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Modeling of the Total Alkalinity and the Total Inorganic Carbon in the Mediterranean Sea

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Abstract: Measurements of the CO2 system parameters in the Mediterranean Sea are relatively scarce and not representative for all its sub-basins. High quality data collected on May 2013 during the 2013 MedSeA cruise covering the whole basin were used to provide for the first time linear relationships estimating the total alkalinity (AT) and the total dissolved inorganic carbon (CT) from salinity in each Mediterranean basin and sub-basin at different depth layers. These correlations show that a substantial quantity of alkalinity is added to the seawater during its residence time in the Mediterranean Sea, whereas the biological processes, the air-sea exchange and the high remineralization rate are responsible of the high CT concentrations in this sea. Moreover, these fits could be used to estimate the AT and CT from salinity where there are not available measurements of the carbonate system parameters.

Keywords: Carbonate System, Total Alkalinity, Total Dissolved Inorganic Carbon, Fits, Mediterranean Sea

1. Introduction

Aiming to understand and quantify the carbonate system in the Mediterranean Sea, several studies have been realized (e.g. [1], [2], [3], [4], [5], [6], [7]). However, the amount of high quality measurements of the carbonate system properties, particularly the total alkalinity (AT) and the total dissolved inorganic carbon (CT), through the whole Mediterranean Sea remained scarce. Recently, during several oceanographic cruises carried out from 2001 until now, the measurement of carbonate system parameters was included [5] [8] [9] [10] [11]. However, many Mediterranean sub-basins remain out of coverage and need to be studied in order to have a better understanding of the carbonate system in this enclosed sea.

The measurement of the AT and CT parameters could be furthermore used to calculate the carbon budget in the Mediterranean and to estimate the acidification variation and the concentrations of the anthropogenic carbon dioxide sequestered in this sea.

The present paper is based on AT and CT data measured during the 2013 MedSeA cruise which covered during the same month almost the entire Mediterranean Sea from the West to the East and from the South to the North. In this study, we present and discuss, for the first time, the AT-Salinity and CT-Salinity relationships in each Mediterranean basin and sub-basin at different depth layers. These correlations could be used to estimate the AT and CT from salinity data where there is a lack in the measurements of
the carbonate system parameters.

2. Study Area and Methodology

2.1. MedSeA Cruise

During the MedSeA (Mediterranean Sea Acidification In A Changing Climate) cruise realized on board of the Spanish R/V Angeles Alvariño, from May 2nd to June 2nd 2013, 23 stations along the Mediterranean Sea were sampled throughout the water column. The overall goal and scientific objectives of the MedSeA project are well described in the following links [12 and 13]. The full cruise track (more than 8000 km long) consisted of two almost longitudinal legs. During the first leg, samples were collected from Atlantic waters off Cadiz harbor, Spain to the Levantine Sub-basin in the Eastern Mediterranean Sea [3879 km long, 15 stations, 279 sampled points, maximum sampled depth = 3720 m]. The second leg was conducted in the Northern part of the Mediterranean from the Western Cretan Straits in the Eastern Mediterranean basin to Barcelona, Spain in the North Western Mediterranean basin, passing through the South of the Adriatic Sub-basin [3232.5 km long, 8 stations, 183 sampled points, maximum sampled depth = 3000 m] (Figure 1).

2.2. Sampling and Measurement

The salinity (S) was measured in situ using a Sea-Bird Electronics CTD system (SBE 911 plus) associated with a General Oceanic rosette sampler, equipped with twenty four 12 L Niskin bottles. The precision of salinity measurements is ± 0.0003.

For the determination of $A_T$ and $C_T$, seawater samples were collected, at all stations and depths, into washed 500 ml borosilicate glass bottles, according to standard operational protocol. A small headspace (< 1 %) was adjusted to prevent pressure build-up and loss of CO$_2$ during storage. Few drops of a saturated solution of HgCl$_2$ were added to the samples in order to avoid any biological activity. Then, the samples were stored in the dark at constant temperature (~ 4 °C) until their analysis on shore (IMAGES laboratory, Perpignan, France). The measurement of these two parameters was performed simultaneously by potentiometric acid titration using a closed cell. The principle and procedure of measurements, as well as a complete description of the system used to perform accurate analysis can be found in [14]. The precision of $A_T$ and $C_T$ analysis was determined to be ± 2 µmol kg$^{-1}$ for $A_T$ and ± 4 µmol kg$^{-1}$ for $C_T$, by titration of 261 samples, collected at the same conditions of temperature and S, from Banyuls Sur Mer, South France. The accuracy of $A_T$ and $C_T$ measurements was determined to be ± 1 µmol kg$^{-1}$ for $A_T$ and ± 4 µmol kg$^{-1}$ for $C_T$ by analyzing a total of 26 bottles of three different batches of Certified Reference Material (Andrew Dickson, CA, USA, batches 85, 86 and 128). More information about the carbonate system measurements and precisions are detailed by [15].

The carbonate system and hydrographic data of the 2013 MedSeA cruise are almost available in Pangaea data repository [16, 17, 18, 19 and 20].

3. Results and Discussion

3.1. $A_T$-$S$ Relationships in the Mediterranean Sea, its Basins and Sub-Basins

Termed as “evaporation basin”, the Mediterranean Sea is characterized by elevated salinities in relation to the adjacent Atlantic Ocean. As a consequence of the surface heat loss and the excessive evaporation [21] [22], the general pattern of salinity in the Mediterranean is an Eastward global increase (Fig.2). The highest salinity values were measured in the Eastern Mediterranean basin (Max. 39.18 in front of Nile Delta, at ~ 5 m), while the lowest salinities were detected at the surface of both the Western Mediterranean basin and the Strait of Gibraltar (Min. 36.29 at the surface of the Strait of Gibraltar, ~ 20 m).
High total alkalinity concentrations were recorded in the Mediterranean Sea (Mean = 2588 ± 46 µmol kg\(^{-1}\)). The highest \(A_T\) concentrations were measured in the Eastern Mediterranean basin (Max. \(A_T = 2666.0\) µmol kg\(^{-1}\), at 300 m in the area of Western Cretan Straits, whereas the lowest \(A_T\) concentrations were measured in both the Strait of Gibraltar and the surface waters of the Western Mediterranean basin (Min. \(A_T = 2377.0\) µmol kg\(^{-1}\) at 25 m in the Strait of Gibraltar). An Eastward increasing tendency for the total alkalinity was also well noticeable, likewise the salinity trend (Fig.3).

Based on the carbonate system parameters data collected during the 2013 MedSeA cruise, an Eastward increasing trend of \(A_T\) was remarked in parallel with the salinity one [15]. Our results indicate the presence of significant correlations between \(A_T\) and \(S\) in the Mediterranean Sea globally, its main basins and many of its sub-basins as well. Table 1 presents the Model II linear regression between these two parameters in each basin and sub-basin and at different depth layers (surface, intermediate and deep layers). These equations were obtained using the Excel Microsoft Office program (2007). For all the equations derived in this study, the root mean square deviation (RMSD), which is a good measure of the accuracy of the fit, the coefficient of correlation (Pearson coefficient ; \(r\)), and the number of data pairs (\(n\)) used to derive each correlation, are also mentioned in the Table 1 for each \(A_T\)-\(S\) fit.

Evaporation would drive a steady increase in salinity and total alkalinity during the propagation of surface waters toward the Eastern part of the Mediterranean Sea. Therefore, the negative intercepts obtained in most \(A_T\)-\(S\) fits (Table 1) may be explained by the high evaporation in the sea along with the increased temperatures.
with the influence of high $A_T$ inputs by freshwater contributions from the local rivers and the Black Sea. These two systems carry very high total alkalinites (between 2000 µmol kg$^{-1}$ and 6500 µmol kg$^{-1}$), at low or zero salinity, to shelf areas, especially in the Eastern basin, where surface S and $A_T$ tend to be higher due to the cumulative effects of evaporation [5]. Moreover, our results indicate the absence of a significant $A_T$-S correlation in the intermediate and deep layers of the Eastern basin, especially in the Levantine Sub-basin in which we detected no significant $A_T$-S relationship at all depth layers (Table 1).

**Table 1.** The $A_T$-S relationships in the different layers of the main basins and sub-basins in the Mediterranean Sea during May 2013 (R.M.S.D. = root mean square deviation, $r$ = coefficient of correlation (Pearson's coefficient), $n$ = number of data pairs used to derive each relationship, [-] means that no significant relationship was found).

<table>
<thead>
<tr>
<th>Basin/Sub-basin</th>
<th>Depth</th>
<th>$A_T$-S relationships</th>
<th>R.M.S.D.</th>
<th>$r$</th>
<th>$n$</th>
<th>Number of equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mediterranean</td>
<td>All</td>
<td>$A_T = 98.48*S - 1208$</td>
<td>± 19</td>
<td>0.9</td>
<td>428</td>
<td>Eq. 1</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 98*S - 1191$</td>
<td>± 18</td>
<td>0.96</td>
<td>58</td>
<td>Eq. 2</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>$A_T = 134*S - 2578$</td>
<td>± 17</td>
<td>0.57</td>
<td>160</td>
<td>Eq. 4</td>
</tr>
<tr>
<td>Western basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 92*S - 956$</td>
<td>± 15.6</td>
<td>0.94</td>
<td>215</td>
<td>Eq. 5</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 101.5*S - 1322$</td>
<td>± 15.6</td>
<td>0.94</td>
<td>105</td>
<td>Eq. 7</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>-</td>
<td>± 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Eastern basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 89*S - 846$</td>
<td>± 19</td>
<td>0.86</td>
<td>27</td>
<td>Eq. 9</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>-</td>
<td>± 30</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>$A_T = 111.42*S - 1713$</td>
<td>± 19</td>
<td>0.54</td>
<td>212</td>
<td>Eq. 8</td>
</tr>
<tr>
<td>Alboran Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 10.65*S + 2005$</td>
<td>± 0.07</td>
<td>0.98</td>
<td>3</td>
<td>Eq. 11</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 82*S - 605.6$</td>
<td>± 0.99</td>
<td>11</td>
<td></td>
<td>Eq. 12</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>$A_T = 171*S - 4020$</td>
<td>± 2</td>
<td>0.7</td>
<td>8</td>
<td>Eq. 13</td>
</tr>
<tr>
<td>Alboran Sub-basin</td>
<td>All</td>
<td>$A_T = 98*S - 1190$</td>
<td>± 11.7</td>
<td>0.95</td>
<td>73</td>
<td>Eq. 14</td>
</tr>
<tr>
<td>Alghero-Provencal</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 100.72*S - 1282.6$</td>
<td>± 14</td>
<td>0.89</td>
<td>9</td>
<td>Eq. 15</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 119.38*S - 2099.7$</td>
<td>± 11.8</td>
<td>0.92</td>
<td>33</td>
<td>Eq. 16</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>-</td>
<td>± 15</td>
<td>0.84</td>
<td>71</td>
<td>Eq. 17</td>
</tr>
<tr>
<td>Liguro-Provencal</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 93.33*S - 1008$</td>
<td>± 12.5</td>
<td>0.9</td>
<td>9</td>
<td>Eq. 18</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 128*S - 2327$</td>
<td>± 11.6</td>
<td>0.89</td>
<td>31</td>
<td>Eq. 19</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>$A_T = 126*S - 2252$</td>
<td>± 15</td>
<td>0.84</td>
<td>71</td>
<td>Eq. 17</td>
</tr>
<tr>
<td>Tyrrenian Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 339.73*S - 10384$</td>
<td>± 3</td>
<td>-0.96</td>
<td>3</td>
<td>Eq. 21</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 96.72*S - 1139$</td>
<td>± 4</td>
<td>0.98</td>
<td>11</td>
<td>Eq. 22</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>-</td>
<td>± 15</td>
<td>0.88</td>
<td>57</td>
<td>Eq. 23</td>
</tr>
<tr>
<td>Ionian Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 97.56*S - 1173.5$</td>
<td>± 17</td>
<td>0.95</td>
<td>8</td>
<td>Eq. 24</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$A_T = 140*S - 2818$</td>
<td>± 16</td>
<td>0.82</td>
<td>27</td>
<td>Eq. 25</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>-</td>
<td>± 15</td>
<td>0.88</td>
<td>57</td>
<td>Eq. 23</td>
</tr>
<tr>
<td>Adriatic Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 239.5*S - 6653.7$</td>
<td>± 8</td>
<td>-0.84</td>
<td>6</td>
<td>Eq. 26</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>-</td>
<td>± 4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>-</td>
<td>± 15</td>
<td>0.88</td>
<td>57</td>
<td>Eq. 23</td>
</tr>
<tr>
<td>Western Cretan Straits</td>
<td>Surface (0-25 m)</td>
<td>$A_T = 81.28*S - 569$</td>
<td>± 0.13</td>
<td>0.99</td>
<td>3</td>
<td>Eq. 27</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>-</td>
<td>± 15</td>
<td>0.88</td>
<td>57</td>
<td>Eq. 23</td>
</tr>
<tr>
<td></td>
<td>Deep (&gt; 400 m)</td>
<td>$A_T = 1236.95*S - 45690$</td>
<td>± 6.3</td>
<td>-0.88</td>
<td>4</td>
<td>Eq. 28</td>
</tr>
<tr>
<td>Levantine Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>-</td>
<td>± 15</td>
<td>0.88</td>
<td>57</td>
<td>Eq. 23</td>
</tr>
</tbody>
</table>

In addition, our results reveal the presence of a very strong positive $A_T$-S correlation (Eq.27) in the surface layer of the Western Cretan Straits, whereas in the deep layer a significant negative $A_T$-S correlation is observed (Eq.28). It is also shown the presence of a negative and significant $A_T$-S fit exclusively in the surface layer of the Adriatic Sub-basin (Eq.26; Table 1). These remarks demonstrate that the relationship between S and $A_T$ does not follow the Eastward strict evaporation trend. However, it reflects the mixture of waters characterized by high $A_T$ concentrations with low salinity waters in the Eastern part of the Eastern Sub-basins and in the Adriatic Sub-basin. This fact is explained by the mixing, between high salinity surface water in the Eastern Sub-basins with waters from rivers flowing through carbonate-dominated terrains and/or the Black Sea, that change the characteristics of surface waters which become less saline with higher $A_T$ concentrations.

Our $A_T$-S equation (Eq.1), that takes into account all available data pairs of both parameters in the entire
Mediterranean basin, is very similar to the one published by 
[23]: \( A_T = 99.6^*S - 1238.4 \pm 4.5 \mu \text{mol kg}^{-1} \) (Eq.I), obtained 
using all the available data in the DYFAMED site in the 
North-Western basin of the Mediterranean Sea from 1998 to 
2005. The reason for the slightly less steep slope and the less 
negative intercept in our correlation (Eq.I) compared to the 
other one (Eq.I) could be attributed to the difference of 
sampling locations (different specific total alkalinites 
between the Western and the Eastern basins). Located in 
the North-Western Mediterranean basin (43° 25'N, 07°52'E), the 
DYFAMED site is more influenced by the contributions of 
waters coming from the continents than most of the stations of 
the 2013 MedSeaA cruise (Fig.1). In the coastal zone, total 
alkalinity inputs by rivers (ex. the nearby Rhone has an \( A_T = 2885 \mu \text{mol kg}^{-1} \) [5]) and potentially by sediments, may induce 
the steep slope of the regression line.

In the Alboran Sub-basin, a positive and highly significant 
\( A_T-S \) correlation was detected (Table 1). This is attributed 
firstly to the parallel increase of salinity and \( A_T \) of the surface 
Atlantic waters incoming towards the Mediterranean Sea, and 
secondly, to the high \( S \) and \( A_T \) in the outgoing Mediterranean 
waters toward the Atlantic at the deepest layers. In addition, it 
was noted that the \( A_T-S \) fit (Eq.10) obtained based on all the 
data collected in the Alboran Sub-basin, is different from the 
one mentioned by [4] in the same sub-basin: \( A_T = 94.85^*S - 
1072.6 \mu \text{mol kg}^{-1} \) (Eq.II). This may be due to the large 
difference in the number of sampled points (23 in our study vs. 
440 in [4]) and the time difference of ~25 years between the 
sampling dates of the two studies. Therefore, the observed 
differences between Eq.10 and the equation of [4] could also 
be attributed to the temporal variability of the temperature and 
\( S \), related to the climate change, in the Mediterranean Sea [24] 
[25] [26] [27].

Similarly, a positive and highly significant \( A_T-S \) correlation 
was noted in the deepest and most isolated sub-basin of the 
Western basin, the Tyrrhenian Sub-basin. The circulation 
patterns of the Mediterranean Sea show generally that most of 
the saline and high-\( A_T \) water, coming from the East to the 
Western basin, enters the Tyrrhenian Sub-basin [28]. Below 
the surface modified Atlantic waters, the Tyrrhenian 
Sub-basin is the first Western Sub-basin reached by the 
Levantine Intermediate Waters (LIW), coming from the 
Eastern basin through the Sicily Channel. The LIW enters the 
Tyrrhenian Sub-basin along the slope of Sicily and leaves it 
along the Sardinian coast [29]. The fact that the intermediate 
layer of this sub-basin is occupied by the LIW explains the 
positive and very significant correlation between \( A_T \) and \( S \) in 
the intermediate depths of the Tyrrhenian. Our \( A_T-S \) fit 
(Eq.20), obtained by all the available data of the Tyrrhenian 
Sub-basin, is similar to the one recorded by [8]: \( A_T = 96.62^*S 
- 1139.1 \mu \text{mol kg}^{-1} \) (Eq.III). The slight differences in the slopes 
and intercepts between the two equations are due firstly to the 
different number of stations and sampled points (one station 
and \( n = 21 \) in our study vs. six stations and \( n = 320 \) in the other 
one), and secondly to the date of sampling (May 2013 in our 
study, November 2006, February, April and July 2007 and 
February 2008 in the other one).

The \( A_T-S \) correlation (Eq.2) for the surface layer of the 
entire Mediterranean Sea differs from the regression reported 
by [5]: \( A_T = 73.7^*S - 285.7 \pm 8.20 \mu \text{mol kg}^{-1} \) (Eq. IV). 
The reason for the steeper slope and the more negative intercept 
in Eq.2 compared to Eq.IV, could be attributed to the different 
sampling locations: our track passed through the Strait of 
Gibraltar toward the Eastern part of the Mediterranean Sea 
and the stations were equally distributed between the two 
main Mediterranean basins, while the track covered in the 
other study was conducted from the South-East of Sardinia 
toward the Levantine Sub-basin and the sampled stations were 
concentrated mainly in the Eastern basin. In addition, the 
sampling periods were different: the data of the present study 
were collected in May 2013, whereas the data of [5] were 
sampled in October/November 2001. The differentiation in 
Eq.2 and Eq.IV could thus be attributed to the temporal 
variability of temperature and \( S \) in the Mediterranean Sea, 
which is in part associated to the climate change (as mentioned 
above for the Alboran Sub-basin). Equation 2 also differs from 
the recently reported \( A_T-S \) fit (Eq.V) for Mediterranean 
surface waters reported by [30]: \( A_T = 79.84^*S - 510 \) (Eq.V) 
that was based exclusively on measurements made at 5m 
below the sea surface.

Furthermore, the \( A_T-S \) relationships noted for the surface 
waters of the entire Mediterranean Sea (Eq.2) and specifically 
for the surface waters of the Western basin (Eq.6), are very 
close to the relationship: \( A_T = 93.996^*S - 1038.1 \pm 2.5 \mu \text{mol} 
\text{kg}^{-1} \) (Eq.VI), calculated for samples located between the 
surface and the maximum of salinity (LIW horizon) at the 
DYFAMED site [31].

The abovementioned similarities of \( A_T-S \) correlations in 
the different Mediterranean areas, imply that the \( A_T \) could 
considered to be conservative in the Mediterranean Sea, as 
previously was stated by [32]. The conservative behavior of 
\( A_T \) with respect to salinity occurs because HCO$_3^-$ (which, 
withgether with CO$_3^{2-}$ and B(OH)$_4^-$, one of the most important 
bases for seawater) is a major constituent of seawater and the 
ratio of HCO$_3^-$ to the salinity or the chlorinity is nearly 
constant [8]. Equations 5 and 8 describing the \( A_T-S \) 
relationship in the Western and Eastern Mediterranean basins, 
respectively, are considerably different although both have 
negative intercepts. The slope and the absolute intercept 
values are higher in the Eastern basin, indicating that the 
salinity-specific alkalinity (i.e. \( A_T/S \) ratio) increases with 
salinity. The specific alkalinity of the Eastern Mediterranean 
waters is therefore higher than that of less saline Western ones. 
As the regression lines do not pass through the origin, the 
different values of the intercept between the different \( A_T-S \) 
equations (Table 1) reflect the different specific total 
alkalinites of the Eastern and Western Mediterranean water 
masses due to the contributions to \( A_T \) besides the salinity. 
However, excessive inputs of \( A_T \) from rivers in the Adriatic 
Sub-basin [33] result in the absence of a significant correlation 
between \( A_T \) and \( S \) at all the depths of this sub-basin, except on 
the surface layer where a significant but negative \( A_T-S \) fit was 
detected. The mixing of saline surface water, coming from the 
Eastern Sub-basins with local waters discharged by the nearby
rivers and characterized by very high $A_T$ concentrations, shaping the specific fit.

### 3.2. $C_T$-S Relationships in the Mediterranean Sea, its Basins and Sub-Basins

Total dissolved inorganic carbon ($C_T$) varied between a minimum of 2095 µmol kg$^{-1}$ at the surface layers (~5 m) of the Alboran Sub-basin in the Western Mediterranean basin and a maximum of 2359.0 ± 0.4 µmol kg$^{-1}$ in the intermediate waters (~350 m) of the Eastern Mediterranean basin (Mean = 2308.5 ± 22 µmol kg$^{-1}$, Fig.4). However, it is obvious that the intermediate, deep and bottom layers of the Western basin are characterized by the highest $C_T$ concentrations (2321 ± 12 µmol kg$^{-1}$ in the intermediate layers of the Algero-Provencal Sub-basin and 2322.0 ± 0.0 µmol kg$^{-1}$ in the deep layers of the Liguro-Provencal Sub-basin) compared to the Eastern basin.

![Fig. 4. Total inorganic carbon (µmol kg$^{-1}$) as a function of depth in the Western (a) and in the Eastern (b) Mediterranean Basins.](image)

The presence of high $C_T$ concentrations in conjunction with high salinities (Fig.2 and 4) in both the Eastern and the Western Mediterranean basins explains the general significant correlation obtained between these two parameters in the entire Mediterranean Sea. Up to our knowledge, the $C_T$-S equations are not assessed for all the Mediterranean basins and sub-basins and at different depth layers (surface, intermediate and deep). The Table 3 presents the $C_T$-S fits in the different layers of the main basins and sub-basins in the Mediterranean Sea obtained by linear regression of Model II, using the data of the 2013 MedSeA cruise.

The variability of $C_T$, apart from salinity, is also controlled by biological processes (i.e. precipitation and dissolution of calcium carbonate, photosynthesis, oxidation of organic matters), and the air-sea exchange of carbon dioxide. Due to the additional impact of these non-conservative processes on $C_T$, significant $C_T$-S correlations are not obtained at all depth layers. In the Eastern basin, there is no significant relationship between these two parameters in the intermediate layer, but we have noted a significant and negative $C_T$-S fit (Eq.8) in the deep layers. The deep waters of this basin are characterized by high $C_T$ concentrations and relatively low salinities in relation to the overlying layers, which explain the negative $C_T$-S correlation. In the Mediterranean Sea, the convective processes and the consequent advection of dense waters assume a relevant role in sustaining the amount of remineralization in deep layers and appear to be more important than the sinking of particulate matter from the upper layers [34]. It is evident that the active overturning circulation of the Mediterranean Sea fuels the deep layers with labile carbon entrained in the newly formed deep waters inducing enhanced production of respiratory CO$_2$. The involvement of remineralization explains the high $C_T$ concentrations measured in the deep layers of both the Eastern and the Western basins and the absence of a significant $C_T$-S correlation in the deep layers of many Mediterranean sub-basins (Table 2).

Our $C_T$-S correlations at the surface (Eq.17) and intermediate (Eq.18) layers of the Liguro-Provencal Sub-basin are different from the ones reported by [32]. However, it has to be mentioned that the $C_T$-S relationships obtained by the two studies are not totally comparable. The differences could be attributed to the different sampling strategy; the equations of [32] are based on data collected in one fixed station in a coastally-influenced area (DYFAMED site) that was sampled monthly for a 2-years period, whereas the equations of the present study derived from data collected in May 2013 in three sampling stations. In addition, the data used in the study of [32] are originating from different depth intervals than ours: the relationship $[C_T = 74.53*S-555.2 \text{ µmol kg}^{-1}]$ corresponds to depths below the salinity maximum (LIW horizon) down to the bottom and the equation $[C_T =155.17*S – 3662.6 \text{ µmol kg}^{-1}]$ was calculated for samples located between the surface and the maximum of salinity in wintertime.
Our results showed that the total alkalinity and total inorganic carbon were higher in the Mediterranean outflow than in the Atlantic inflow, in agreement with [35]. It seems that there is an important flux of $C_T$ from the Mediterranean to the Atlantic (at the Strait of Gibraltar, $C_T$ is equal to $2327 \pm 2 \mu mol\ kg^{-1}$ in the outflowing Mediterranean waters vs. $2123 \pm 7 \mu mol\ kg^{-1}$ in the inflowing Atlantic waters). This is probably due to the supply of carbon by the rivers and the Black Sea, to the transformation of 40% of the organic carbon entering the Mediterranean to inorganic carbon [4] and to the high remineralization rates in the Mediterranean deep layers [34]. Moreover, our results confirm that the Mediterranean Sea exports $C_T$ to the Atlantic Ocean. These findings are in agreement with those of [36] whom estimated that there is a net export of inorganic carbon from the Mediterranean Sea to the Atlantic Ocean varying from 0.02 to 0.07 pg C yr$^{-1}$, whereas [37] estimated that this export amounted to 0.025 PgC yr$^{-1}$.

### Table 2. The $C_T$-$S$ relationships in the different layers of the main basins and sub-basins in the Mediterranean Sea during May 2013 (R.M.S.D. = root mean square deviation, $r = \text{coefficient of correlation}$, $n = \text{number of data pairs used to derive each relationship}$, $\equiv$ means that no significant relationship was found).

<table>
<thead>
<tr>
<th>Basin/Sub-basin</th>
<th>Depth</th>
<th>$C_T$-$S$ correlation</th>
<th>R.M.S.</th>
<th>$r$</th>
<th>$n$</th>
<th>Number of equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mediterranean</td>
<td>All</td>
<td>$C_T = 90.91*S - 1213$</td>
<td>± 29</td>
<td>0.72</td>
<td>428</td>
<td>Eq. 1</td>
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<td>Surface (0-25 m)</td>
<td>$C_T = 63.65*S - 198$</td>
<td>± 18</td>
<td>0.93</td>
<td>58</td>
<td>Eq. 2</td>
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<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 80.75*S - 822$</td>
<td>± 26.5</td>
<td>0.69</td>
<td>207</td>
<td>Eq. 3</td>
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<tr>
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<td>Deep (&gt; 400 m)</td>
<td>-</td>
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<tr>
<td></td>
<td>All</td>
<td>$C_T = 107.68*S - 1836.6$</td>
<td>± 19</td>
<td>0.93</td>
<td>215</td>
<td>Eq. 4</td>
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<tr>
<td>Western basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 74*S - 583.5$</td>
<td>± 14</td>
<td>0.94</td>
<td>30</td>
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<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 99.3*S - 1515$</td>
<td>± 18</td>
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<td>105</td>
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<tr>
<td>Eastern basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 66*S - 292.6$</td>
<td>± 20</td>
<td>0.68</td>
<td>28</td>
<td>Eq. 7</td>
</tr>
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<td>Intermediate (&gt;25-400 m)</td>
<td>-</td>
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<tr>
<td>Alboran Sub-basin</td>
<td>Deep (&gt; 400 m)</td>
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<tr>
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<td>All</td>
<td>$C_T = 269.6*S - 8145.8$</td>
<td>± 16</td>
<td>-0.53</td>
<td>81</td>
<td>Eq. 8</td>
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<tr>
<td>Liguro-Provençal Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 148*S - 3282$</td>
<td>± 4</td>
<td>0.83</td>
<td>3</td>
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<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 102*S - 1611$</td>
<td>± 5</td>
<td>0.99</td>
<td>11</td>
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<td>Deep (&gt; 400 m)</td>
<td>$C_T = 244*S - 7083$</td>
<td>± 2</td>
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<td>All</td>
<td>$C_T = 123.78*S - 2445.5$</td>
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<tr>
<td>Alboran Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 85.61*S - 1012$</td>
<td>± 12</td>
<td>0.88</td>
<td>9</td>
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<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 136.62*S - 2934.5$</td>
<td>± 12</td>
<td>0.93</td>
<td>32</td>
<td>Eq. 15</td>
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<tr>
<td>Liguro-Provençal Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 56.89*S + 66$</td>
<td>± 5.6</td>
<td>0.95</td>
<td>8</td>
<td>Eq. 17</td>
</tr>
<tr>
<td></td>
<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 113.5*S - 2059$</td>
<td>± 13.6</td>
<td>0.8</td>
<td>33</td>
<td>Eq. 18</td>
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<td>All</td>
<td>$C_T = 126.6*S - 2285$</td>
<td>± 8</td>
<td>0.96</td>
<td>21</td>
<td>Eq. 19</td>
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<tr>
<td>Tyrrenian Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 335.17*S - 10537$</td>
<td>± 3</td>
<td>-0.95</td>
<td>3</td>
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<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 103.24*S - 1683.5$</td>
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<tr>
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<td>All</td>
<td>$C_T = 111*S - 2003$</td>
<td>± 21</td>
<td>0.77</td>
<td>57</td>
<td>Eq. 22</td>
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<td>Ionian Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 72.71*S - 540$</td>
<td>± 16</td>
<td>0.91</td>
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<td>Intermediate (&gt;25-400 m)</td>
<td>$C_T = 149*S - 3481$</td>
<td>± 23.6</td>
<td>0.61</td>
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<td>Western Cretan Straits</td>
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<td>Deep (&gt; 400 m)</td>
<td>$C_T = 104.18*S - 1805$</td>
<td>± 0.8</td>
<td>-0.68</td>
<td>4</td>
<td>Eq. 25</td>
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<tr>
<td>Levantine Sub-basin</td>
<td>Surface (0-25 m)</td>
<td>$C_T = 39.22*S + 1082$</td>
<td>± 4</td>
<td>-0.54</td>
<td>4</td>
<td>Eq. 26</td>
</tr>
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</table>
4. Conclusion

Based on high quality and recent carbonate system data collected on May 2013 during the MedSeA cruise, this paper provides for the first time $A_{T-S}$ and $C_{T-S}$ fits in each Mediterranean basin and sub-basin and at different depth layers. These equations could be used to estimate, based on salinity data, the carbonate system parameters in cases where there is a lack in this kind of measurements. This study show that a substantial quantity of alkalinity is added to the seawater during its residence time in the Mediterranean Sea, whereas the biological processes, the air-sea exchange and the high remineralization rate are responsible of the high $C_T$ concentrations in this sea.

A continuous monitoring of the $CO_3^2-$ system parameters in the main sub-basins of the Mediterranean Sea is recommended to evaluate the spatial and temporal evolution of this system in the context of climate change and ocean acidification.

Acknowledgements

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