

The carbonate system in the Ligurian Sea

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£.1. Introduction

In a little more than 200 years, human activities have released about 660 billion tons of carbon (Pg C) to the atmosphere [LEQ 18], which has major consequences on climate, ecosystems and people [IPC 14]. The oceans have absorbed, and still absorb about a quarter of anthropogenic CO_2 emissions [LEQ 18], limiting the increase in atmospheric carbon dioxide (CO_2), but increasing ocean acidity [GAT 11]. The study of the oceanic carbonate system is therefore linked to two important environmental issues: (1) ocean CO_2 uptake and (2) ocean acidification and its impact on organisms, ecosystems and ecosystem services [GAT 15].

CO_2 uptake is difficult to measure due to its variability induced by physical and biological processes. Methods to estimate the penetration of anthropogenic CO_2 in the ocean interior exist but they are derived empirically and subject to scientific debate [SAB 10]. Moreover, it has recently been recognized that changes in ocean circulation drive significant variability in carbon uptake [DEV 17]. Long-term

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observations of carbonate system variables (dissolved inorganic carbon, C_T, total alkalinity, A_T, CO_2 partial pressure, pCO_2, and pH) in the ocean remain challenging but highly needed in order to understand how the ocean is changing, how those changes relate to climate variability, and predict future changes in the global carbon cycle.

Studies on the oceanic carbonate system have been mostly performed in the frame of international programs (JGOFS, WOCE, GO-SHIP) that coordinate oceanographic cruises to collect samples along the water column and perform accurate measurements of carbonate parameters (mostly C_T and A_T). Trends and variability in these ocean variables, including pH (e.g., [BAT 14]), have been quantified and compared with corresponding changes in atmospheric CO_2 through dedicated long-term efforts to maintain ocean time-series stations initiated through JGOFS program (e.g. HOT, BATS, ESTOC, DYFAMED and others; WMO, 2014). These programs have generated high quality databases of carbonate chemistry variables (e.g., GLODAP v2, [OLS 16]) that provide long-trend estimates of the oceanic carbon content based on A_T and C_T inventories. In addition to this ocean interior programs, continuous shipboard surface pCO_2 measurements on research and opportunity vessels, buoys or moorings are feeding the SOCAT database [BAK 16], which now allows annual estimates of ocean carbon uptake introduced in global carbon budgets [LEQ 18].

A recent study highlighted an "overaccumulation" of anthropogenic carbon in some oceanic regions and particularly in the Mediterranean Sea [LEE 11, PAL 15, SCH 10, TOU 11]. The study of the Mediterranean carbonate system is unique because of the intrinsic characteristics of this basin: warm waters and high total alkalinity (> 2500 $\mu mol.kg^{-1}$) associated with a permanent and rapid thermohaline circulation loop (residence time around 100 years; [MIL 05]). Several studies have characterized the Mediterranean carbonate system from samples collected along zonal transect at basin scale (e.g. [ALV 14]) and have shown that the Mediterranean exports dissolved inorganic carbon to the Atlantic Ocean with a net flux of 38 Tg C yr^{-1} [SCH 10]. Due to the important evaporation, A_T and S are higher in the Mediterranean Sea compared to the Atlantic water entering into the Mediterranean Sea [JIA 14]. On average, A_T in the Mediterranean Sea is 10% higher than in the global ocean [PAL 15]. The relationship between S and A_T is partly controlled by inputs from rivers and the Black Sea, which are generally high in A_T [COP 93, SCH 07]. Due to its important role in carbon sequestration and ecological sensitivity to anthropogenic change with economic consequences [LAC 16], the Mediterranean Sea could provide insight to global trends [LEJ 18].

Table 1. *List of cruises with A_T and C_T sampling in the Ligurian Sea from 1998 to 2016. Surface CO_2 data provided by the fixed observatories (autonomous sensors) and by the surface ocean observations database (SOCAT) are also listed*

CRUISE & PLATFORMS	START TIME	END TIME	DATA	DATASET DOI
ANTARES	06/18/2010	10/16/2016	502	10.18142/233
CASCADE	03/02/2011	03/02/2011	10	10.17600/11010020
POINT B	01/09/2007	12/22/2015	1660	10.5194/ os-13-411-2017
DEWEX	02/19/2013	04/14/2013	68	10.17600/13020010
MOOSE-GE	05/25/2010	05/26/2016	380	10.18142/235
DYFAMED	02/06/1998	12/10/2016	1809	10.17882/43749
DYFAMED (CARIOCA sensor)	1995-1997; 2013-2015		31600	10.17882/56709
W1M3A (PRO-CO_2 sensor)	2015	2017	15950	-
SOCAT (database)	1998	2016	53527	10.5194/ essd-8-383-2016

In this chapter, we mainly focus on seasonal cycles and long-term trends of ocean carbonate system based on a synthesis of data collected in the Ligurian Sea from 1998 to 2016. It includes seawater sampling for A_T and C_T measurements and pCO_2 and pH calculated using the CO2SYS program [PIE 06] with the recommended constants from Mehrbach et al. [MEH 73] refit by Dickson and Millero [DIC 87] and Dickson [DIC 90]. These samples were collected during oceanographic cruises (CASCADE, DEWEX, MOOSE-GE) and during regular monitoring operations (weekly for SOMLIT-Point B and monthly for DYFAMED and ANTARES, see Table 1). We also use high frequency pCO_2 data measured from CARIOCA sensor at the DYFAMED/BOUSSOLE site [HOO 01, MER 18b] and from CO_2-PRO sensor at the W1M3A buoy [BOZ 13, CAN 15]. In addition, pCO_2 data available in the SOCAT database version 6 [BAK 16] are used to compare pCO_2 and pH long-term trends deduced from A_T and C_T data.

Carbonates system chemical reactions

Any two of the four CO_2 variables (total carbon C_T, pCO_2, pH, and total alkalinity A_T) can be used to determine the CO_2 system:

$C_T \equiv [CO_{2(aq)}] + [H_2CO_3] + [HCO_3^-] + [CO_3^{-2}]$

At seawater pH, we can simplify to : $C_T \equiv [HCO_3^-] + [CO_3^{-2}]$

C_T is also known as Dissolved Inorganic Carbon (DIC)

A_T represents ability of seawater to resist pH change upon addition of acid:

$A_T \equiv 2[CO_3^{-2}] + [HCO_3^-] + [H_2BO_3^-] + 2[HBO_3^{-2}] + 3[BO_3^{-3}] + [OH^-] + [\text{organic/inorganic } H^+ \text{ acceptors}] - [H^+]$

Acidity is a measure of H^+ concentration; the freer H^+ ions, the lower the solution's pH and the greater the acidity ($pH = -\log[H^+]$)

The pH of seawater varies only between about 7.5 and 8.4

Carbon dioxide reacts with water to form carbonic acid: $CO_2 + H_2O \leftrightarrow H_2CO_3$

The carbonic acid then almost instantly dissociates in the seawater, releasing the H^+ ions and bicarbonate molecules: $H_2CO_3 \leftrightarrow H^+ + HCO_3^-$

The bicarbonate ions also dissociate, releasing additional hydrogen ions and forming carbonate ions: $H^+ + HCO_3^- \leftrightarrow 2\,H^+ + CO_3^{2-}$

Excepted for DYFAMED site in 1998-2000 [COP 02], all A_T and C_T water samples collected in 2004-2016 were shipped back to LOCEAN (Paris) where they are stored at 4°C and analyzed within three months of collection by "Service National d'Analyse des Paramètres Océaniques du CO_2" ($SNAPCO_2$ at Sorbonne University in Paris, France). C_T and A_T are measured via potentiometric titration following methods described by Edmond [EDM 70] and Doe [DOE 94]. Accuracy

of C_T and A_T was between 1.5 and 3 µmol kg^{1} depending the sequence of measurements in 2004-2017. Repeatability of replicate samples conducted at SOMLIT-Point-B in 2007-2015 was better than 3 µmol kg^{-1} for both C_T and A_T [KAP 17]. During the C_T and A_T sampling, CTD casts (Seabird SBE25 for SOMLIT and SBE911 for open ocean studies) have been performed to collect Temperature (T) and Salinity (S) profiles which were used to estimate pCO_2 and pH. Nutrient samples have been also collected systematically during the regular cruises during CTD casts by using Niskin bottles mounted on rosette. Usually, most of samples have been collected from surface to bottom depth in the open ocean zone and at two depths (near surface and 50m) in the coastal area (SOMLIT Point B).

£.2. Distribution of the carbonate system in the Ligurian Sea

In the Ligurian Sea, episodes of dense water formation and deep mixing occur in winter. They are related to the deep convection process in the Gulf of Lion, which occurs every winter with higher intensity than in the Ligurian Sea [BOS 17, HOU 16]. The Ligurian Sea is also characterized by atmospheric inputs (see Chapter Migon), rich in nutrients, influencing phytoplankton production and the export of organic matter to the mesopelagic zone [MAR 02a].

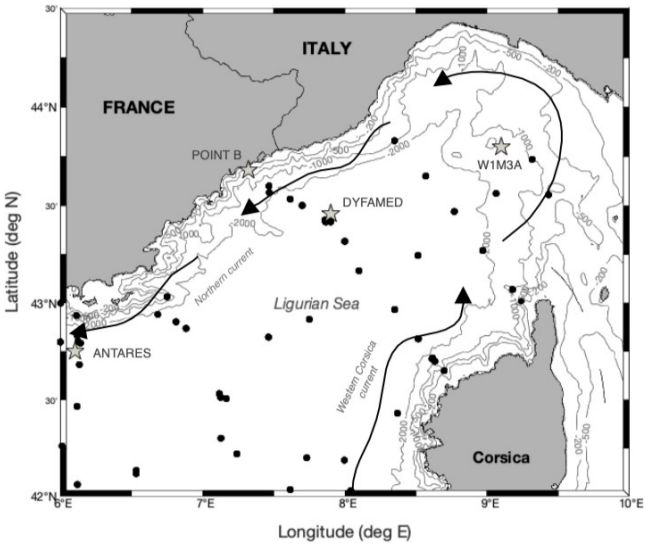


***Figure £.1**. The Ligurian Sea is located in the Northern part of the Western Mediterranean basin. It is located in the pathway of the Levantine Intermediate Water (LIW), which follows two main surface currents (the Western Corsican Current, WCC and the Northern Current, NC, black arrows) that form a front between coastal and*

offshore waters (See chapter Prieur). The sampling stations from 1998 to 2016 are represented by black dots. The grey stars represent the time series of fixed observatories (DYFAMED, ANTARES, POINT B and W1M3A).

Water column monthly climatology of potential T (theta) and practical S distributions in the Ligurian Sea have been plotted in figure £.2. They include all samples collected during time series monitoring and regular cruises from 1998 to 2016 (Table 1). Results are consistent with those already described by Marty et al. [MAR 02a] and in Coppola et al. [COP 18] at the DYFAMED site: the Modified Atlantic Water (MAW) in the first 200 m with strong T-S seasonal variability, the Levantine Intermediate Water (LIW) more saline than in the rest of the Northwestern basin (200-800 m) with a core around 350 m (maximum of theta and S) and the Western Mediterranean Deep Water (WMDW) warmer and more saline for the last decade due to intense vertical mixing during some winters and the deep-water spreading. These episodes of deep convection are now well documented [HOU 16, SCH 08, SCH 17].

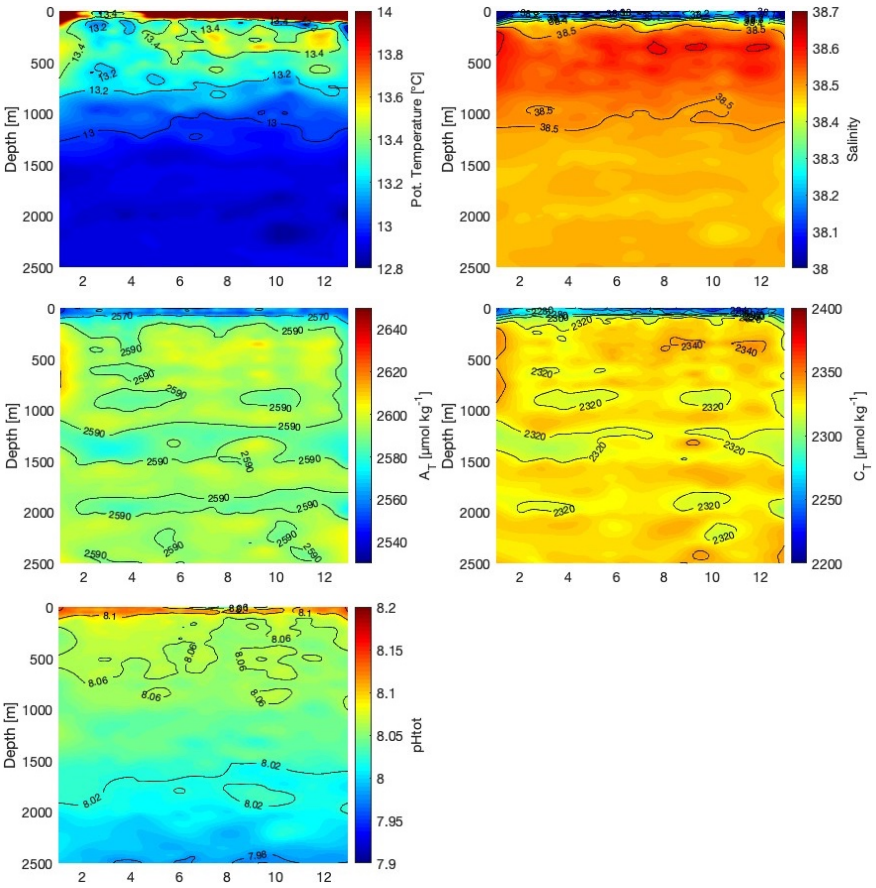


Figure £.2. *Water column monthly climatology of potential T, S and carbonate variables (A_T, C_T and pH at total scale) in the Ligurian Sea derived from cruises conducted from 1998 to 2016 (all stations shown in figure £.1). In the Ligurian Sea, the average C_T concentration ranges from 2200 in surface to 2350 µmol kg^{-1} in deep waters). Total alkalinity follows the same pattern with depth and ranges from 2500 to 2600 µmol kg^{-1}. pH (total scale) is higher in the upper 100 m (8.15) and decreases progressively with depth (< 8 in deep waters). Based on all dataset in 1998-2016 (about 1200 samples in deep waters) the mean C_T and A_T below 300 m are respectively 2328 ± 9 and 2593 ± 7 µmol kg^{-1}. In the next section we will also explore whether changes can be detected in deep layers.*

They modified considerably the deep-water structure and form a stratification of deep-water column where successive new deep waters are overlapped depending on the convection intensity and the newly formed deep-water volume. In the Ligurian

Sea, the wind forcing and heat loss flux are less important than in the Gulf of Lion but deeper vertical mixing can occur in February/March, allowing ventilation of part of the LIW (figure £.2). When the mixed layer is too shallow, the LIW is reinforced (warmer and denser) and the minimum dissolved oxygen concentration is lower [COP 18].

In addition to the effect of T on CO_2 solubility, the distribution of C_T in the water column is driven by the antagonistic effects of (1) the biological carbon pump that increases the vertical gradient of C_T (lowering C_T at the surface and increasing it in the ocean interior) and (2) the exchange of CO_2 at the air-sea interface.

£.3. The seasonal cycle in surface water

The seasonal cycle of carbonate system and ancillary variables in surface water is shown in figure £.3. The monthly variability of T and S at the DYFAMED site has already been reported by Marty and Chiavérini [MAR 10] and Coppola et al. [COP 18]. At the coastal SOMLIT - Point B site, seasonality has been described by Kapsenberg et al. [KAP 17]. For the Ligurian Sea sub-basin (all cruises listed in Table 1), the same seasonal trend is observed: a maximum sea surface temperature (SST) from July to September and a minimum SST in March when evaporation and heat loss prevail.

The seasonal variability of surface S is more complex. S ranges from 37.2 to 38.6 with higher variability in coastal zone. The haline content in surface is highly variable and driven by evaporation and precipitation in the open ocean while groundwater discharges could affect the surface S in coastal zone [BEJ 17]. During the re-stratification period in offshore, the newly formed deep waters will mix with the Atlantic waters and the LIW that will reinvest the mixed patch, a phenomenon that seems to be more pronounced in the Ligurian Sea, probably because the mixed patch contains more salt. This is due to shallower vertical mixing and a saltier LIW, which is close to the sources in the basin: the Corsica Channel and southern Sardinia [BOS 15].

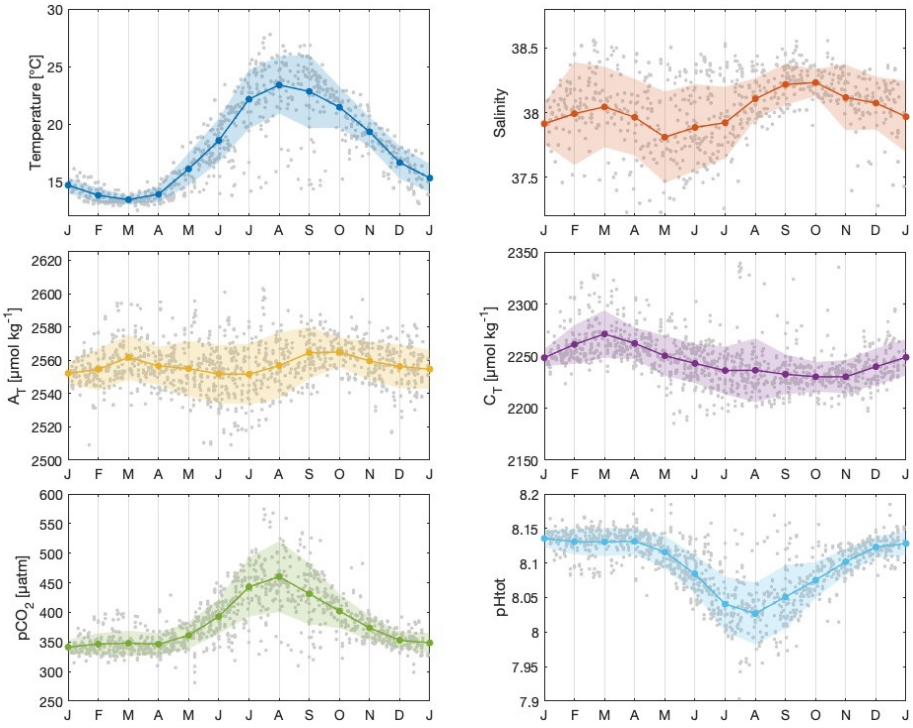


Figure £.3. *Surface (0-20 m) seasonal variability of T, S, A_T, C_T, pCO_2 and pH (total scale) derived from 1998 to 2016 with monthly sampling (grey dots). The coloured dots represent the mean values and the coloured area the standard deviation of the respective values. The main processes underlying observed variations are evaporation, heat loss, precipitation, ground water discharge, mixing of different water masses, and interactions between parameters themselves (see for example figure £.4).*

The seasonal A_T cycle generally mimics the one of S, with highest values in March and September. In surface waters, the A_T variability is controlled by freshwater addition, the effect of evaporation and S that contributes to more than 80% [MIL 98]. In the Mediterranean Sea, several studies have shown that the relationship between A_T and S is linear [COP 02, COP 93, HAS 15, JIA 14, RIV 10, SCH 07]. The same linear relationship was observed between A_T and S with higher A_T associated to the presence of LIW (highest S values; figure £.4). In the coastal zone, the relationship is more complex and variable from year to year [KAP 17]. Since S is high in the Mediterranean Sea (concentration basin), total alkalinity is high too: values range from 2500 to 2600 µmol kg^{-1} (annual average 2557 ± 15

µmol kg^{-1} in surface waters in the Ligurian Sea). Low values (2500 µmol kg^{-1}) are observed only in the coastal site (Point B). Offshore, the lowest values are mainly due to calcium carbonate sedimentation ($CaCO_3$) and Atlantic water inflows.

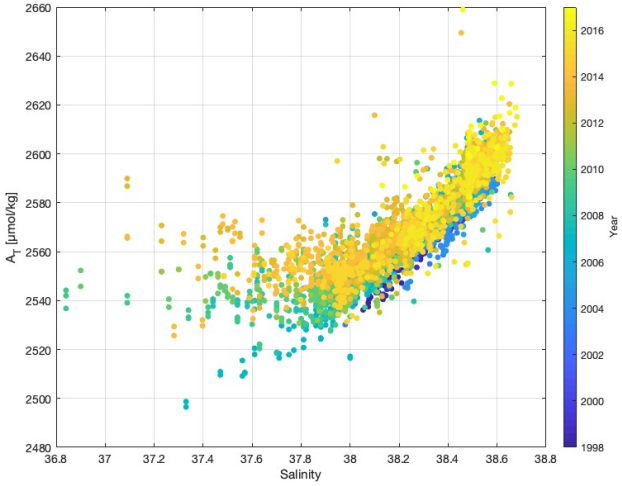


Figure £.4. *Relationship between A_T and S for the entire water column (0-2400m) in the Ligurian Sea (see map in figure £.1). The different values of A_T and S are attributable to the different water masses composing the water column and to long term variations (the colour indicates the range of year: 1998-2016).*

In the Ligurian Sea, C_T concentrations in surface waters range between 2200 and 2320 µmol kg^{-1}. As opposed to A_T, the seasonal cycle of C_T is pronounced and mirrors the SST cycle: C_T is maximum in March, followed by a sharp decline until July and a gradual decrease until November after which it increases again. The seasonal cycle, here represented from all data available in the Ligurian Sea is a robust feature at local scale, as seen at both Point B [KAP 17] and DYFAMED sites [COP 02, HAG 16].

The seasonal pattern of pCO_2 is also pronounced and mainly controlled by SST and C_T. It is higher during the stratification and warm period in summer and lower during "cold" winter. For the Ligurian Sea, pCO_2 values range from 300 to 550 µatm as already reported for the DYFAMED site [COP 02, COP 04, HOO 01, MER 18b] and Point B [KAP 17]. This is also the range of pCO_2 values observed in 1998-2016 in this region from various platforms and included in SOCAT database [BAK 16]. The pCO_2 is highly dependent on the T variability: T increase of +12°C from winter to summer would lead to increase pCO_2 by 200 µatm.

To separate this effect, pCO_2 has been normalized to constant T (here 13°C for winter, thereafter named pCO_2@13C) using the method described by Takahashi et al. [TAK 93] (figure £.5). pCO_2@13C increases when the mixed layer deepens in winter (C_T maximum). When primary production increases in March/April, the productive layer is mostly between 0 to 40 m and pCO_2@13C, like C_T, decreases [COP 02].

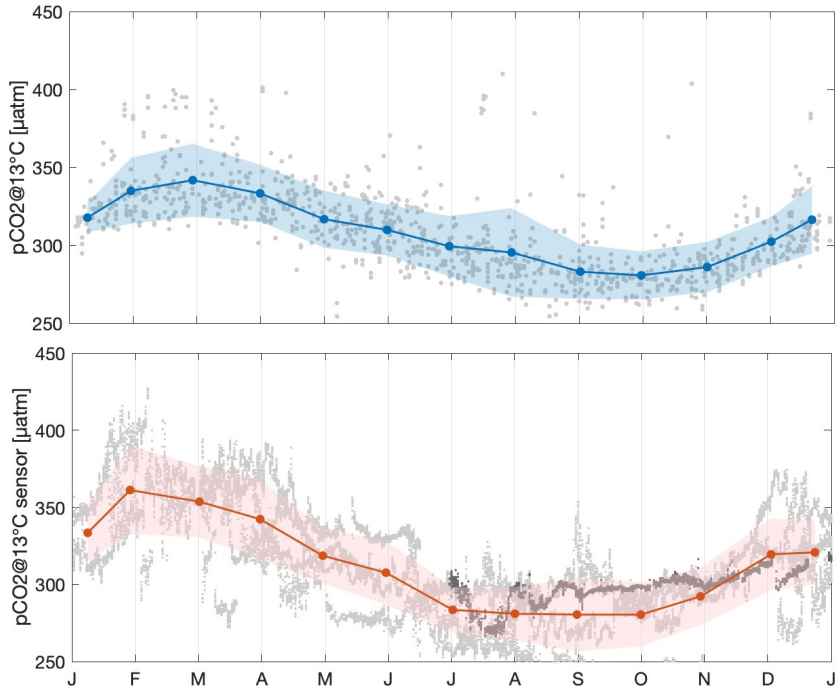


Figure £.5. *Top: seasonal variations of pCO_2@13C in surface (0-20m) derived from discrete measurement of C_T and A_T (grey dots) in the Ligurian Sea (see map in figure £.1). Bottom: seasonal variations of pCO_2@13C derived from hourly surface measurements of pCO_2 with CARIOCA sensor at the DYFAMED/BOUSSOLE (grey light) and from CO_2-PRO sensor in W1M3A sites (grey dark). Discrete and semi-continuous estimations exhibit similar seasonal variations ranging from 250 to 400 µatm, and follows the C_T seasonal cycle (figure £.3). Although there are uncertainties attached to pCO_2 calculations based on C_T/A_T pairs, the pCO_2 and pCO_2@13C seasonal cycles presented in figures £.3 and £.5 confirm the overall quality of C_T/A_T data that are used to detect long-term trends.*

Finally, SST and C_T influence strongly the seasonal signal of pH [HAG 16, YAO 16]. In the Ligurian Sea, surface pH at total scale ranges between 8 and 8.15 (figure

£.3). It is highest in winter when vertical mixing of surface water with cold and C_T enriched deeper water is predominant and the exchanges of CO_2 with the atmosphere is important. Surface pH is still high in March/April when primary production increases as a result of the displacement of the carbonate equilibrium related to CO_2 consumption [COP 02]. Finally, surface pH is lowest in summer during the warm stratification period.

£.4. Long-term changes of the carbonate system and acidification

Long-term trends of carbonate system in the surface, intermediate and deep waters provide crucial information on climate and anthropogenic impacts and allow to emphasize some anomalies. These observations are essential to explain the processes that govern these trends in the Mediterranean Sea [TOU 09, YAO 16]: warming, increase in atmospheric CO_2, ocean dynamics and changes in biological communities.

In this chapter, trends have been estimated using monthly or annual data measured at different depths: surface (0-20 m), intermediate (300-800 m) and deep (> 2000 m). Even though climate change impacts are usually detectable after 30 years (e.g., [MCK 11]), we establish here for the first time, trend values for carbonate system in the Ligurian Sea based on 18-year time series.

£4.1. Surface trends

At the surface (0-20 m), both C_T and A_T exhibit a positive trend: 0.59 ± 0.34 µmol kg^{-1} yr^{-1} for C_T and 0.50 ± 0.21 µmol kg^{-1} yr^{-1} for A_T (figure £.6). pCO_2 and pH (total scale) show respectively an increase of 3.3 ± 0.7 µatm yr^{-1} and a decrease of -0.003 ± 0.001 unit yr^{1} from 1998 to 2016. This is consistent with the coastal observations performed at Point B [KAP 17]. It can therefore be concluded that, at the basin scale, the different series (Point B, Dyfamed, Antares) lead to the same result: pCO_2 increases, leading to a decline in pH.

The pCO_2 trend derived here from monthly discrete measurements of C_T and A_T is consistent with the trend estimated by Merlivat et al. [MER 18b] using the pCO_2 sensor deployed during two different periods (1995-1997 and 2013-2015). Based on CARIOCA hourly measurements, an annual increase of C_T, +1.40 ± 0.15 µmol kg^{-1} yr^{-1}, increase of pCO_2, 2.30 ± 0.23 µatm yr^{-1}, and a decrease of pH -0.0022 ± 0.0002 are computed. Additionally, the fugacity of CO_2 (fCO_2) from surface water measured during all cruises in the Ligurian Sea [BAK 16] provides a fCO_2 trend of

+3.73 ± 0.05 µatm yr^{-1} for 1998-2016 (figure £.7), although we note that no data were available in SOCAT during 2001-2009 (in surface pCO_2 and fCO_2 are similar).

The estimated increase in pCO_2 of +2.3 to +3 µatm yr^{-1} are higher than in the atmosphere (about 2 ppm yr^{-1} as recorded at station Lampedusa; [DLU 18]) suggesting that the CO_2 sink is decreasing. Most of this signal is due to both C_T increase and warming observed in recent years (figure £.6), but opposed to the unexpected positive trend in A_T.

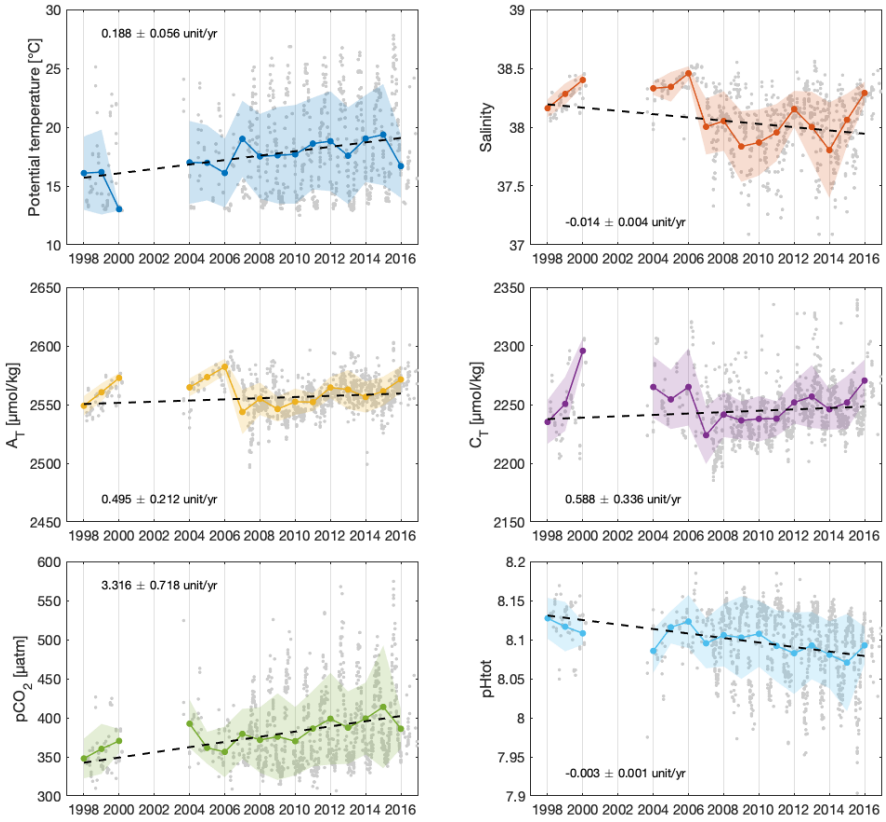


Figure £.6. *Despite the scattering of data, long-term trends of potential T, S, A_T, C_T, pCO_2 and pH (total scale) are visible in the surface waters (0-20 m) from 1998 to 2016. The coloured dots represent the mean values and the coloured area the standard deviation of the respective values.*

Using surface pCO_2 observations available in the Ligurian Sea region (42.5°N-44.5°N, 6°E-10°E) in SOCAT version 6 [BAK 16] and assuming a A_T/S relationship based on Ligurian Sea dataset (figure £.4), we calculate a pH trend of -0.0026 units yr^{-1} for the period 1998-2016, close to the CARIOCA sensor result (-0.0022 ± 0.0002) and close to the pH trend (-0.003 ± 0.001 units yr^{-1}) evaluated from C_T and A_T (figure £.6). The difference of pH trend between these three estimates may be linked to the changes in A_T that are disregarded when A_T is derived from S. Therefore, pH trend also depends on A_T in this region although the origin of the observed positive A_T trend is not explained yet [KAP 17]. However, all results based on different observations indicate a clear pH decrease in the Ligurian Sea in the last two decades. These results reinforce the acidification issue already reported in the Mediterranean Sea [WMO 14].

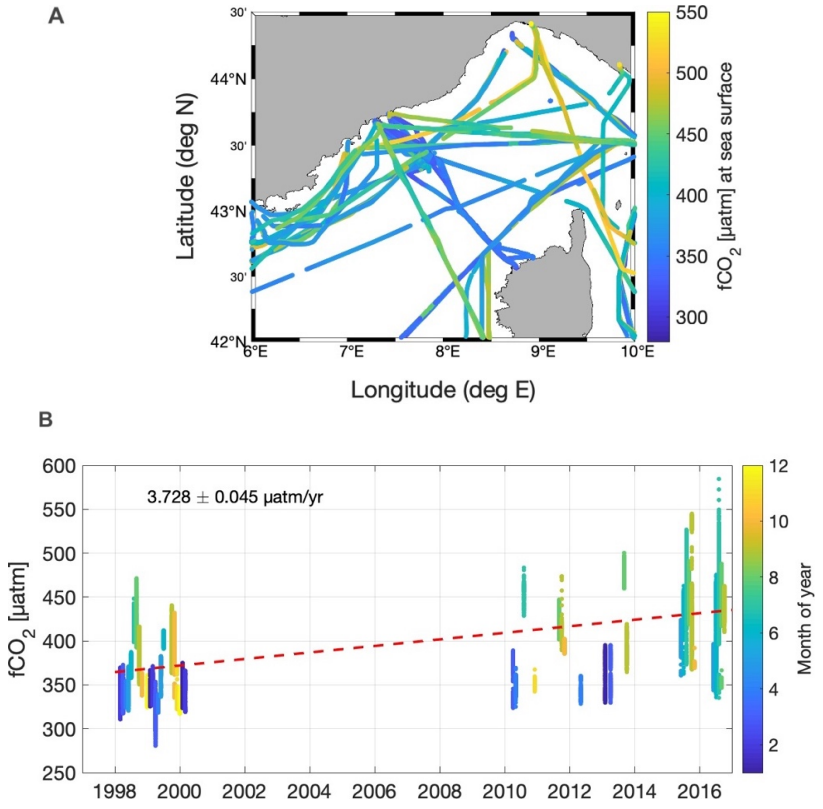


Figure £.7. *A) Location of fCO_2 observations in the Ligurian Sea from the SOCAT-v6 database [BAK 16]. Colour code is fCO_2 at sea surface (µatm). B) SOCAT fCO_2 data for the period 1998-2016 in the Ligurian Sea (colour code is the month). The red line is the trend of 3.73 ± 0.05 µatm yr^{-1} derived from all seasons. Despite the lack of data*

from 2001 to 2009, the averaged trend seems significant when the series of the different seasons are merged.

£.4.2. Interior trends

Recent changes observed in the LIW and WMDW characteristics becoming warmer and saltier in the Northwestern basin modified the biogeochemical distributions in the water column in the Ligurian Sea [COP 18, PAS 15] and probably the carbonate variables trends.

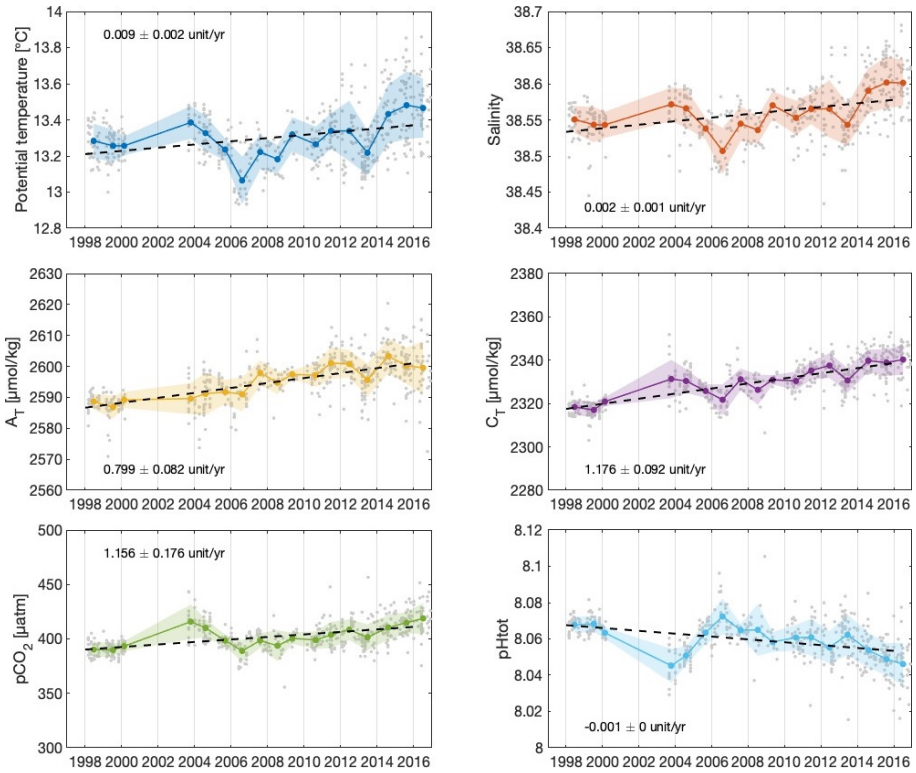


Figure £.8. *Long-term trend in the intermediate waters (300-800 m) of potential T, S, A_T, C_T, pCO_2 and pH (total scale) from 1998 to 2016. The coloured dots represent the mean values and the coloured area the standard deviation of the respective values.*

In the layer 300-800m, we used observations from DYFAMED, ANTARES, DEWEX and MOOSE-GE cruises. At that depth, no seasonal signal is observed (figure £.2). Total alkalinity and carbon show a positive trend with a more sustained increase for the C_T and A_T than in surface (respectively + 1.18 ± 0.09 and + 0.80 ± 0.08 µmol kg^{-1} yr^{-1}; figure £.8). pCO_2 shows an increase around 1.16 ± 0.18 µatm yr^{1}, less important than in surface, which results in a lower decrease of pH (-0.001 unit yr^{-1}). Although C_T increase is significant with depth, the difference of pCO_2 and pH trends in surface and deeper layer is likely linked to the warming up of the surface waters.

In deep waters, below 2000 m, A_T, C_T, pCO_2 and pH (total scale) show the same trend as in the 300-800m layer, with slightly higher values for pCO_2 and pH (1.27 ± 0.30 µatm yr^{-1} and -0.002 unit yr^{-1}, respectively; figure £.9).

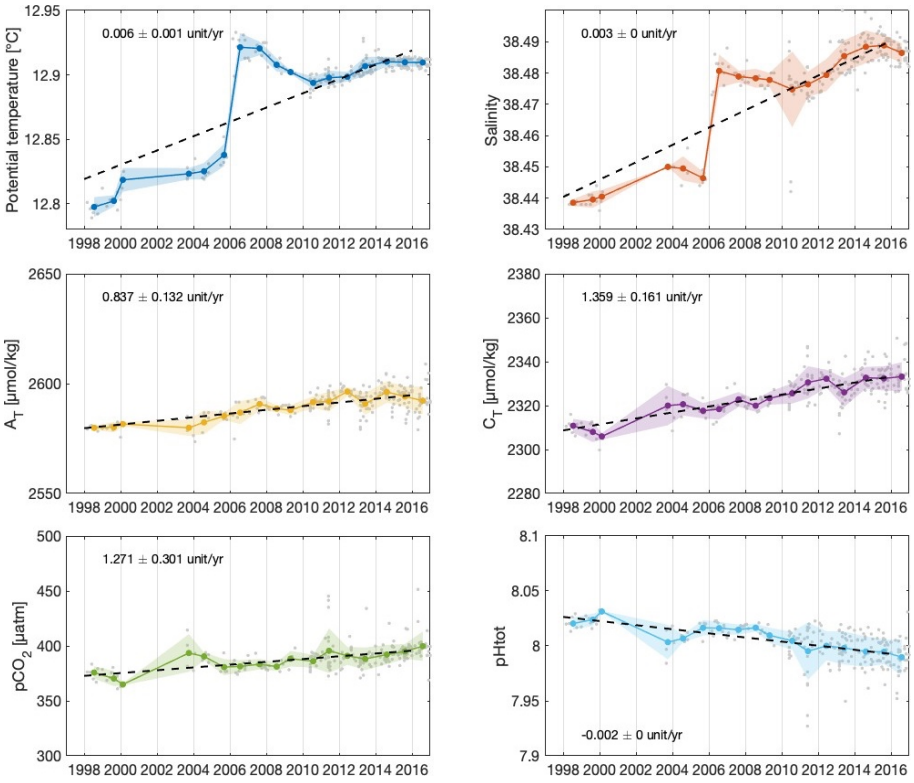


Figure £.9. *Long-term trend in the deep waters (below 2000 m) of potential T, S, A_T, C_T, pCO_2 and pH (total scale) from 1998 to 2016. The coloured dots represent the*

mean values and the coloured area the standard deviation of the respective values. Note the anomaly observed in 2005/2006 only for T and S, discussed in the text.

The trends in deep waters have been also impacted by the 2005/2006 anomaly where an abrupt vertical mixing in the Ligurian Sea conducted to warmer, more saline and more oxygenated newly formed deep water that had invaded the western basin [MAR 10, SCH 08, SMI 08]. This rapid change is clearly visible on potential T and S trend (figure £.9) and was already discussed in many papers [HOU 16, MAR 10, SCH 08, SMI 08, ZUN 12].

The abrupt pH increase observed in 2005/2006 in the layer 300-800m (figure £.8) coincides with an increase in S, potential T, total carbon and alkalinity [TOU 09, TOU 11]. This event could be related to the modification of the main deep-water formation site in the Eastern Mediterranean basin. Indeed, in the late 1980s - early 1990s, nearly 20% of the eastern basin bottom waters were replaced by very dense waters initially formed in the Aegean Sea instead of the original deep-water formation site in the Adriatic Sea (see Chapter Prieur). This phenomenon, known as the Eastern Mediterranean Transient (EMT), has disrupted the distribution of the main water masses [ROE 07]. One of the consequences for the waters of the Ligurian Sea, is that an older water mass, and therefore poorer in oxygen (reinforcement of the Oxygen Minimum Layer) and richer in anthropogenic carbon, has probably been introduced at intermediate depths.

Another hypothesis to explain this anomaly would be the absence and/or low intensity of convection processes for several years, which led to a warmer, saltier and more oxygen-depleted LIW. The outbreak of intense convection in 2005 in the Gulf of Lion and in 2006 in the Ligurian Sea, due to successive cold winters, led to a massive supply of warmer and saltier water from surface to the bottom. In 2005, this would have occurred through deep water dispersion mechanism following the very intense bottom reaching convection event in the central Gulf of Lion (called Western Mediterranean Transient, WMT) and in 2006 by intense vertical mixing in the Ligurian Sea, which led to a very rapid increase of T, S and O_2 [COP 18].

£.5. Changes in the carbonate system in the Ligurian Sea in the Mediterranean Sea and global contexts

A model simulation of anthropogenic carbon storage and acidification indicate that the surface water acidification rate in the Mediterranean Sea increased since 1800 (estimation of delta pH of -0.08 unit; [PAL 15]). In the Ligurian Sea, in situ dataset from 1998 to 2016 presented here provide the same delta pH range (-0.08 to

-0.05 units in the surface and deep waters, respectively). For this period, Merlivat et al. [MER 18b] compute a change of - 0.040 ± 0.004 for surface waters. From basic marine carbonate chemistry, it is well known that, as atmospheric CO_2 increases, surface-ocean pCO_2 increases, reducing seawater pH. Deep waters of the Mediterranean Sea exhibit changes in pH which are higher than typical global ocean deep waters due to faster ventilation times. Furthermore, typical Mediterranean Sea anomalies as EMT and WMT signals, have severely disrupted the distribution of water masses. As the Mediterranean Sea is warmer and more alkaline than others offshore areas, this could potentially represent a larger and faster decrease in pH and then higher acidification impacts.

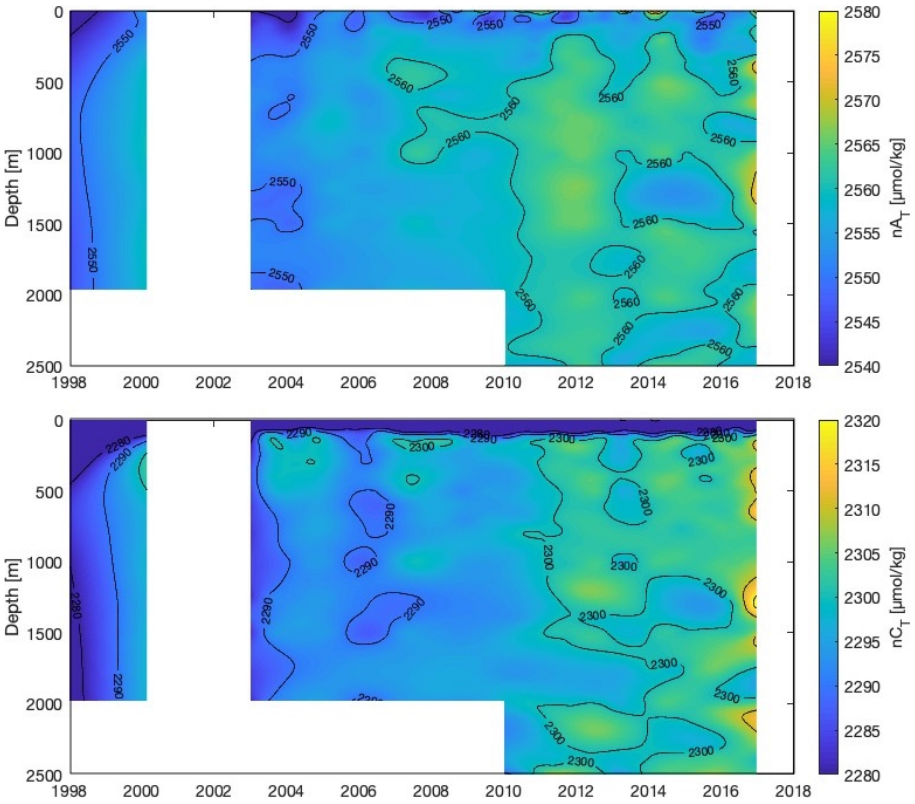


Figure £.10. *Time series of normalized A_T (nA_T) and normalized C_T (nC_T) in the Ligurian Sea from 1998 to 2016 (all data shown in figure £.1 are merged). The increase of these parameters visible after 2010 from 300 to 2500 m could result from anthropogenic impact and water mass characteristic modifications.*

To observe change in the water column, we estimate a normalized A_T (nA_T) and C_T (nC_T) adapted for the Mediterranean Sea (nX = X * 38/S where X corresponds to C_T and A_T values). In figure £.10, variability of nA_T and nC_T shows an accumulation of CO_2 and A_T after 2010 from 300 to 2500 m. This could be a signal of anthropogenic impact but also due to a modification of intermediate and deep-water masses characteristics. After the WMT, local intense deep convection occurred in the Ligurian Sea in 2010, 2012 and 2013. These events were short and accompanied by a new deep-water spreading recently formed in the Gulf of Lion [COP 18]. They produced a large input of S and heat fluxes from surface to deep waters. It is possible that this supply induces a large transport of CO_2 from surface to the intermediate and deep waters in addition to the rapid increase of S that stratified the deep-water column.

These observations highlight that the Ligurian Sea is a key region to observe changes in the carbonate chemistry and it highlights the importance of maintaining long-time series of the oceanic carbonate system in relation to their hydrological and biogeochemical properties. This is particularly true in a very dynamic oceanic region like the Mediterranean Sea in terms of water-mass changes and ventilation process.

£.6. Conclusions

This synthesis shows the consistency of different analyses carried out through different oceanographic cruises and time-series stations located in the Ligurian Sea that now help to detect and understand long-term of A_T, C_T, pCO_2 and pH trends in this region. It is also a unique database to validate biogeochemical simulations to better understand the future role of Mediterranean Sea for both CO_2 uptake and acidification issues in the context of global changes. The observations conducted since 1995 in the Ligurian Sea show a clear increase of pCO_2 and associated decrease of pH over 18 years. This is observed in surface from direct pCO_2 measurements, as well as in the water column (from A_T, C_T observations). The seasonality of the carbonates system is now well observed in both coastal and open-ocean waters, and long-term trends start to be detected. However, the synthesis presented here also highlights significant interannual variability as observed in 2004-2007 at depth. In this context, autonomous sensors for pCO_2, pH, oxygen and nutrients, not only in surface but also in water column (e.g., moorings, Argo floats), and included in integrated observing system should improve our vision of ocean carbon variables that become mandatory to constrain ocean acidification projections and the role of the Mediterranean Sea in the fate of the carbon pump and marine ecosystems.

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