S in the Mediterranean Sea (Copin-Montégut, 1993; Copin-Montégut and Bégovic, 2002; Schneider et al., 2007; Touratier and Goyet, 2009). These relationships apply either to a specific region (Alboran Sea for Copin-Montégut, 1993; DYFAMED site for Copin-Montégut and Bégovic, 2002, and Touratier and Goyet, 2009) or only to the surface layer of the Mediterranean Sea (Schneider et al., 2007). Earlier work (Touratier and Goyet 2011) showed that A_T data from the METEOR 51 cruise (that cover both the western and the eastern parts of the Mediterranean Sea) could not be simply fitted as a function of S, but could be fitted as a function of both S and θ , as did Lee et al. (2006) for several regions in the world ocean.

Concerning the CASCADE dataset, no significant relationship can be proposed between A_T and S, or A_T and S and θ . However A_T is significantly and linearly correlated to C_T (Fig. 8). Among the 215 samples from which A_T and C_T were measured during the cruise, only 5 surface samples (very close to the coast in section A to D) were eliminated in order to obtain this following linear equation (model II regression):

$$A_T = 0.64 C_T + 1102.6 \quad (r = 0.98) \tag{7}$$

Using Eq. (7), the A_{Tc} values can be calculated either from the measured values of C_T or from the calculated values of C_T (C_{Tc} ; see above). In each case, a statistical analysis of the

residuals R (A_T - A_{Tc}) is performed. When A_{Tc} is derived from the measured C_T we obtain $\bar{X}_R = 0.3 \ \mu\text{mol.kg}^{-1}$ and $SD_R = 2.4 \ \mu\text{mol.kg}^{-1}$. Similarly, when A_{Tc} is derived from the calculated C_{Tc} , $\bar{X}_R = 0.3 \ \mu\text{mol.kg}^{-1}$ and $SD_R = 2.4 \ \mu\text{mol.kg}^{-1}$. These results indicate that A_{Tc} can be accurately estimated either from C_T (from surface to the bottom) or from the 3 properties S, θ , and O_2 (from 200 m to the bottom), using the CASCADE data. The level of precision obtained for A_{Tc} in the present study (2.4 μ mol.kg⁻¹; i.e. 0.09 % of the averaged A_T property from the CASCADE dataset) is significantly better than the precision of 4.5 μ mol.kg⁻¹ obtained by Touratier and Goyet (2009) for A_{Tc} derived from S at the DYFAMED site, and also better than the precision of 6 μ mol.kg⁻¹ obtained by Touratier and Goyet (2001) using the METEOR 51 cruise dataset, when A_{Tc} is estimated from both S and θ .

4.3 Distributions of CTD-derived properties and level of acidification

The results obtained for the distributions of C_{Tc} and A_{Tc} for section L and M are presented in Figs. 9A-B and 10A-B, respectively. When compared to their respective bottle samples distributions (Figs. 6B-C and 7B-C), numerous details are revealed (for instance, new maxima and minima appears) which are all in agreement with the distribution of the physical forcing properties (θ , S, and σ_{θ} ; compare with Figs. 2A-C and 3A-C).

Looking now at the equations used to estimate C_{ANT} (see Eqs. 1 to 4), we can also replace C_T and A_T by C_{Tc} and A_{Tc} , respectively. This leads to a new CTD-derived product of C_{ANT} , called C_{ANTc} , which provides estimates every meter for all stations (see Figs. 9C and 10C).

One of the main reason we estimate the level of anthropogenic CO_2 is that its accumulation in the ocean is the main cause of acidification. Since the beginning of the industrial era it is generally admitted that the pH has already decreased by ~0.1 pH unit in the ocean surface layer (equivalent to an increase of ~30% in the [H+]; Orr et al. 2005; Martin et al. 2008). For the Mediterranean Sea, a relatively high level of acidification is expected due to the high concentration levels recorded for total alkalinity which, combined to a typical Revelle factor of ~ 9 for the surface Mediterranean waters, allow to absorb relatively more C_{ANT} than in the open ocean (CIESM, 2008; Goyet et al., 2009).

The acidification (ΔpH) during the 2011 CASCADE cruise is calculated from the difference between the 2011 distribution of pH (pH₂₀₁₁) and the pre-industrial distribution of pH (pH_{preind}):

$\Delta pH = pH_{2011} - pH_{preind}$

We then follow the procedure detailed in Touratier and Goyet (2011) and Touratier et al. (2012) to estimate pH_{2011} and pH_{preind} . Using the model CO2SYS developed by Lewis and Wallace (1998), the pH_{2011} is estimated from the 2011 C_{Tc} and A_{Tc} distributions. Concerning the pH_{preind} , it is estimated from the 2011 A_{Tc} values (since we know that this property is not affected by the accumulation of anthropogenic CO₂ in seawater), and the pre-industrial C_{Tc} which is computed from the difference between the 2011 C_{Tc} and the 2011 C_{ANTc} values.

Using Eq. (8), the results for the Δ pH distributions are shown for sections L and M (Figs. 9D and 10D, respectively). These results indicate that all water masses sampled in the Gulf of Lions during the CASCADE cruise were significantly acidified (the range is from -0.15 to - 0.11 pH unit over a period of approximately 140 years). This range is very similar to those obtained with historic data from the western Mediterranean Sea (METEOR 2001 cruise, Touratier and Goyet 2011; BOUM 2008 cruise, Touratier et al., 2012).

5. Discussion and conclusion

From the analysis of the previous property distributions (Figs. 2, 3, 9, and 10) it is challenging to assess the role played by the deep convection on the sequestration of anthropogenic CO₂. In order to clarify the impact of such event on the carbon cycle, we calculate the mean values of several key properties (θ , S, σ_{θ} , O₂, C_{Tc}, and C_{ANTc}) within the layer 200-1000 m (see Fig. 11). The mixed layer (0-200 m) is not considered here since estimates of C_{Te}, and consequently those of C_{ANTc}, cannot be determined with the appropriate accuracy (see above). Another reason to remove this layer is the large variability of most properties which results from the permanent interaction with the atmosphere through the air/seawater interface. The bottom layer (below 1000 m) is also excluded from the calculation to improve the signals since this layer is relatively less affected by convection. The seafloor depth for stations CL01, CL02 (section L) and CM12, CM11 (section M) is less than 1000 m, they are thus removed from the analysis.

The impact of deep convection on properties is clearly visible in section L for distance < 135 km (stations CL03 to CL08 are represented by black square symbols; see Fig. 11). Other stations in section L with a distance > 135 km, and all stations in section M are representative

of relatively stratified conditions. The deep convection is clearly associated to a decrease of the mean θ value in the layer 200-1000 m (Fig. 11A). Heat losses through the sea surface and mixing of the mixed layer with the underlying water masses certainly explain a large part of the cooling. The mean salinity value in the layer 200-1000 m (Fig. 11B) does not seem to be significantly affected by convection. Consequently, the decrease of temperature appears to be the main forcing variable to explain the increase of the mean density σ_{θ} (Fig. 11C). Concerning the chemical properties, the convection region allows O₂ (Fig. 11D) and C_{ANTc} (Fig. 11F) to propagate rapidly from the mixed layer, where they accumulated initially (probably during stratified conditions), to the intermediate and bottom layers. Convection is also responsible for a slight decrease of C_{Tc} (Fig. 11E), which is in agreement with the traditional mirror effect obtained between O₂ and C_{Tc} (compare Figs. 11D and 11E).

The three phases described by Marshall and Schott (1999) to explain the offshore deep convection could potentially highlight the way by which anthropogenic CO_2 penetrates so quickly the deepest layers of the western Mediterranean Sea. During the vertical mixing phase (phase 2), the strong and cold winds increase the instability and the depth of the mixed layer. We hypothesize that it could maintain a depression of CO₂ in the mixed layer favorable to a net transfer of atmospheric CO_2 to the ocean. This transfer is however a slow process (several months to one year to reach equilibrium); and the duration of the vertical mixing phase is certainly a key parameter to understand such phenomenon. As shown by Houpert (2013), using time-series data from the Lion mooring line, the vertical mixing reached 1500 m in mid-December 2010. This phase was however episodically interrupted by short (several days) events of re-stratification of variable intensities (phase 3). As evidenced by Figs. 9C and 11F, significant amounts of anthropogenic CO_2 were exported during a typical 'phase 2 event' of medium intensity thanks to the convective region. Phase 2 corresponds to a period of intense and rapid transfer of CO_2 (previously accumulated during phase 1 in the mixed layer) to deeper layers. During the phase 3 of re-stratification and 'spreading', the new dense water, richer in oxygen and anthropogenic CO₂, would be then incorporated into the northern current by lateral transfers. If true, such deep convection events would represent a very efficient pumping, penetration and spreading of atmospheric gas like O2 and CO2 to the deepest layers of the north western Mediterranean Sea (this is also true for many other compounds like organic maters that will enhance the biological activity and therefore impact the O_2 and CO_2 budgets in the deep ocean).

Using mean values calculated for the layer 200-1000m (see Fig. 11), the next step is to detect any significant relationships among the key properties (results are shown in Fig. 12). Both the O_2 and the C_{ANTc} concentrations increase significantly with σ_{θ} (Fig. 12A and 12C, respectively). We conclude here that the homogeneization of the water column induced by the convection is a factor which stimulates the penetration of O₂ and C_{ANTc} from the atmosphere to the ocean interior. This is also true for the concentration of total carbon (C_{Tc}) which is significantly correlated to σ_{θ} (r²=0.45 and p-value= 0.0006; see Fig. 12B). As expected, a mirror effect exits between C_{Tc} and O₂ (Fig. 12D): C_{Tc} is negatively but significantly $(r^2=0.9)$ correlated to the mean oxygen concentration. Among the selected properties, the most significant relationship is between CANTC and O2 (r2=0.99; Fig. 12E): this positive correlation is characterized by a slope of 0.57, which means that the increase of 1 mole of CANTC corresponds to an increase of 1.75 mole of O2, probably reflecting a more efficient pumping of O_2 through the air/ sea interface (a plausible explanation – not exhaustive - is the higher solubility of O_2 in seawater when compared to that of CO_2). Using C_T and A_T measurements along sections L and M, the sea surface partial pressure of CO_2 (pCO2) is also estimated (we use the K1 and K2 constants published by Govet and Poisson, 1989) and compared to the atmospheric pCO_2 (Fig. 13). Stations of section L, representative of deep convection (phase 2), are all characterized by a sea surface $pCO_2 > atmospheric$ pCO₂. On the contrary, most other stations, representative of relatively stratified conditions, show the opposite trend. This means that during the period of convection, CO_2 should be released by the ocean while it should be captured during stratified conditions. This provides only an instantaneous picture of the CO_2 air/sea flux direction. To identify the potential areas and periods of source and sink, however, the velocity and the intensity of CO₂ transfer should be known and integrated over a timescale ranging from several months to a year. We know from the analysis of historical data that climatic changes already impacted the dynamics of the western Mediterranean Sea, with rapid repercussions on the properties of the deepest layers through the deep convection sites located both in the Western and the Eastern basins. One of the most striking example was the so-called 'Eastern Mediterranean Transient' (EMT) which corresponds to the apparition of a new deep convection site in the eastern Mediterranean, at the end of 80s (Roether et al., 1996). A combination of meteorological and hydrological factors imposed the Aegean Sea as a new source of deep waters in addition to those of the Adriatic source which traditionally feed the Eastern Mediterranean Deep Water (EMDW; see Roether et al., 1999; Klein et al., 1999; Lascaratos et al., 1999; Theocharis et

al., 2002). The main consequence was that as much as ~20% of the EMDW has been replaced by the new Aegean deep waters (Roether et al., 1996). As stated by Klein et al. (2003) and Manca et al. (2004), when compared to deep waters from the Adriatic source, the new deep waters originating from the Aegean Sea were characterized by higher salinity, temperature, higher density, and they were also produced at a higher rate. As evidenced by Schröder et al. (2006), the EMT signal propagated rapidly into the Western basin. This signal, by following different pathways of circulation, mainly affected the intermediate and the deep layers. Using data from the DYFAMED time-series station (northwestern Mediterranean Sea), Touratier and Goyet (2009) pointed a significant increase of S, θ , C_T, A_T, associated with a significant decrease of O₂ and C_{ANT} in both LIW and the upper portion of WMDW over the period 1993-2005. According to the authors, these changes probably resulted from the impact of the EMT.

However the evolution of deep water properties in the western basin are primarily the result of surface properties modified by climatic changes and transferred through the local deep water formation site (the Gulf of Lions convection area). Significant increases of S and θ in the WMDW have been detected and published by several authors (Béthoux et al., 1990; Krahmann and Schott, 1998; Rixen et al., 2005; Schroeder et al., 2009; and Touratier and Goyet, 2009): for the period 1955-2006, the increase rates range from 0.8 to 8 10^{-3} y⁻¹ for S, and from 1.6 to 19 10^{-3} °C y⁻¹ for θ . It also affects chemical properties like the concentrations of phosphates and nitrates (Béthoux et al. 2002). Another challenge for the future comes from the regular increase of σ_{θ} in the WMDW. To allow the ventilation of the WMDW, the density of any new surface dense water should increase in parallel, which means that S should increase or/and θ should decrease. In case of a high precipitation/evaporation ratio and/or an inefficient cooling during a particular year, the risk is to slow down or even to stop the ventilation of WMDW (Keeling and Garcia, 2002; Bopp et al., 2002) Numerous questions still exists on the mechanisms of transfer (both vertical and horizontal) and on quantitative aspects that cannot be answered with the sole dataset of the CASCADE cruise. One big challenge is to understand the meso-scale variability of the gyres in the area. A promising and complementary approach to oceanographic cruises like CASCADE would be to use a 3D model, coupled with a carbon cycle sub-model, to analyze specific physical/biogeochemical aspects. What are the impacts of the succession of phases 1 and 2, and of their respective timing and intensities on the sequestration of anthropogenic CO_2 and the resulting acidification? The global warming, by increasing the sea surface temperature,

could decrease the intensity and the frequency of the deep convection events in the area. On the other hand, Sanchez-Gomez et al. (2009) observed an increase of evaporation and a decrease of precipitations above the Mediterranean Sea, both processes leading to an increase of surface salinity (this could stimulate the deep convection). Using models, different scenario could be tested to evaluate the impact of such changes on the dynamics of the convection area (Dubois et al. 2011).

As shown above there is a huge complexity of the mechanisms involved in the spatiotemporal evolution of the western Mediterranean properties. A striking feature of the Mediterranean Sea is the speed by which these properties are changing. Dense water formation processes probably explain a large part of these changes since they perform a rapid and an efficient transfer of properties from the surface to depths. In the present paper, we focus mainly on the offshore deep convection, yet cascading of dense water along the continental slope also contributes significantly to the overall budget (Canals et al. 2006; Durrieu de Madron et al. 2013).

Results from this study will undoubtedly contribute (with ongoing studies) to disentangle the complex interactions among the various physical and biogeochemical processes involved in the CO_2 sequestration associated to the western Mediterranean deep water formation site.

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Figure 1: Sampling map of the CASCADE cruise. Sections M (stations CM01 to CM012) and L (stations CL01 to CL12) are analyzed in the present study.

Figure 2: Distributions of properties (from CTD profiles) and for section L. A) potential temperature $(\theta, {}^{\circ}C)$; B) salinity (S); C) potential density (σ_{θ}) ; and D) concentration of dissolved oxygen (O₂, μ mol.kg⁻¹).

Figure 3: Distributions of properties (from CTD profiles) and for section M. A) potential temperature $(\theta, {}^{\circ}C)$; B) salinity (S); C) potential density (σ_{θ}) ; and D) concentration of dissolved oxygen (O₂, μ mol.kg⁻¹).

Figure 4: Time-series data from the Lion mooring line : A) daily net heat flux (W.m⁻²); B: temporal distribution of the potential temperature. The position of the mixed layer depth (MLD) is shown by the yellow line. The black box corresponds to the period of the CASCADE cruise (4-11th March 2011)

Figure 5: A) θ /S diagram for the CASCADE cruise. The three water masses identified in the area are indicated: AW/WIW (Atlantic Water/Western Intermediate Water), LIW (Levantine Intermediate Water), and WMDW (Western Mediterranean Deep Water). Isopycnals are also added on the graphic. B) σ_{θ} profiles for stations CL10 (representative for stratified conditions) and CL07 (representative for a convective cell). C) C_{ANT} profiles for stations CL10 (representative for stratified conditions) and CL07 (representative for a convective cell).

Figure 6: Distributions of properties (from bottle samples) and for section L. A) Concentration of dissolved oxygen (O_2 , μ mol.kg⁻¹); B) concentration of total dissolved inorganic carbon (C_T , μ mol.kg⁻¹); C) concentration of total alkalinity (A_T , μ mol.kg⁻¹); and D) concentration of anthropogenic CO₂ (C_{ANT} , μ mol.kg⁻¹).

Figure 7: Distributions of properties (from bottle samples) and for section M. A) Concentration of dissolved oxygen (O_2 , μ mol.kg⁻¹); B) concentration of total dissolved inorganic carbon (C_T , μ mol.kg⁻¹); C) concentration of total alkalinity (A_T , μ mol.kg⁻¹); and D) concentration of anthropogenic CO₂ (C_{ANT} , μ mol.kg⁻¹).

Figure 8: Linear relationship between A_T and C_T obtained using measurements of the CASCADE cruise (see text for details).

Figure 9: Distributions of properties (calculated from CTD profiles) and for section L. A) Concentration of calculated total dissolved inorganic carbon (C_{Tc} , μ mol.kg⁻¹); B) concentration of calculated total alkalinity (A_{Tc} , μ mol.kg⁻¹); C) concentration of calculated anthropogenic CO₂ (C_{ANTc} , μ mol.kg⁻¹); acidification since the pre-industrial era (Δ pH; pH unit).

Figure 10: Distributions of properties (calculated from CTD profiles) and for section M. A) Concentration of calculated total dissolved inorganic carbon (C_{Tc} , μ mol.kg⁻¹); B) concentration of calculated total alkalinity (A_{Tc} , μ mol.kg⁻¹); C) concentration of calculated anthropogenic CO₂ (C_{ANTc} , μ mol.kg⁻¹); acidification since the pre-industrial era (Δ pH; pH unit).

Figure 11: Mean values of key properties within the layer 200-1000m, and for sections L and M. A) potential temperature (θ , °C); B) salinity (S); C) potential density (σ_{θ}); D) concentration of dissolved oxygen (O₂, µmol.kg⁻¹); E) concentration of calculated total dissolved inorganic carbon (C_{Tc}, µmol.kg⁻¹); and F) concentration of calculated anthropogenic CO₂ (C_{ANTc}, µmol.kg⁻¹). Black square symbols indicate stations from section L which belongs to the convective cell (CL02 to CL08).

Figure 12: Regressions between several key properties using mean values of Figure 11. A) O_2 against σ_{θ} ; B) C_{Tc} against σ_{θ} ; C) C_{ANTc} against σ_{θ} ; D) C_{Tc} against O_2 ; and E) C_{ANTc} against O_2 . Black square symbols indicate stations from section L which belongs to the convective cell (CL02 to CL08).

Figure 13: Comparison of CO₂ partial pressures (μ atm) for surface waters of section L and M (computed from A_T and C_T measurements), with an atmospheric CO₂ partial pressure of 396 μ atm.

Black square symbols indicate stations from section L which belongs to the convective cell (CL02 to CL08).

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