An updated survey of the carbonate system in the Mediterranean Sea

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Abstract: The Mediterranean Sea, considered as a "laboratory" basin, is facing large oceanographic and biogeochemical changes driven by both natural and anthropogenic pressures. Measurements of the carbonate system parameters of this highly diverse region are relatively scarce. High quality data collected on May 2013 during the MedSeA cruise are displayed and used to update the pre-existing knowledge about the overall trends of hydrographic, biogeochemical and carbonate system parameters in the Mediterranean Sea. The complexity of the Mediterranean biogeochemistry is shown by the spatial and vertical variability, revealing significant differences between the various Mediterranean sub-divisions. Moreover, the water masses characterization reveals that the Levantine Intermediate Water (LIW), which is the main intermediate water mass in the entire Mediterranean Sea, is well recognized by a maximum intermediate total alkalinity (A_T). It shows furthermore that deep Levantine waters are still filled by Aegean Eastern Mediterranean Deep Waters (EMDW) from the Eastern Mediterranean Transient (EMT) period, while the Adriatic and Ionian deep waters were occupied by new Adriatic EMDW. The biogeochemical data of the 2013 MedSeA cruise can now be found on PANGAEA search engine (www.pangaea.de)with the identifier doi:10.1594/PANGAEA.841933. With this effort, we hope to improve the accessibility and long-term storage of these data for future research.

Key-Words: Carbonate system; Total alkalinity; total dissolved inorganic carbon; water masses; Mediterranean Sea.

Data coverage:

Repository-Reference:

doi:10.1594/PANGAEA.841933
Coverage: 33.21536-41.83675 N, -6.6421 W-33.22604 E
Location Name: The Mediterranean Sea
Date/Time Start: 02 May 2013
Date/Time End: 31 May 2013

1. Introduction

The Mediterranean Sea represents less than 1% of the global world's ocean surface (UNEP/MAP-Plan Bleu, 2009). Being relatively small and with a limited exchange with the open ocean, this sea is considered as a "laboratory basin" where processes occurring on a global scale can be approximated to shorter time and space scales (Bergamasco and Malanotte-Rizzoli, 2010). This holds not only for general circulation, but also for biogeochemical features. In this sea, biogeochemical cycles are affected by climate change (Durrieu de Madron *et al.*, 2011), particularly the carbon cycle. This latter is of major concern since it is directly impacted by the elevated anthropogenic CO_2 emission rates that have increased the atmospheric CO_2 partial pressure since the beginning of the industrial era.

Several studies have been undertaken to measure the carbonate system properties (pH ; total alkalinity, A_T ; total dissolved inorganic carbon, C_T ; and partial pressure of CO_2, pCO_2) in the Mediterranean Sea. The majority of these measurements have been performed in the Western Mediterranean basin (Alekin, 1972 ; Millero *et al.*, 1979 ; Copin-Montégut, 1993 ; Bégovic and Copin-Montégut, 2002 ; Copin-Montégut and Bégovic, 2002 ; Copin-Montégut *et al.*, 2004 ; De Carlo *et al.*, 2013), in the Catalano-Balearic region (Delgado and Estrada, 1994), in the Strait of Gibraltar and the Gulf of Cadiz (Dafner *et al.*, 2001 ; Santana-Casiano *et al.*, 2002 ; Huertas *et al.*, 2006 ; De la Paz *et al.*, 2008 ; De la Paz *et al.*, 2009 ; Ribas-Ribas *et al.*, 2011), whereas fewer ones have been achieved in the other Mediterranean Sea areas : Sicily strait (Chernyakova, 1976) ; Eastern basin (Schneider *et al.*, 2007 ; Pujo-Pay *et al.*, 2011). Recently, during several oceanographic cruises carried out from 2001 until now, the measurement of carbonate system parameters was included (Hassoun *et al.*, 2015c). 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 present study aims to contribute in quantifying and understanding the carbonate system in the Mediterranean Sea based on recent data collected from the one-month 2013 MedSeA cruise that covered a wide area of the Mediterranean Sea from the West to the East and from the South to the North during May 2013. Moreover, this paper contributes to the updating of the preexisting knowledge about the Mediterranean water masses characteristics and the carbonate system, using temperature, salinity, dissolved oxygen, pH, total alkalinity and total dissolved inorganic carbon spatial variations during May 2013.

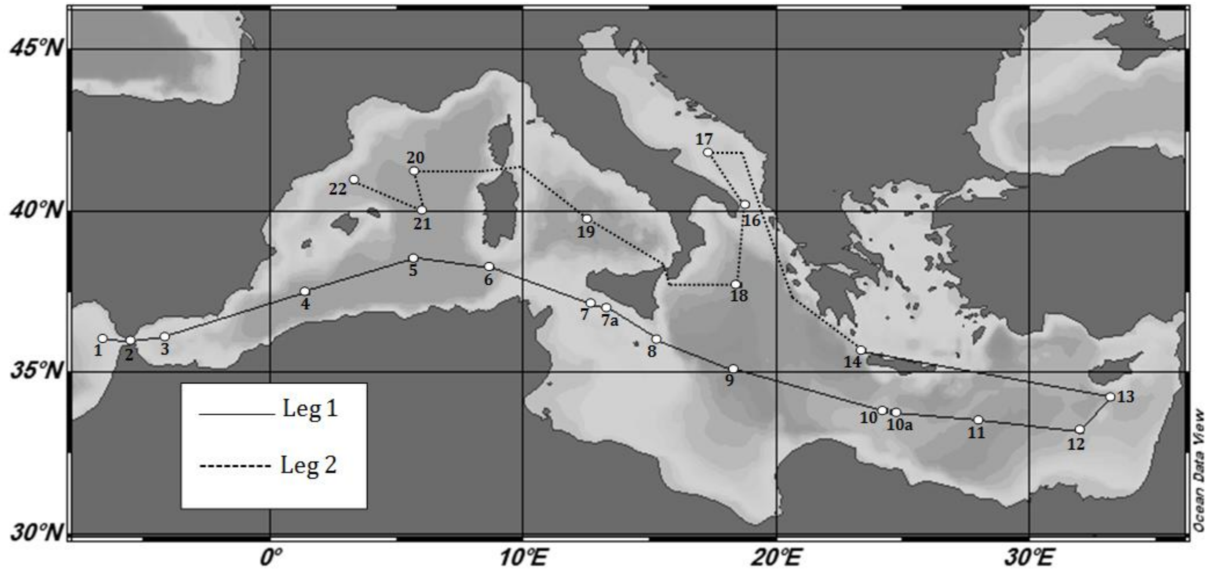


Fig.1. Tracks of the 2013 MedSeA cruise in the Mediterranean Sea. The numbers from 1 to 22 refer to the sampled stations.

2. Material and Methods

2.1.Study area

Twenty three stations, along the Mediterranean Sea, were sampled throughout the water column during the 2013 MedSeA cruise conducted on board of the Spanish vessel *R/V Angeles Alvariño*, from May 2nd to June 2nd 2013. The major cruise objective was to study, at the basin scale, the impact of elevated CO_2 on the Mediterranean Sea biogeochemistry by conducting a comprehensive water column sampling from each of the main Mediterranean basins. The overall goal and scientific objectives of this cruise are further described at the following links: http://medsea-project.eu/ ; http://medseaoceancruise.wordpress.com/. The full cruise track (more than 8000 km long) consisted of two quasi-latitudinal 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 ; Fig.1).

2.2.Measured parameters

The methodology used to sample and measure each parameter is detailed by Hassoun *et al.* (2015c). Salinity S and temperature T were measured *in situ*. The precision of measurements is ± 0.001 ºC for T and ± 0.0003 for S. Seawater samples for dissolved oxygen (O_2) determination were measured via a Winkler iodometric titration. The analytical precision and accuracy of O_2 measurements are ± 1.5 µmol kg^{-1}. For A_T and C_T, seawater samples were collected at all stations and depths. The measurement of these two parameters was performed by potentiometric acid titration using a closed cell (DOE, 1994). 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 T and S, from Banyuls Sur Mer, South France. Whereas 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 types of Certified Reference Material in order to test the sensitivity of the electrodes to the various A_T and C_T concentrations and the precision of the analysis (Hassoun *et al.*, 2015c).

2.3. Derived parameters

The potential temperature (θ) and depth (m) were calculated from the three measured parameters: S, T (ºC), and pressure (db ; IOC, SCOR and IAPSO, 2010).

The degree of saturation of calcite (Ω Ca) and aragonite (Ω Ar) and the pH were calculated via the CO2SYS program for seawater CO_2 calculations, configured for Excel by Pierrot *et al.* (2006). The calculation was done according to the output conditions of temperature and pressure (*in situ* condition), based on A_T-C_T combination and choosing the set of constants (K1 and K2) of Goyet and Poisson (1989), the sulfate constants of Dickson (1990), the seawater scale and the borate constants of Uppström (1974).

The statistical differences between the various Mediterranean sub-divisions (Northern *Vs.* Southern sections and Western *Vs.* Eastern sections) were tested by applying a t-test: two-sample assuming unequal variances via Excel program. The sub-divisions were considered significantly different when the P value (two-tailed test) was smaller than 0.05 [$P < 0.05$*] and highly significantly different when the P value was smaller than 0.001 [$P < 0.001$**], whereas P values greater than 0.05 [$P > 0.05$] indicated the absence of any significant difference.

The hydrographic and carbonate system data of the 2013 MedSeA cruise are available on Pangaea data repository (Goyet *et al.*, 2015a ; 2015b ; Ziveri and Grelaud, 2013a ; 2013b ; 2013c.).

3. Results

3.1. Vertical distribution of the hydrographic and carbonate system parameters in the Mediterranean Sea

The distributions of hydrographic and biogeochemical properties shown hereafter refer to the 3950.6 km section, from the Atlantic waters (off Cadiz, Spain) to the Levantine Sub-basin (between Lebanon and Cyprus, Fig.1). In order to present the detailed variations of the different parameters in the upper layers (highly influenced by biological seasonal variability) and within the water column, the following diagrams are splitted into two depth ranges: from 0 to 300 m and from 300 m to the bottom.

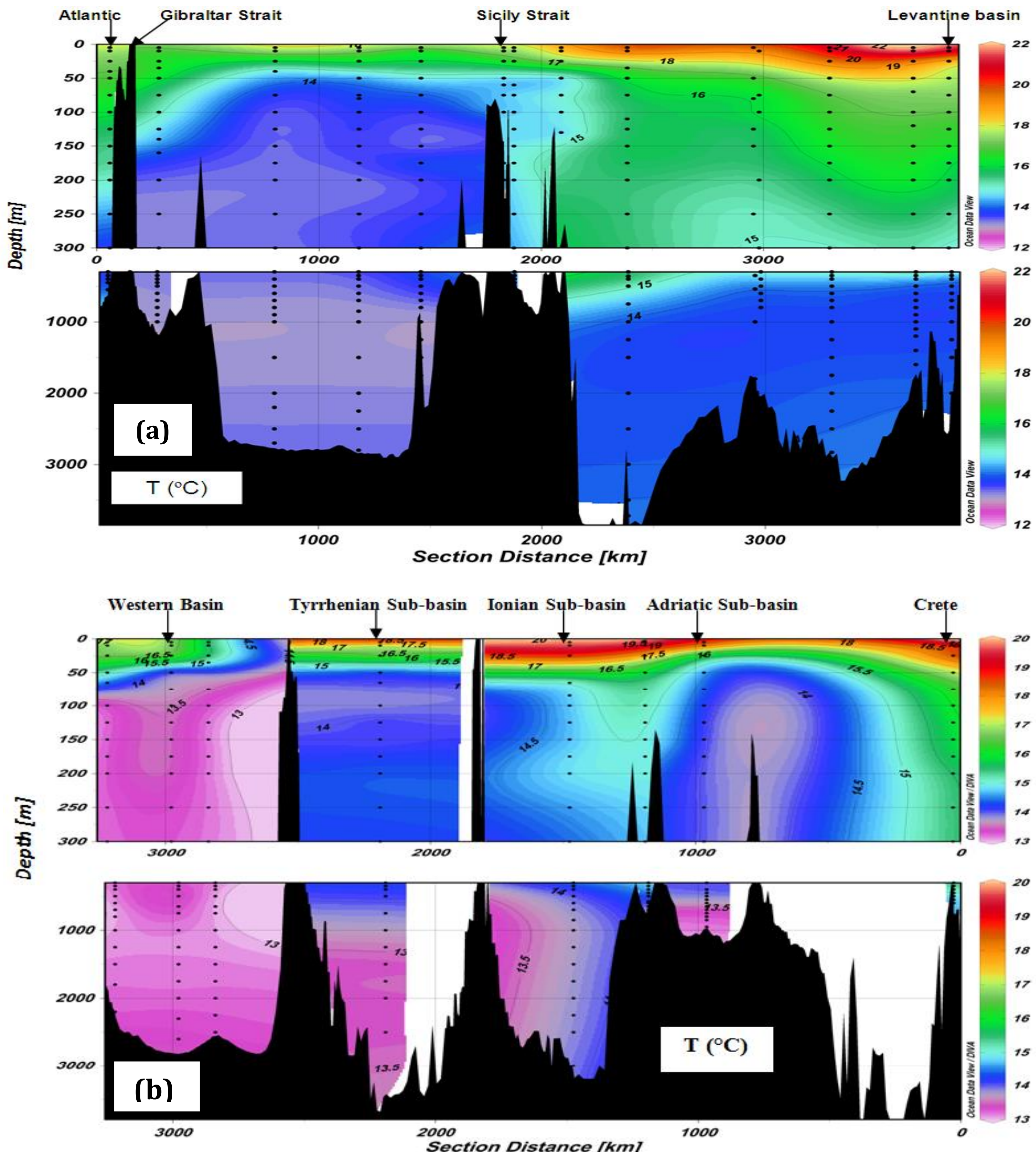


Fig.2. Vertical distribution of the temperature (T ; ºC) along the Southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

The general pattern of T (ºC) is an Eastward global increase ; a marked rise (4 ± 1 ºC) in surface layers and a slight one (2 ± 0.5 ºC) in deep layers (Fig.2 ; a, b). Mediterranean seawater temperature varied, during May 2013, between a minimum of 13.02 ºC at 650 m in the Liguro-Provençal Sub-basin, and a maximum of 21.8 ºC in front of the Nile Delta at the surface of the Eastern Mediterranean Basin.

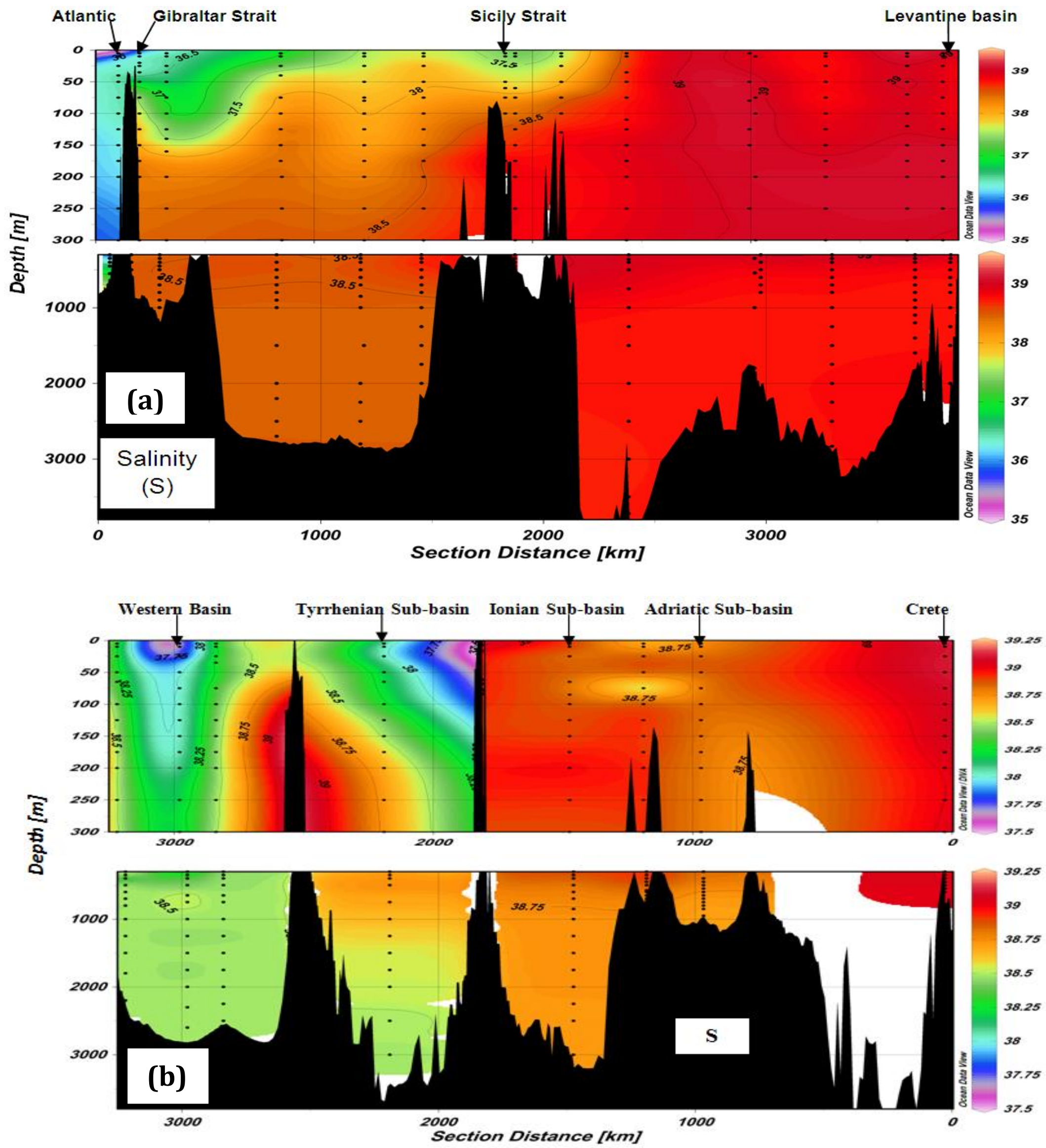


Fig.3. Vertical distribution of the salinity (S) along the southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

As expected, the highest salinity was 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 ; Table 2).

Contrary to the dissolved oxygen trends recorded during the same cruise (Hassoun *et al.*, 2015c), the highest apparent oxygen utilization (AOU) has been observed in the intermediate layers of the Alboran Sub-basin (87.5 µmol kg^{-1}), whereas the lowest values have been detected at the surface layers of the Eastern Mediterranean basin (around 0 µmol kg^{-1}, Fig.4).

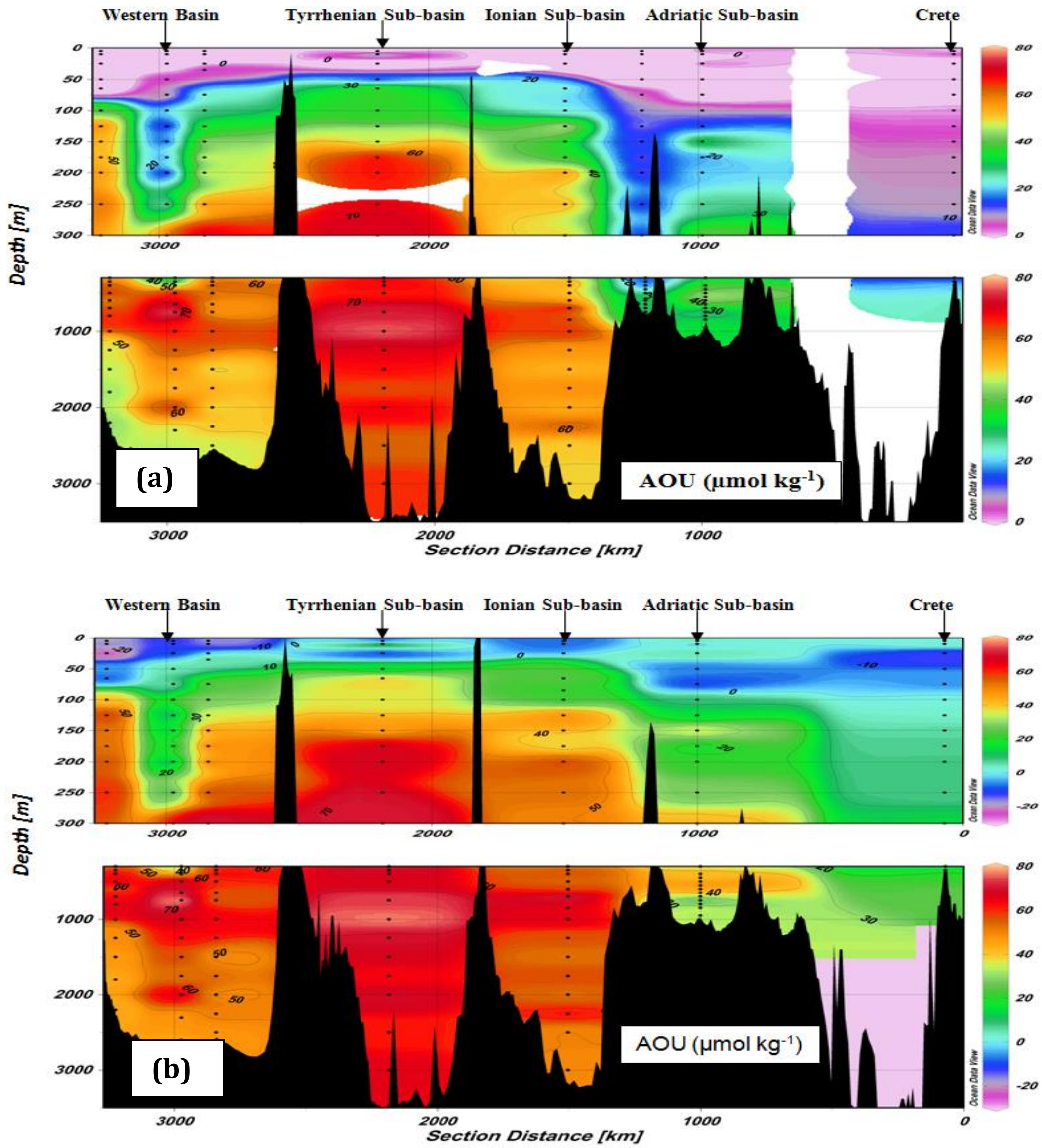


Fig.4. Vertical distribution of the apparent oxygen utilization (AOU ; µmol kg^{-1}) along the southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

High total alkalinity concentrations were recorded in the Mediterranean Sea (2588 ± 46 µmol kg^{-1}). The highest A_T concentrations were measured in the Eastern Mediterranean Basin (Max. A_T = 2666.0 ± 0.5 µmol kg^{-1}, at 300 m in the Antikythera Channel, near Crete), whereas the lowest A_T concentrations were measured in both Gibraltar Strait and the surface waters of the Western Mediterranean Basin (Min. A_T = 2377.0 ± 0.5 µmol kg^{-1} at 25 m in the Strait of Gibraltar). An Eastward increasing tendency for the total alkalinity is also well noticeable at all depths (Fig.5).

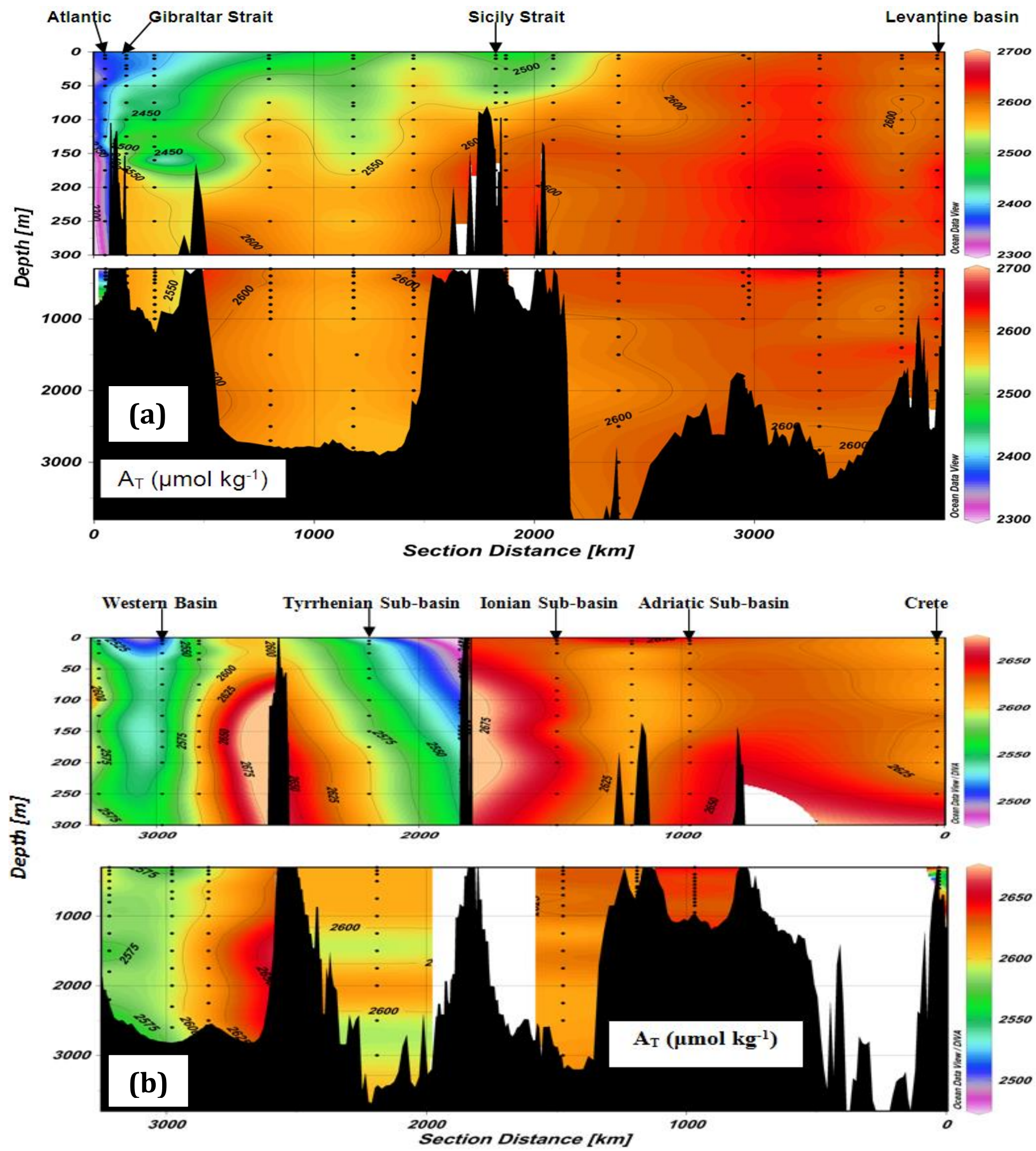


Fig.5. Vertical distribution of the total alkalinity (A_T ; µmol kg^{-1}) along the southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

Propagating Eastward, total dissolved inorganic carbon (C_T) varied between a minimum of 2095.0 ± 0.4 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 (Fig.6). However, it's 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.

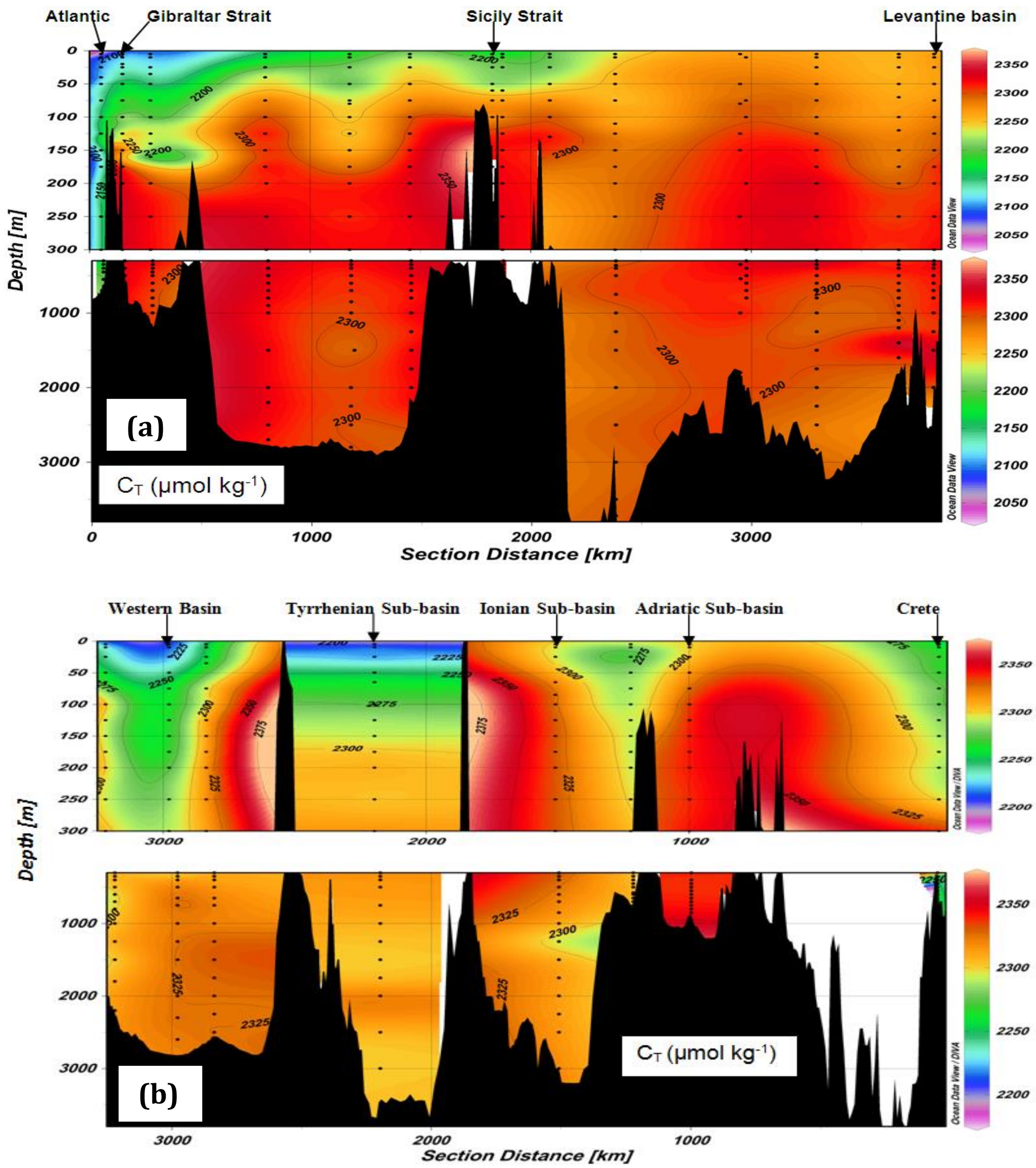


Fig.6. Vertical distribution of the total dissolved inorganic carbon (C_T ; µmol kg^{-1}) along the southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

In general, the C_T/A_T ratio decreases propagating from the West to the East of the Mediterranean Sea with the highest levels observed in the Western Basin, particularly in the intermediate layers (around 150 and 500 m, Fig.7).

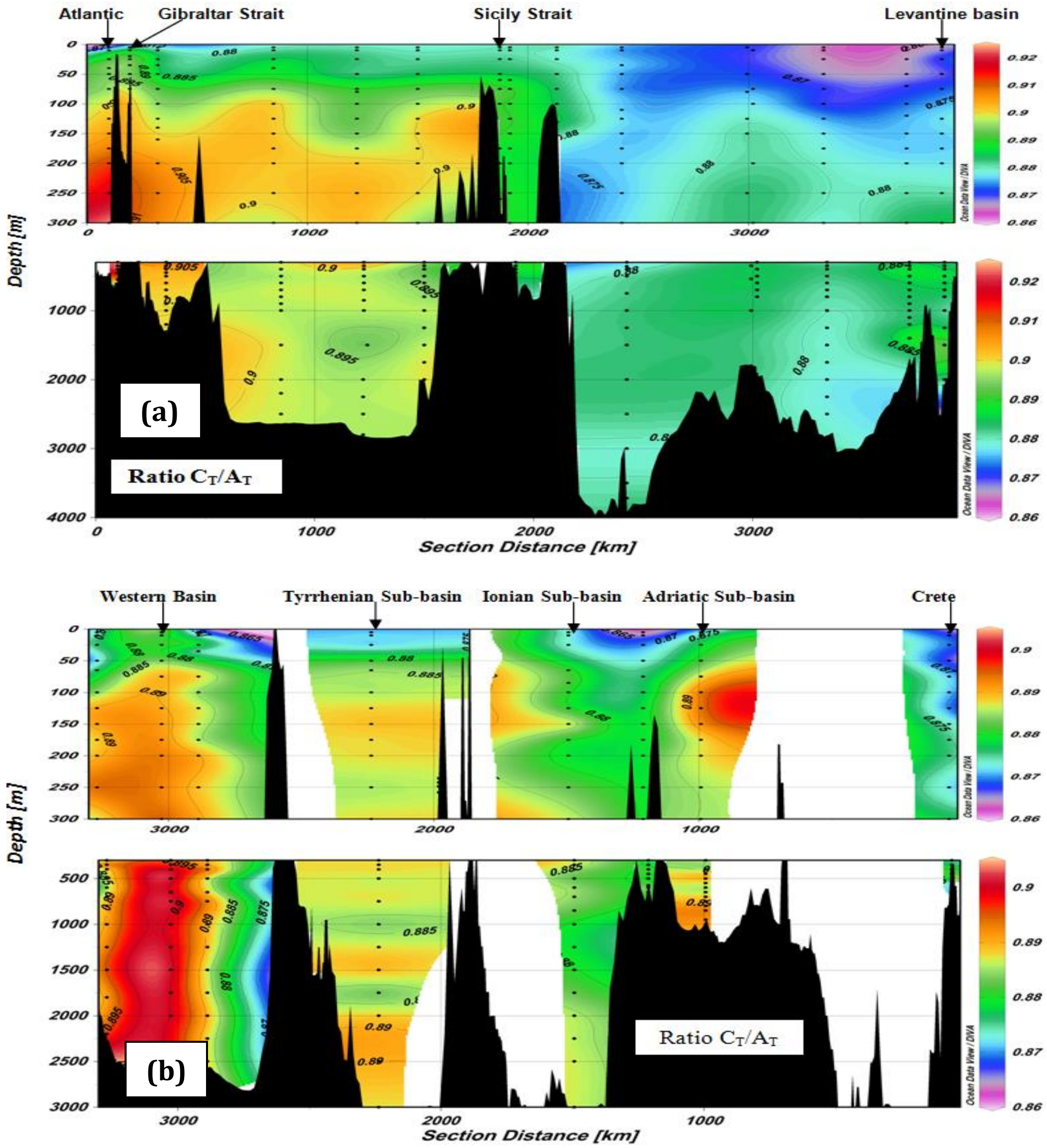


Fig.7. Vertical distribution of the ratio C_T/A_T (µmol kg^{-1}) along the southern (a) and the northern (b) sections of the 2013 MedSeA cruise.

The pH results, already published by Hassoun *et al.* (2015c), show that this parameter exhibits high and variable values in the surface layer (from 8.034 to 8.148 between 0 and 150 m), then an abrupt drop with depth to approximately 250 m, followed by a slight increase up to 1000 m and constant values, or a slight decrease, below this depth (Fig. 10). Horizontally, the surface mean pH values increase, propagating from the West to the East of the Mediterranean, from 8.078 ± 0.025 at the surface of the Alboran Sub-basin to 8.091 ± 0.018 and 8.112 ± 0.017 at the surface of the Levantine and Aegean Sub-basins respectively (Fig.10).

3.2.The carbonate system at basin and sub-basin scales

The average and standard deviation of the hydrographic, biogeochemical and carbonate system parameters are shown for both the Northern and Southern sections of the Mediterranean Sea in table 1 and for each sub-basin in table 2. The results indicate that the Southern and the Northern Mediterranean Sea are significantly different ($p < 0.05$) in terms of T, S and O_2, whereas the differences in terms of carbonate system parameters (A_T, C_T and pH) for both parts are highly significant ($p < 0.001$, Table 1).

Table.1. Average and standard deviation of hydrological, chemical and CO_2 system parameters in the Southern (1st leg) and Northern (2nd leg) sections of the Mediterranean Sea during the 2013 MedSeA cruise. P values were derived by applying a t-test: two-sample assuming unequal variances. P > 0.05 means the absence of any significant difference (-), P < 0.05 means the presence of a significant difference (*), and P < 0.001 indicates the presence of a highly significant difference (**).

	T (ºC)	S	O_2 (µmol kg^{-1})	A_T (µmol kg^{-1})	C_T (µmol kg^{-1})	pH	Ω Ca	Ω Ar
Southern Mediterranean Sea (1st leg ; n = 242)	14.92 ± 1.86	38.5 ± 0.5	205 ± 23	2578 ± 52	2285 ± 48	8.067 ± 0.032	4.54 ± 0.72	2.94 ± 0.46
Northern Mediterranean Sea (2nd leg ; n = 181)	14.43 ± 1.54	38.6 ± 0.3	213 ± 22	2602 ± 30	2300 ± 30	8.083 ± 0.034	4.63 ± 0.5	2.99 ± 0.45
P > 0.05 - P < 0.05 * P < 0.001 **	*	*	*	**	**	**	-	-

Table.2. Average and standard deviation of the hydrological, chemical and CO_2 system parameters in the main basins and sub-basins of the Mediterranean Sea during the 2013 MedSeA cruise.

	T (ºC)	S	O_2 (µmol kg^{-1})	A_T (µmol kg^{-1})	C_T (µmol kg^{-1})	pH	Ω Ca	Ω Ar

Surface (0-150m)								
Atlantic (n = 9)	17 ± 1	36.2 ± 0.8	233 ± 11	2362 ± 9	2103 ± 25	8.048 ± 0.048	4.38 ± 0.54	2.83 ± 0.35
Gibraltar Strait (n = 10)	15 ± 1	37 ± 1	217 ± 20	2446 ± 70	2196 ± 76	8.043 ± 0.16	4.26 ± 0.19	2.74 ± 0.12
Western Basin (n = 81)	15 ± 1	37.9 ± 0.5	231 ± 26	2526 ± 54	2236 ± 54	8.089 ± 0.025	4.86 ± 0.35	3.13 ± 0.23
Alboran Sub-basin (n = 9)	16 ± 1	36.7 ± 0.4	230 ± 5	2417 ± 28	2143 ± 45	8.078 ± 0.025	4.62 ± 0.33	2.98 ± 0.21
Algero-Provencal Sub-basin (n = 25)	14 ± 1	37.9 ± 0.4	232 ± 3	2522 ± 36	2243 ± 50	8.075 ± 0.024	4.69 ± 0.34	3.02 ± 0.22
Liguro-Provencal Sub-basin (n = 24)	14 ± 1	38.2 ± 0.3	234 ± 25	2563 ± 32	2261 ± 32	8.108 ± 0.02	5.04 ± 0.33	3.25 ± 0.22
Tyrrhenian Sub-basin (n = 8)	15 ± 2	38.2 ± 0.2	222 ± 15	2556 ± 18	2250 ± 34	8.105 ± 0.146	5.09 ± 0.34	3.29 ± 0.23
Eastern Basin (n = 79)	17 ± 2	38.8 ± 0.3	231 ± 12	2608 ± 28	2282 ± 29	8.094 ± 0.02	5.44 ± 0.34	3.53 ± 0.23
Ionian Sub-basin (n = 23)	16 ± 2	38.6 ± 0.4	228 ± 14	2591 ± 46	2275 ± 42	8.09 ± 0.023	5.26 ± 0.25	3.4 ± 0.17
Adriatic Sub-basin (n = 16)	16 ± 2	38.8 ± 0.1	237 ± 13	2621 ± 14	2302 ± 24	8.097 ± 0.02	5.32 ± 0.45	3.44 ± 0.3
Aegean Sub-basin (n = 8)	17 ± 1	39.07 ± 0.02	232 ± 7	2614 ± 6	2273 ± 10	8.112 ± 0.017	5.65 ± 0.16	3.66 ± 0.11
Levantine Sub-basin (n = 32)	18 ± 2	38.9 ± 0.2	228 ± 8	2613 ± 11	2278 ± 18	8.091 ± 0.018	5.58 ± 0.27	3.62 ± 0.19
Intermediate (150-500m)								
Atlantic (n = 7)	14 ± 1	36.3 ± 0.2	212 ± 12	2354 ± 18	2156 ± 24	7.954 ± 0.024	3.23 ± 0.26	2.09 ± 0.17
Gibraltar Strait (n = 5)	13.3 ± 0.2	38.3 ± 0.1	181 ± 18	2567 ± 11	2322 ± 11	8.021 ± 0.009	3.98 ± 0.09	2.57 ± 0.05
Western Basin (n = 66)	13.6 ± 0.5	38.5 ± 0.2	187 ± 16	2583 ± 33	2310 ± 25	8.062 ± 0.027	4.38 ± 0.29	2.83 ± 0.19
Alboran Sub-basin (n = 8)	13.3 ± 0.2	38.3 ± 0.2	170 ± 5	2537 ± 58	2294 ± 57	8.019 ± 0.011	3.91 ± 0.05	2.52 ± 0.03
Algero-Provencal Sub-basin (n = 20)	13.5 ± 0.2	38.5 ± 0.1	179 ± 10	2583 ± 20	2321 ± 12	8.045 ± 0.014	4.22 ± 0.14	2.72 ± 0.09
Liguro-Provencal Sub-basin (n = 21)	13 ± 0.1	38.4 ± 0.2	201 ± 18	2583 ± 22	2303 ± 17	8.082 ± 0.023	4.48 ± 0.22	2.88 ± 0.14
Tyrrhenian Sub-basin (n = 7)	14.21 ± 0.09	38.69 ± 0.05	178 ± 2	2604 ± 6	2310 ± 6	8.083 ± 0.004	4.69 ± 0.09	3.03 ± 0.06
Eastern Basin (n = 64)	15 ± 0.7	38.94 ± 0.09	208 ± 17	2622 ± 21	2311 ± 23	8.095 ± 0.012	4.94 ± 0.23	3.19 ± 0.15
Ionian Sub-basin (n = 14)	15 ± 0.6	38.9 ± 0.06	206 ± 15	2626 ± 15	2311 ± 19	8.099 ± 0.01	5 ± 0.2	3.23 ± 0.14
Adriatic Sub-basin (n = 15)	14 ± 0.4	38.86 ± 0.06	222 ± 11	2626 ± 12	2319 ± 20	8.097 ± 0.012	4.88 ± 0.18	3.15 ± 0.12
Aegean Sub-basin (n = 8)	15 ± 0.3	39.03 ± 0.02	226 ± 6	2598 ± 41	2278 ± 32	8.103 ± 0.014	5.04 ± 0.29	3.26 ± 0.19
Levantine Sub-basin (n = 27)	15 ± 0.7	38.9 ± 0.1	197 ± 14	2626 ± 17	2317 ± 15	8.088 ± 0.01	4.92 ± 0.25	3.18 ± 0.16
Deep (500-2500m)								
Atlantic	–	–	–	–	–	–	–	–
Gibraltar Strait (n = 2)	13.223 ± 0.009	38.492 ± 0.005	176.8 ± 0.5	2578 ± 1	2327 ± 2	8.024 ± 0.003	3.87 ± 0.02	2.5 ± 0.01
Western Basin (n = 65)	13.2 ± 0.1	38.49 ± 0.04	191 ± 9	2586 ± 17	2314 ± 11	8.029 ± 0.031	3.61 ± 0.42	2.36 ± 0.26
Alboran Sub-basin (n = 7)	13 ± 0.03	38.47 ± 0.01	187 ± 4	2559 ± 2	2305 ± 3	8.019 ± 0.008	3.65 ± 0.16	2.37 ± 0.1
Algero-Provencal Sub-basin (n = 26)	13.2 ± 0.1	38.48 ± 0.03	191 ± 9	2579 ± 9	2315 ± 10	8.018 ± 0.026	3.52 ± 0.43	2.3 ± 0.27
Liguro-Provencal Sub-basin (n = 25)	13 ± 0.1	38.47 ± 0.01	196 ± 10	2595 ± 17	2318 ± 12	8.037 ± 0.035	3.66 ± 0.44	2.38 ± 0.27
Tyrrhenian Sub-basin (n = 7)	13.5 ± 0.2	38.57 ± 0.06	182 ± 6	2602 ± 11	2308 ± 9	8.052 ± 0.026	3.76 ± 0.45	2.45 ± 0.28
Eastern Basin (n = 64)	13.8 ± 0.3	38.76 ± 0.05	196 ± 14	2614 ± 12	2309 ± 18	8.077 ± 0.023	4.2 ± 0.42	2.73 ± 0.26
Ionian Sub-basin (n = 16)	13.8 ± 0.1	38.74 ± 0.04	198 ± 7	2612 ± 13	2306 ± 12	8.066 ± 0.027	3.96 ± 0.49	2.59 ± 0.3
Adriatic Sub-basin (n = 14)	13.6 ± 0.3	38.74 ± 0.05	218 ± 8	2622 ± 14	2324 ± 20	8.083 ± 0.016	4.42 ± 0.21	2.86 ± 0.13
Aegean Sub-basin (n = 2)	14.7 ± 0.03	39.015 ± 0.004	219 ± 1	2594 ± 1	2261 ± 1	8.124 ± 0.000005	4.97 ± 0.02	3.23 ± 0.01
Levantine Sub-basin (n = 32)	13.8 ± 0.1	38.75 ± 0.02	187 ± 5	2611 ± 7	2305 ± 12	8.077 ± 0.02	4.17 ± 0.37	2.72 ± 0.23
Bottom (>2500m)								
Atlantic	–	–	–	–	–	–	–	–

Gibraltar Strait	–	–	–	–	–	–	–	–
Western Basin (n = 4)	13.4 ± 0.1	38.477 ± 0.004	199 ± 9	2580 ± 11	2310 ± 10	7.974 ± 0.017	2.76 ± 0.06	1.83 ± 0.05
Alboran Sub-basin	–	–	–	–	–	–	–	–
Algero-Provencal Sub-basin (n = 2)	13.34 ± 0.01	38.475 ± 0.001	200 ± 3	2573 ± 10	2308 ± 10	7.968 ± 0.001	2.72 ± 0.04	1.8 ± 0.02
Liguro-Provencal Sub-basin (n = 1)	13 ± 0.0	38.5 ± 0.0	208 ± 0.0	2582 ± 0.0	2322 ± 0.0	7.962	2.75	1.82
Tyrrhenian Sub-basin (n = 1)	13.5 ± 0.0	38.5 ± 0.0	187 ± 0.0	2594 ± 0.0	2302 ± 0.0	7.999	2.84	1.89
Eastern Basin (n = 5)	14 ± 0.06	38.73 ± 0.02	201 ± 4	2604 ± 2	2293 ± 4	8.007 ± 0.018	2.9 ± 0.2	1.94 ± 0.13
Ionian Sub-basin (n = 4)	14 ± 0.06	38.719 ± 0.002	203 ± 1	2607 ± 4	2295 ± 2	8.003 ± 0.017	2.84 ± 0.18	1.89 ± 0.11
Adriatic Sub-basin	–	–	–	–	–	–	–	–
Aegean Sub-basin	–	–	–	–	–	–	–	–
Levantine Sub-basin (n = 1)	14.00 ± 0.04	38.76 ± 0.00	194.5 ± 0.0	2601 ± 0.0	2288 ± 0.0	8.027	3.13	2.08

Moreover, our results indicate that the hydrographic, biogeochemical and carbonate system characteristics of both the Western and the Eastern Mediterranean Basins are very significantly different (Table 3).

Table.3. Average and standard deviation of hydrological, chemical and CO_2 system parameters in the Western and Eastern Mediterranean basins during the 2013 MedSeA cruise. P values were derived by applying a t-test: two-sample assuming unequal variances. P > 0.05 means the absence of any significant difference (-), P < 0.05 means the presence of a significant difference (*), and P < 0.001 indicates the presence of a highly significant difference (**).

	T (ºC)	S	O_2 (µmol kg^{-1})	A_T (µmol kg^{-1})	C_T (µmol kg-1)	pH	Ω Ca	Ω Ar
Western Basin (n=214)	14 ± 1.3	38.26 ± 0.5	205 ± 26	2563 ± 48	2284 ± 51	8.06 ± 0.038	4.3 ± 0.65	2.78 ± 0.41
Eastern Basin (n=209)	15 ± 2	38.84 ± 0.2	212 ± 20	2614 ± 23	2299 ± 28	8.087 ± 0.024	4.8 ± 0.68	3.15 ± 0.43
P > 0.05 - P < 0.05 * P < 0.001 **	**	**	*	**	**	**	**	**

3.3.Water masses characterization in the Mediterranean Sea

Vertical distributions of temperature, salinity, pH, A_T and C_T and θ/S diagrams applied for to the 2013 MedSeA cruise data, outline the presence of distinct water masses in both the Eastern and Western Mediterranean basins from the surface to the bottom (Fig. 2 to 10 ; Table 2).

-Atlantic Water (AW): The characteristics of this water mass change while propagating from the Strait of Gibraltar (15 ± 1 ºC, 36.3 ± 0.9, 217 ± 20 µmol kg^{-1}, 8.043 ± 0.16, 2446 ± 70 µmol kg^{-1}, 2196 ± 76 µmol kg^{-1}, 4.26 ± 0.19 µmol kg^{-1} and 2.74 ± 0.12 µmol kg^{-1} for T, S, O_2, pH, A_T, C_T, Ω Ca and Ω Ar respectively) to become warmer, saltier, more oxygenated, more oversaturated with respect to calcite and aragonite, with higher pH, A_T and C_T concentrations in the Levantine Sub-basin (Table 2 ; Fig.2 to 10).

-Levantine Surface Water (LSW): This water is easily distinguished in the surface layer of the Eastern Sub-basins (above 100 m) by the maximum temperatures (> 17 ºC) and salinities (> 38.8) measured in the entire Mediterranean Sea (as seen in the θ/S diagrams shown in Fig.8). The LSW is characterized by high O_2 (228 ± 8 µmol kg^{-1}), A_T (2612 ± 10 µmol kg^{-1}) and C_T (2271 ± 13 µmol kg^{-1}) concentrations.

-Levantine Intermediate Water (LIW): It is detected in both Levantine and Ionian Sub-basins (Fig.8), around 250 m, with O_2 equal to 212 ± 10 µmol kg^{-1}, high pH (8.094 ± 0.009), high A_T (2635 ± 15 µmol kg^{-1}) and C_T (2315 ± 16 µmol kg^{-1}) concentrations and a high degree of saturation with respect to calcite (> 5) and aragonite (> 3.3). However, this water was found around 400 m in the Western Basin (Fig.9), with a maximum salinity (38.55 ± 0.12) corresponding to O_2 = 184 ± 4 µmol kg^{-1}, A_T = 2590 ± 16 µmol kg^{-1}, C_T = 2314 ± 10 µmol kg^{-1}, pH = 8.064 ± 0.026, **Ω** Ca = 4.36 ± 0.26 and **Ω** Ar = 2.82 ± 0.17.

-Cretan Intermediate Water (CIW): It has been detected between 250 and 300 m, in the Aegean Sub-Basin. The highest A_T concentrations (2650 ± 22 µmol kg^{-1}) were measured in this intermediate water during the entire 2013 MedSeA cruise (Fig.8). The warm (15.4 °C) and saline (39) CIW was well oxygenated (204 ± 3 µmol kg^{-1}). In addition, it presents higher C_T levels (2318 ± 28 µmol kg^{-1}) than those measured in the surface and deep layers of the Aegean Sub-basin.

-Tyrrhenian Deep Water (TDW): This water mass is colder (13.5 ± 0.1 °C), less saline (38.55 ± 0.05) and more oxygenated (184 ± 6 µmol kg^{-1}) than the LIW in the Tyrrhenian Sub-basin. At the same time, it is warmer, more saline and less oxygenated than the WMDW. TDW is also characterized by A_T (2601 ± 12 µmol kg^{-1}) and C_T (2307 ± 10 µmol kg^{-1}) concentrations higher than those of the WMDW.

-Western Mediterranean Deep water (WMDW): This water mass occupies layers below 1500 m in the Western Mediterranean Basin (Fig.9, 10). WMDW is colder (13.3 ± 0.05 ºC) and fresher (38.474 ± 0.005) than the EMDW. Moreover, it has lower A_T (2588 ± 18 µmol kg^{-1}), and higher C_T concentrations (2316 ± 10 µmol kg^{-1}) than the EMDW.

-Eastern Mediterranean Deep Water (EMDW): Pre-EMT (Eastern Mediterranean Transient) EMDW water, typified by a minimum salinity value (38.738 ± 0.003), was noted at around 1000 m in the Levantine Sub-basin. The temperature of this water mass is equal to 13.74 ± 0.02 °C, O_2 = 186 ± 2 µmol kg^{-1}, A_T = 2612 ± 11 µmol kg^{-1} and C_T = 2303 ± 10 µmol kg^{-1}, pH = 8.088 ± 0.006, **Ω** Ca = 4.3 ± 0.1, and **Ω** Ar = 2.8 ± 0.06. Below Pre-EMT, temperature and salinity increase again, indicating the presence of the EMT-EMDW produced in the Aegean Sub-basin. The θ–S diagram indicates that the deep layers of the Levantine Sub-basin are still occupied by the warmest (13.9 ± 0.08 ºC) and the most saline (38.763 ± 0.003) EMDW, originated in the Aegean Sub-basin, with O_2 = 193 ± 1 µmol kg^{-1}, A_T = 2605 ± 7 µmol kg^{-1}, C_T = 2293 ± 10 µmol kg^{-1}, pH = 8.046 ± 0.015, **Ω** Ca = 3.5 ± 0.3, and **Ω** Ar = 2.3 ± 0.2 (Fig.8). Post EMT-EMDW was occupying the bottom layers of the Ionian Sub-basin and the South of Crete (> 2500 m), with T = 13.9 ± 0.06 ºC, S = 38.72 ± 0.001, O_2 = 203 ± 1 µmol kg^{-1}, A_T = 2608 ± 6 µmol kg^{-1} and C_T = 2303 ± 13 µmol kg^{-1}, pH = 7.99 ± 0.01, Ω Ca = 2.77 ± 0.13, and Ω Ar = 1.85 ± 0.08 (Fig.8 and 10).

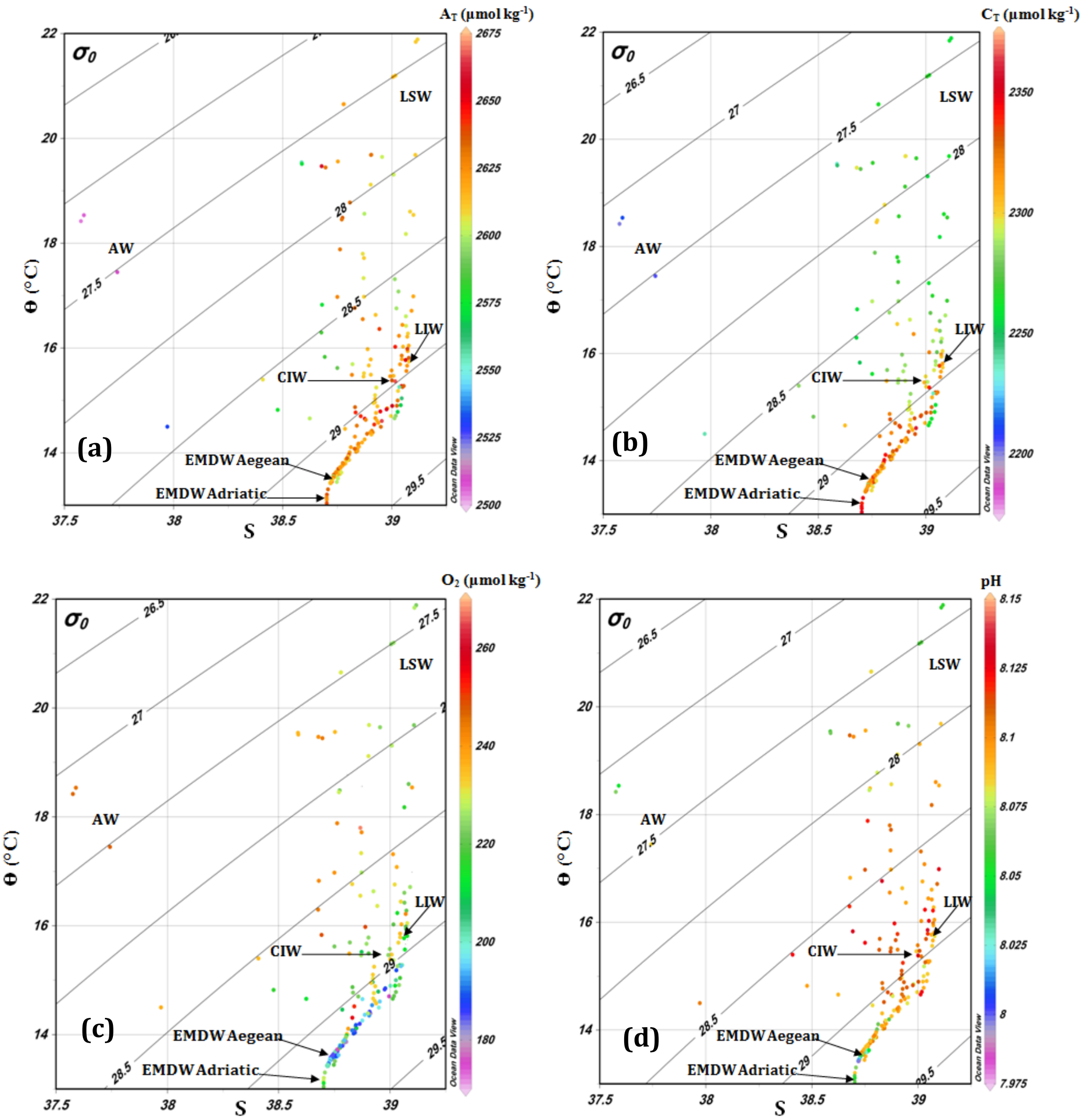


Fig.8. θ/S diagrams with total alkalinity (A_T, µmol kg^{-1} ; a), total dissolved inorganic carbon (C_T, µmol kg^{-1} ; b), dissolved oxygen (O_2, µmol kg^{-1} ; c) and pH (d) for the Eastern Mediterranean Basin during the 2013 MedSeA cruise.

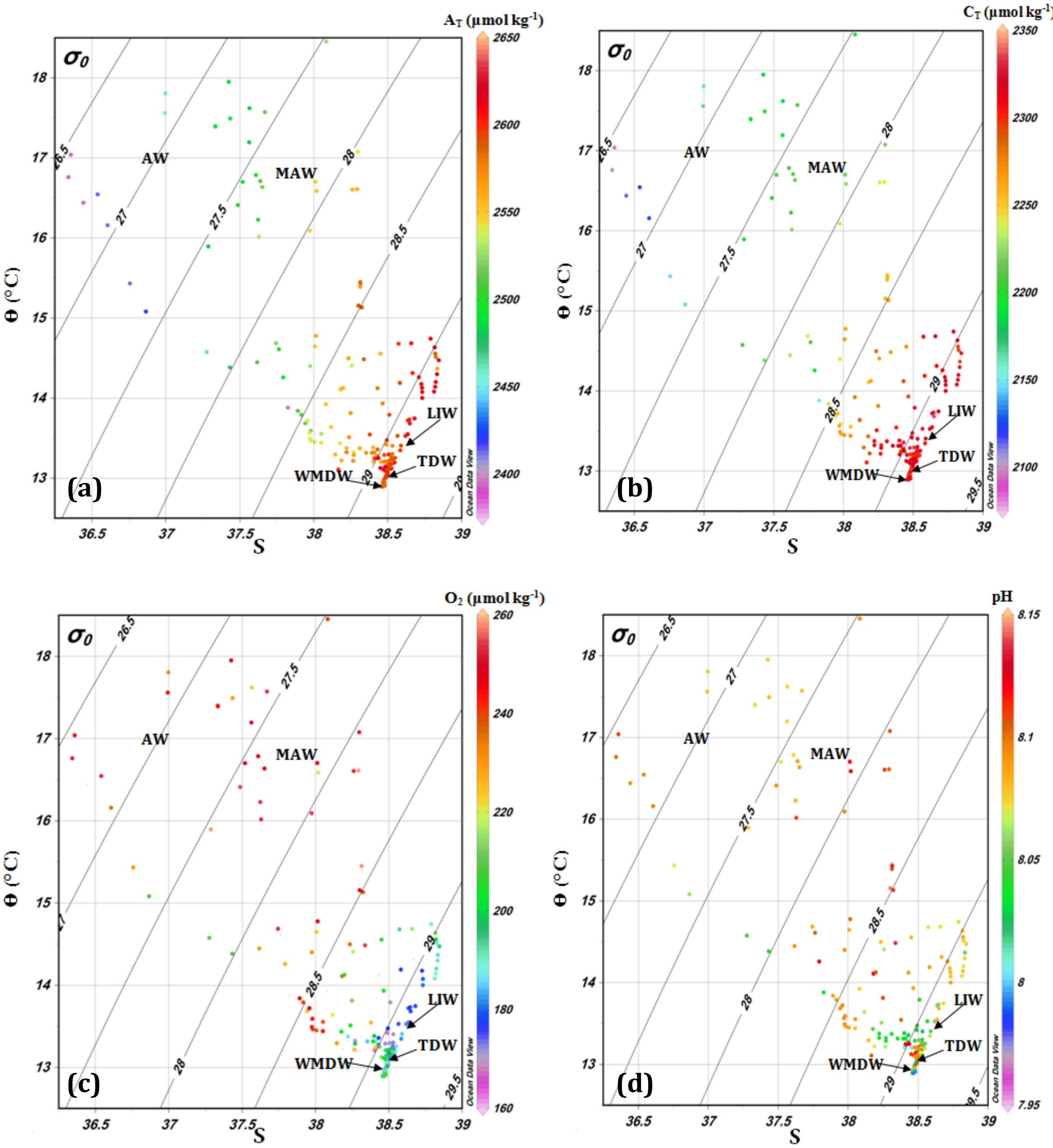


Fig.9. θ/S diagrams with total alkalinity (A_T, µmol kg^{-1} ; a), total dissolved inorganic carbon (C_T, µmol kg^{-1} ; b), dissolved oxygen (O_2, µmol kg^{-1} ; c) and pH (d) for the Western Mediterranean Basin during the 2013 MedSeA cruise.

4. Discussion

4.1. Overall trend of the hydrographic, biogeochemical and carbonate system parameters in the Mediterranean Sea

As a consequence of the surface heat loss and the excessive evaporation, specifically in the Levantine Sub-basin (Hassoun *et al.*, 2015b), the general pattern of T (ºC) in the Mediterranean Sea is an Eastward global increase (Fig.2 ; a, b). Termed as “evaporation basin”, this sea is characterized by high salinities with a remarkable Eastward increase, similar to that of the temperature, in both the Southern and Northern parts (Fig.3 ; a, b). The annual mean of the budget "evaporation minus precipitation (E-P)" is positive over the whole Mediterranean Sea (350-750 mm yr^{-1}), particularly in the Levantine Sub-basin where E-P is over 750 mm yr^{-1}. Thus, the Mediterranean Sea is considered as a "concentration basin" and the Levantine Sub-basin is believed to be one of the regions providing the maximum water supply to the atmosphere in this semi-enclosed sea (Mariotti *et al.*, 2002). In addition, the annual precipitation is about half the evaporation and river discharges with an estimated freshwater deficit of about 2500 km^3 y^{-1} (EEA, 1999). These facts explain the high salinities measured in this sea and the Eastward increasing trend of this parameter. Our salinity results are in a good agreement with the ones recently published by Álvarez *et al.* (2014) with a slight difference of + 0.036 in the entire Mediterranean Sea.

As shown by Zenetos *et al.* (2002), our results reveal that surface layers of this sea are almost saturated by dissolved oxygen. In the intermediate layers, the highest O_2 concentrations were located in the Eastern Basin (Fig.4), probably because of the drowning of oxygenated, warm and salty (thus dense) waters from the surface to the intermediate layers in this basin. Western Basin presents, slightly lower O_2 concentrations than those in the Eastern Basin, due to the different residence time of the waters in these two sub-basins.

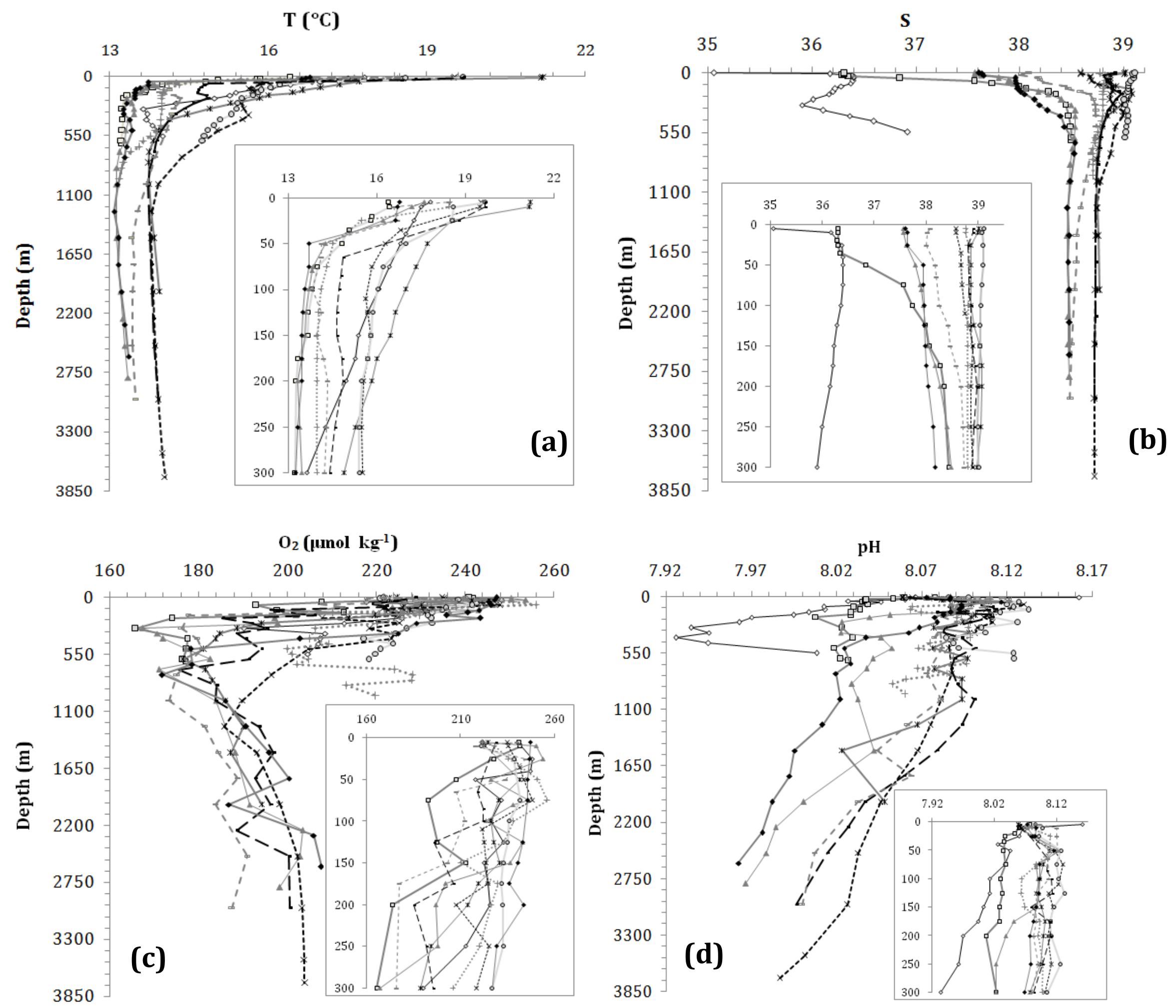
The low AOU detected in the intermediate layers of the Eastern Basin are probably because of the drowning of oxygenated, warm and salty (thus dense) waters from the surface to the intermediate layers (Fig.4). Also, the AOU demonstrate that the low O_2 concentrations observed at the intermediate and deep layers of the Western Basin, particularly in the Alboran Sub-basin, are directly correlated to the high oxidation rate at these depths. El Boukhary *et al.* (2002) indicated a significant decrease of O_2 concentrations (~ 0.2 % per year) since 1988, in the deep Alboran Sub-basin exclusively linked to the intense primary productivity in the surface layer, and an increase in the Eastern Basin related to the oxygen input coming from the Aegean Sub-basin new deep water.

Since it has high salinities and it is oversaturated by calcite and aragonite ($\Omega >> 1$), the total alkalinity of the Mediterranean Sea is also high. This sea presents A_T concentrations higher than those registered in the Atlantic station (Hassoun *et al.*, 2015b), confirming the concentrating behavior of the Mediterranean Sea and its role as a re-mineralization area. Atlantic water inflowing from the Strait of Gibraltar into the Mediterranean Sea can be clearly identified by its low A_T signature (Fig.5). Our A_T measurements are in agreement with the results of Schneider *et al.* (2007), Souvermezoglou *et al.* (2010), Touratier and Goyet (2011). Furthermore, it is slightly higher than those published by Álvarez *et al.*, (2014) with a difference of ± 16 µmol kg^{-1}. This difference could be attributed firstly to the seasonal variation of the A_T in this sea, since our cruise was conducted during May 2013 and the other cruise (Meteor 84/3) during April 2011 and secondly this discrepancy could also be induced by variations in the freshwater inputs by the rivers and the Black Sea. Freshwater inputs into coastal zones play a crucial role in the spatial variations of A_T concentrations within this semi-enclosed sea. A total alkalinity budget shows that the main total alkalinity inputs come from the Black Sea and from rivers (between 2000 µmol kg^{-1} and 6500 µmol kg^{-1}), whereas the Strait of Gibraltar and the carbonate sedimentation appear to be net sinks (Schneider *et al.*, 2007). This explains the high A_T concentrations measured nearby the coastal zones or in sub-basins highly influenced by riverine inputs, such as the Po river impacts on the A_T concentrations in the Adriatic Sub-basin (Fig.5, 10 ; Table 2).

The fact that the intermediate and deep layers of the Western Basin have high C_T levels, while the surface layers of this basin have, comparatively, low C_T concentrations (Fig.6, 10 ; Table 2, 3), indicates that the Western Basin might play a role in the sequestration of the atmospheric CO_2 absorbed mainly by the Eastern Basin (where high C_T levels were detected on its surface waters). This statement is in harmony with the clear Eastward pCO_2 trend outlined by Gemayel *et al.* (2015) during the same cruise (2013 MedSeA). Moreover, the high C_T concentrations in the Western Basin were detected in the minimum oxygen zone observed within the entire Mediterranean Sea (Fig.6 a). This can be a direct consequence of the CO_2 released by the respiration of organisms and the decomposition of organic matter (Touratier and Goyet, 2011). Respiration in the deepest Mediterranean waters accounts for a greater percentage of the upper aphotic zone respiration (over 45%) than that found in the open oceans (below 21% ; La Ferla *et al.*, 2003). The C_T concentrations measured in this study were higher than the ones noted by Álvarez *et al.* (2014) with a difference of + 18 µmol kg^{-1}. This difference could be due to the seasonal variability of the C_T concentrations in the Mediterranean Sea, since it is directly related to the biological activity which is connected to the availability of nutrients loaded mainly by the rivers inputs. It could also be attributed to the high anthropogenic CO_2 invasion in the Mediterranean seawater (Hassoun *et al.*, 2015c).

The variability of the carbonate system in the surface layer can be ascribed in certain areas (e.g. The Western Mediterranean Basin) to the upwelling of CO_2-rich deep waters and to biological production. The vertical mixing of the surface water with deeper water causes a decrease of the pH, while primary production increases the pH of seawater as a result of the displacement of the carbonate equilibrium related to CO_2 consumption. The pH vertical Eastward trend, illustrated by Hassoun *et al.* (2015c), is similar to those reported by Santana-Casiano *et al.* (2002) and Rivaro *et al.* (2010). Taking into account that the Mediterranean Sea is considered as one of the most impacted regions by acidification, the low pH values in the Western Basin are attributed to the excessive accumulation of anthropogenic CO_2 in this basin where high C_T concentrations were measured in its intermediate and deep layers in parallel with high invasion of anthropogenic CO_2 in those layers (Hassoun *et al.*, 2015c).

One of the important processes controlling the concentrations of C_T and A_T in both surface and deep waters is the formation and dissolution of calcium carbonate ($CaCO_3$) tests. Within surface waters, plankton convert dissolved bicarbonate ions (HCO_3^-) to $CaCO_3$ and dissolved carbon dioxide. In deep water, some of the $CaCO_3$ dissolves and the remainder is buried in the sediment (Sabine *et al.*, 2002). A recent study by Oviedo *et al.* (2014) shows that coccolithophores are a dominant phytoplankton group in the entire Mediterranean Sea ; they have life stages that are expected to respond differently to the variability in seawater carbonate chemistry and nutrient concentrations. Otherwise, C_T/A_T ratio is an indicative of the concentration of carbonates ; the lower the ratio the higher the CO_3^{2-} concentration (Álvarez *et al.*, 2014). Our results indicate that the Eastern Basin (0.879 ± 0.006) has lower C_T/A_T ratio than the Western Basin (0.891 ± 0.008, Fig.8), which means that the Eastern Basin has higher carbonate concentrations than the Western Basin. Dissolving in seawater, CO_2 causes a suite of changes in the carbonate system : the concentrations of dissolved CO_2, total dissolved inorganic carbon, and the bicarbonate ion increase, while pH, and carbonate ion concentration decrease (Cooley *et al.*, 2012). These facts explain the high C_T/A_T ratio in the Western Basin.



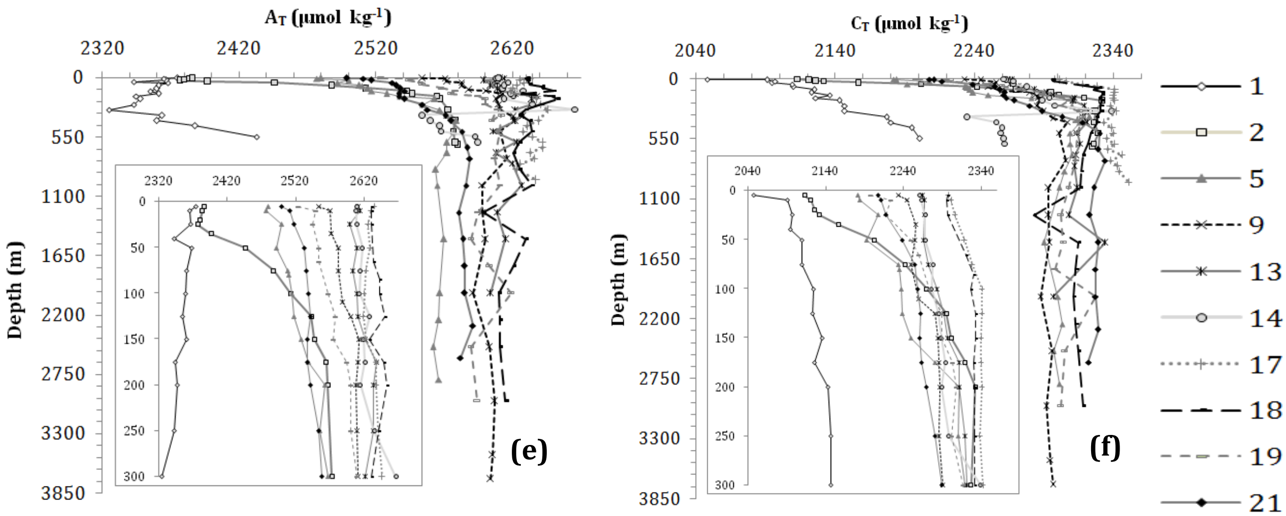


Fig.10. Profiles of Temperature (T, ºC ; a), salinity (S ; b), dissolved oxygen (O_2, µmol kg^{-1} ; c), pH (d), total alkalinity (A_T, µmol kg^{-1} ; e) and total dissolved inorganic carbon (C_T, µmol kg^{-1} ; f) for selected stations.

4.2. Are the main sections of the Mediterranean Sea different biogeochemically?

4.2.1. Southern section Vs. Northern section

Water circulation within the Mediterranean Sea itself is very slow, largely because of major sills that isolate the various basins (e.g. sills between the Western and Eastern Basins). This partitioning leads to differentiation between these isolated areas in terms of biogeochemical properties, as seen clearly in the above schemes (Fig.2-7). Comparing the two cruise's legs (Table 1) based on t-test statistical analysis, we noticed that the Northern and the Southern sections of the Mediterranean Sea are either significantly different ($P < 0.05$) or highly significantly different ($P < 0.001$) in terms of hydrographic and carbonate system features. Since the damming of the Nile River in 1964, most of the freshwater entering the Mediterranean comes from southward flowing rivers. The Rhône [main freshwater and sediment supplier to the Mediterranean Sea (Sempéré *et al.*, 2000)], Po (Cozzi and Giani, 2011) and Ebro are the major inputs of freshwater into the Mediterranean (Crivelli *et al.*, 1995). Skliris and Lascaratos (2004) described the influence of the construction of the Assouan dam on the thermohaline circulation in the Mediterranean, and they mentioned that all rivers' contributions flowing into the Mediterranean Sea were reduced by 50% since 150 years because of the establishment of numerous dams. These facts explain the low T and high A_T concentrations measured in the North, always fed by freshwater inputs, compared to the South of the Mediterranean Sea. Moreover, the results indicate that the Northern Mediterranean waters are more oxygenated and have higher pH values and C_T concentrations than those of the South. This could be ascribed to the massive A_T and nutrients inputs, coming from the Northern rivers, especially during the ice melting season (from March to May) which stimulates the primary production in this area and increase then the oxygen levels generated by the photosynthesis on the sea surface and the amount of re-mineralization in the intermediate layers (Hassoun *et al.*, 2015b).

4.2.2. Western Basin Vs. Eastern Basin

Since the evaporation exceeds precipitation and river runoff, the Mediterranean Sea continuously transforms Atlantic Surface Water (T = 15 ± 1 ºC, S = 37.0 ± 0.9) into cooler (13.223 ± 0.009 ºC) (hence denser) and saltier (38.492 ± 0.005) water. This AW sinks in the sub-basins of the Eastern (the Levantine, the Aegean, and the Adriatic) and the Western Mediterranean (the Liguro-Provencal ; Lacombe and Tchernia, 1960 ; Hassoun *et al.*, 2015a).

The Western and Eastern Mediterranean Basins have also significant biogeochemical characteristic differences, due to the complex distinct topography of the two basins, the diversity of mixing processes involved, the variability of atmospheric forcing at various time scales, the variety of water mass formation processes and other biologically-driven phenomena present in each basin. This fact explains our results which show that the waters of the Eastern Basin are warmer, saltier, more oxygenated, and have higher A_T and C_T concentrations than the Western Basin Waters. Moreover, the degree of saturation of calcite and aragonite, calculated in the Mediterranean Sea, indicates that the Eastern waters are more saturated with respect to calcite and aragonite (Hassoun *et al.*, 2015c). These differences are due to the inflow of freshwater characterized by high alkalinity, from the Northeastern rivers as well as from the Black Sea, which contributes to the oxygen production by primary production at surface and thus to an enhanced re-mineralization rates/C_T and carbonate ions production at intermediate layers. The deep Mediterranean waters are more saturated with respect to calcite and aragonite than the Atlantic waters at the same depths ; which is attributed to the relatively higher pH values in deep Mediterranean waters (Millero *et al.*, 1979). Hassoun *et al.* (2015c) have also indicated that the Western Basin waters are more acidic than the Eastern waters which is directly correlated to the high anthropogenic carbon sequestration in the Western Basin, where ΔpH is rarely less than −0.1 pH unit.

Our A_T and C_T concentrations are in a good agreement with those mentioned by Rivaro *et al.* (2010) with small difference with respect to the Eastern Basin measurements (± 2 µmol kg^{-1} and ± 5 µmol kg^{-1} for A_T and C_T respectively) and bigger one with respect to the Western Basin measurements (± 14 µmol kg^{-1} and ± 15 µmol kg^{-1} for A_T and C_T respectively). These differences are ascribed mainly to the different cruises tracks and to the distribution of the stations between the North and the South, the Eastern and the Western Basins of the Mediterranean Sea.

4.3. Water masses characterization in Western and Eastern Mediterranean Basins and Sub-basins

The above figures and tables reveal the presence of distinct water masses, from the surface to the bottom :

-Atlantic Water (AW): The Mediterranean Sea has an active water exchange with the Northern Atlantic through the Strait of Gibraltar. The surface Atlantic flow entering the Mediterranean Sea does not only fill the water deficit of 1 m per year, but it also replace the Mediterranean deep outflow, which represents a loss of 20 m of water per year for the whole Mediterranean Sea

(Béthoux, 1980). As a consequence of the excess of evaporation over precipitation (~ 0.62 – 1.16 m $year^{-1}$; Hopkins, 1978), heating and various physical phenomena (gyres, eddies,...), the characteristics of the AW change while propagating from the Strait of Gibraltar to become warmer, saltier, more oxygenated, more oversaturated with respect to calcite and aragonite, with higher pH, A_T and C_T concentrations in the Levantine Sub-basin (Table 3 ; Fig.2-7). As the typical Mediterranean Waters circulate (together with AW in general) within the sea and outflow (contrary to AW) from the Eastern Basin into the Western Basin through the Channel of Sicily and into the ocean through the Strait of Gibraltar, there is some mixing between them so that they can be more or less differentiated. The mixing of the AW with some of the typical Mediterranean waters in some specific places is so intense that they can be completely ‘‘lost’’ (Millot *et al.*, 2006). However, our results indicate that these two waters masses could be differentiated based on their oversaturation with respect to calcite and aragonite ; since the Mediterranean waters (LSW in the upper layers) are more oversaturated by 0.8 ± 0.03 and 0.58 ± 0.03 for calcite and aragonite respectively.

-Levantine Surface Water (LSW): This water is formed by intensive heating and evaporation in the Eastern part of the Mediterranean Sea. As a consequence of the high alkalinity inputs, from rivers as well as from the Black Sea, in the Levantine and Aegean Sub-basins, the LSW could also be differentiated by its relatively high pH values (> 8.06) and its remarkable oversaturation with respect to calcite (> 5.5) and aragonite (> 3.5). The calcite and aragonite saturation state increases as a function of increasing pH. However, the surface acidity increases, thus there is relatively less carbonate ion (CO_3^{2-}) in seawater. Consequently, the value of Ω decreases and so does the saturation state of seawater with respect to calcite and aragonite. The deeper penetration of the LSW that was found at station 11 in the Eastern Basin (Fig.8) could be due to the presence of the anti-cyclonic gyre able to push surface waters down to 200 m, as the one shown in the Sea Level Anomaly (SLA) map on 15 June 2007 (Kovačević *et al.*, 2009).

-Levantine Intermediate Water (LIW): Levantine Intermediate Water (LIW) is a warm salty water formed in one out of four main zones of dense water formation in the Mediterranean Sea (Millot, 2013). The main formation area of LIW is located in the Northern Levantine Sub-basin (Arsouze *et al.*, 2013). This water spreads Westward and contributes predominately to the non-returning efflux, mixed with both EMDW and WMDW, in the Strait of Gibraltar, and then into the Atlantic Ocean (Özsoy *et al.*, 1993 ; Robinson *et al.*, 2001 ; Manca *et al.*, 2004). Our results show that the LIW is the main intermediate water mass in the entire Mediterranean Sea. It is well recognized on the θ–S diagrams, anywhere in this sea as far as the Western Basin, by the typical form "scorpion tail", defined by Lacombe and Tchernia (1972) and Lacombe *et al.* (1985), which makes it the easiest water mass to follow. The main CO_2 property identifying LIW in any Mediterranean Sub-basin is a maximum intermediate A_T (Álvarez *et al.*, 2014). In our study, the LIW was detected, in both Levantine and Ionian Sub-basins, around 250 m, above the layer of maximum organic matter mineralization, whereas it was found around 400 m in the Western Basin, in agreement with the findings of Manca *et al.* (2004), Millot *et al.* (2006), Rivaro *et al.* (2010).

The Mediterranean Sea presents two internal thermohaline cells that circulate dense water masses. This latter are formed by convective events in the Northern Mediterranean sub-basins, mainly in correspondence to topographically controlled cyclonic gyres both in the Western and in the Eastern Mediterranean Sea.

-Western Mediterranean Deep water (WMDW): This homogenous water mass is formed in the Liguro-Provencal Sub-basin (Millot *et al.*, 2006), mainly in the Gulf of Lions, where strong cold and dry winds induce the LIW and AW mixing, and fills the deeper levels of the Western Basin (Manca *et al.*, 2004). WMDW is colder and fresher than the EMDW, since its zone of formation witnesses a continuous freshwater input from the Mediterranean main rivers. The ranges of our measured parameters in the WMDW are in a good agreement with those mentioned by Rivaro *et al.* (2010) and Álvarez *et al.* (2014). Data collected since the 1960s (Lacombe *et al.*, 1985) have shown (Béthoux *et al.*,1990) that WMDW is submitted to a significant warming and salinification (linear trends: ~ +0.03 °C/decade, ~ +0.01/decade), attributed up to now either to anthropogenic modifications (Rohling and Bryden,1992), especially the Nile damming, or to change in Mediterranean climatic conditions (Béthoux *et al*., 1990). A study by Vargas-Yáñez *et al*. (2010) further suggests that the intermediate and surface waters of the Western Mediterranean Sea are warming too.

At the Strait of Gibraltar, Santana-Casiano *et al.* (2002) and Rivaro *et al.* (2010) mentioned that the LIW and the WMDW are characterized by the same salinity and they could only be differentiated by pH values. However, our results show that LIW and WMDW have similar T (13.2 °C), S (38.45 ± 0.05) and C_T concentrations (2327 ± 2 μmol kg^{-1}), whereas the LIW is less oxygenated (169 ± 5), have lower A_T concentrations (2570 ± 4), and it is more acidic (8.015 ± 0.011) and more oversaturated with respect to calcite (3.96 ± 0.06) and aragonite (2.55 ± 0.04) than the WMDW (O_2 = 177 ± 0.5 μmol kg^{-1}, A_T = 2578 ± 1 μmol kg^{-1}, pH = 8.024 ± 0.005, Ω Ca = 3.91 ± 0.07, Ω Ar = 2.52 ± 0.04). The high A_T concentrations, pH values and saturation states in the WMDW, compared to the LIW in this strait, are due to the massive freshwater inputs from the Rhône River in the Western Basin.

-Tyrrhenian Deep Water (TDW): It was detected in the deep layers of the Tyrrhenian Sub-basin, the deepest and the most isolated sub-basin of the Western Mediterranean Sea, where enters the greater part of the water going from the Eastern to the Western Basin (Sparnocchia *et al.*, 1999). This water, which is a product of the mixing between LIW and WMDW, was noted during our cruise below the LIW entering the channel of Sicily, around 1000 m. As noted by Budillon *et al.* (2009), the θ–S diagram shows that TDW fills the Tyrrhenian Sub-basin down to the bottom (Fig.9). The characteristics of this water mass highlighted in this study are in a good agreement with the findings of Rivaro *et al.* (2010) and Copin-Montégut who reported that the A_T measured in the deep layer in the South of the Tyrrhenian Sea during the PROSOPE cruise (http://www.obsvlfr.fr/jgofs/html/prosope/home.htm) was higher than in deep water at the DYFAMED site, suggesting that the TDW contributes to the Ligurian–Provencal Basin deep water. The pH and salinity are positively and significantly correlated (r = 0.759) in the TDW which explains the high mean pH (8.045 ± 0.03), thus the high saturation states of calcite (3.64 ± 0.53) and aragonite (2.38 ± 0.33) in this water mass.

-Cretan Intermediate Water (CIW): The high A_T concentrations and pH values characterizing this water body are due to the freshwater inputs coming from the nearby Black Sea and the Northern Rivers.

-Eastern Mediterranean Deep Water (EMDW): Throughout the period of oceanographic observation, until the late 1980s/early 1990s, the Adriatic Sub-basin was found to be the main source area of EMDW formation (Pollak 1951 ; Wüst 1961). A combination of meteorological and hydrological factors caused the Aegean Sub-basin to become a new source of deep waters in addition to the Adriatic source, which traditionally feeds the Eastern Mediterranean Deep Water (EMDW ; Roether *et al.*, 1996 ; Klein *et al.*, 1999 ; Lascaratos *et al.*, 1999 ; Theocharis *et al.*, 2002). This abrupt shift in the Mediterranean circulation has been named as the “Eastern Mediterranean Transient = EMT”. EMDW is formed, therefore, in two separate regions, the Adriatic Sub-basin and the Aegean Sub-basin which are subject to orographically channeled continental air outbursts in winter (Rohling *et al.*, 2009). Pre-EMT EMDW water, typified by a minimum salinity, is still noted at around 1000 m in the Levantine Sub-basin. This water mass was detected during the Meteor cruise (M84/3) as well on April 2011 (Álvarez *et al.*, 2014). The fact that deep layers of the Levantine Sub-basin are still occupied by the EMDW originated in the Aegean Sub-basin, could be attributed to the long residence time of deep water masses in the Levantine Sub-basin due the robust topography which could trap the deep waters in this sub-basin for a long period. The post EMT-EMDW, occupying the bottom layers of the Ionian Sub-basin and the South of Crete, is a newly formed water mass, thus fresher and more oxygenated. It is less oversaturated with respect to calcite and aragonite than the Pre-EMT and has low pH values. Its low calcite/aragonite and low pH values could be a response to the increased CO_2 concentration in the atmosphere due to anthropogenic activities. The decrease in pH has a significant effect on the carbonate chemistry of the seawater and causes a decrease in the calcium carbonate saturation state, which explain the weak calcite and aragonite oversaturation state in the Pre-EMT waters.

5. Conclusions

High quality data collected on May 2013 during the MedSeA cruise, from the Atlantic waters off Cadiz harbor to the Easternmost part of the Mediterranean Sea, then Westward, are used to describe the West-East gradients of hydrographic, chemical and CO_2 system parameters in the Mediterranean Sea. A comparison between the Northern and Southern sections, as well the Western and the Eastern Basins indicates that massive A_T and nutrients inputs, originating from the Northern rivers, especially during the ice melting season, are making these Mediterranean compartments biogeochemically significantly different.

Furthermore, the water masses characterization shows that the deep Levantine waters are still occupied by Aegean Eastern Mediterranean Deep Waters (EMDW), while the Adriatic and Ionian deep waters were filled by Adriatic EMDW.

A continuous monitoring of the CO_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. A similar study is newly undertaken off the Lebanese coast, in the Levantine Sub-basin, to measure the A_T and C_T concentrations in this area for the first time.

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References

Aït-Ameur N. and Goyet C., 2006. Distribution and transport of natural and anthropogenic CO2 in the Gulf of Cadiz. *Deep-Sea Research II*, 53, 11-13, 1329-1343.

Alekin O.A., 1972. Saturation of Mediterranean Sea water with calcium carbonate. *Geochemistry*, 206, 239-242.

Álvarez M., 2011. The CO2 system observations in the Mediterranean sea: Past, present and future. In: Designing Med-SHIP: a Program for repeated oceanographic surveys. N°43 in CIESM Workshop Monographs [F. Briand Ed.], 164 p., Monaco.

Álvarez M., Sanleón-Bartolomé H., Tanhua T., Mintrop L., Luchetta A., Cantoni C., Schroeder K., and Civitarese G., 2014. The CO2 system in the Mediterranean Sea : a basin wide perspective. *Ocean Science*, 10, 69–92.

Arsouze T., Palmiéri J., Dutay J.-C., Béranger K., Beuvier J., Orr J., Somot S., 2013. Modeling the Levantine Intermediate Water: sensitivity of CFC distribution on the Eastern Mediterranean Transient representation and implications on anthropogenic CO2 uptake. *EGU General Assembly* 2013, held 7-12 April, 2013 in Vienna, Austria, p.13197.

Bégovic M., Copin-Montégut C., 2002. Processes controlling annual variations in the partial pressure of CO2 in surface waters of the central northwestern Mediterranean Sea (Dyfamed site). *Deep Sea Research Part II: Topical Studies in Oceanography*, 49, (11), 2031–2047.

Bergamasco A. and Malanotte-Rizzoli P., 2010. The circulation of the Mediterranean Sea: a historical review of experimental investigations. *Advances in Oceanography and Limnology*, 1:1, 11-28.

Béthoux J.-P., 1980. Mean water fluxes across sections in the Mediterranean Sea, evaluated on the basis of water and salt budget and of observed salinities. *Oceanol. Acta*, 3, 79–88.

Béthoux J. P., Gentili B., Raunet J., and Tailliez D., 1990. Warming trend in the western Mediterranean deep water. *Nature*, 347, 660 – 662, doi: 10.1038/347660a0

Budillon G., Gasparini G.P., Schröder K., 2009. Persistence of an eddy signature in the central Tyrrhenian basin. *Deep-Sea Research II*, 56, 713–724.

Cacho I., Grimalt J.O., Canals M., Sbaffi L., Shackleton N.J., Schönfeld J., and Zahn R., 2001. Variability of the western Mediterranean Sea surface temperature during the last 25,000 years and its connection with the Northern Hemisphere climatic changes. *Paleoceanography*, 16(1), 40–52, doi:10.1029/2000PA000502.

Chernyakova A.M., 1976. Elements of the carbonate system in the Straits of Sicily (Tunis Strait) area. *Oceanology*, 16, 36-39.

Cooley S., Mathis J., Yates K., and Turley C. eds., 2012. Frequently Asked Questions about Ocean Acidification. U.S. Ocean Carbon and Biogeochemistry Program and the UK Ocean Acidification Research Programme. Version 2. 24 September. www.whoi.edu/OCB-OA/FAQs

Copin-Montégut C., 1993. Alkalinity and carbon budgets in the Mediterranean Sea. *Global Biogeochemical Cycles*, 7, (4), 915–925, doi:10.1029/93GB01826.

Copin-Montégut C. and Bégovic M., 2002. Distributions of carbonate properties and oxygen along the water column (0 – 2000 m) in the central part of the NW Mediterranean Sea (Dyfamed site). Influence of winter vertical mixing on air – sea CO2 and O2 exchanges. *Deep-Sea Research, II. Topical studies in oceanography*. 49 (11), 2049-2066.

Cozzi S. and Giani M. 2011. River water and nutrient discharges in the Northern Adriatic Sea: current importance and long term changes. *Continental Shelf Research*, 31, 1881-1893.

Crivelli A.J., 1995. Are fish introductions a threat to endemic freshwater fishes in the northern Mediterranean region? *Biological Conservation*, 72, 311–319.

De Carlo E.H., Mousseau L., Passafiume O., Drupp P.S., Gattuso J., 2013. Carbonate chemistry and air-sea CO2 flux at a fixed point in a NW Mediterranean bay over a four-year period: 2007-2011. *Aquatic Geochemistry*, 19, 399-442.

Delgado O. and Estrada M., 1994. CO2 system in a Mediterranean frontal zone. *Scientia Marina*, 58 (3), 237-250.

Dickson A. G., 1990. Standard potential of the reaction: AgCl(s) + 1/2 H2(g) = Ag(s) + HCl(aq), and the standard acidity constant of the ion HSO4- in synthetic seawater from 273.15 to 318.15 K. *Journal of Chemical Thermodynamics*, 22, 113-127.

DOE, 1994. Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water ; version 2, A. G. Dickson and C. Goyet, eds., ORNL/CDIAC-74.

Durrieu de Madron X., Guieu C., Sempéré R., Conan P., Cossa D., D'Ortenzio F., Estournel C., Gazeau F., Rabouille C., Stemmann L., Bonnet S., Diaz F., Koubbi P., Radakovitch O., Babin M., Baklouti M., Bancon-Montigny C., Belviso S., Bensoussan N., Bonsang B., Bouloubassi I., Brunet C., Cadiou J.-F., Carlotti F., Chami M., Charmasson S., Charrière B., Dachs J., Doxaran D., Dutay J.-C., Elbaz-Poulichet F., Eléaume M., Eyrolles F., Fernandez C., Fowler S., Francour P., Gaertner J.C., Galzin R., Gasparini S., Ghiglione J.-F., Gonzalez J.-L., Goyet C., Guidi L., Guizien K., Heimbürger L.-E., Jacquet S.H.M., Jeffrey W.H., Joux F., Le Hir P., Leblanc K., Lefèvre D., Lejeusne C., Lemé R., Loÿe-Pilot M.-D., Mallet M., Méjanelle L., Mélin F., Mellon C., Mérigot B., Merle P.-L., Migon C., Miller W.L., Mortier L., Mostajir B., Mousseau L., Moutin T., Para J., Pérez T., Petrenko A., Poggiale J.-C., Prieur L., Pujo-Pay M., Pulido-Villena, Raimbault P., Rees A.P., Ridame C., Rontani J.-F., Ruiz Pino D., Sicre M.A., Taillandier V., Tamburini C., Tanaka T., Taupier-Letage I., Tedetti M., Testor P., Thébault H., Thouvenin B., Touratier F., Tronczynski J., Ulses C., Van Wambeke F., Vantrepotte V., Vaz S., Verney R., 2011. Marine ecosystems' responses to climatic and anthropogenic forcings in the Mediterranean. *Progress in Oceanography*, **91** (2), 97-166.

EEA, 1999. State and pressures of the marine and coastal Mediterranean environment, *Environmental Assessment Series*, No 5.

El Boukhary M. S., Ruiz-Pino D., Béthoux J. P., 2002. Is The Oxygen Decreasing In The Mediterranean Sea ? EGS XXVII General Assembly, Nice, 21-26 April 2002, abstract #6463.

Gascard J.C. and Richez C., 1985. Water masses and circulation in the western Alboran Sea and in the Strait of Gibraltar. *Progress in Oceanography*, 15, 157–216.

Goyet C., and Poisson A., 1989. New determination of carbonic acid dissociation constants in seawater as a function of temperature and salinity. *Deep-Sea Research*, 36, 1635-54.

Goyet C., Hassoun A.E.R., and Gemayel E., 2015a. Carbonate system during the May 2013 MedSeA cruise., doi:10.1594/PANGAEA.841933.

Goyet C., Gemayel E., and Hassoun A.E.R., 2015b. Underway pCO2 in surface water during the 2013 MedSEA cruise, doi:10.1594/PANGAEA.841928.

Hansen H.P., 1999. Determination of oxygen. In: Grasshoff, K., Kremling, K., Ehrhardt, M., Methods of Seawater Analysis, 3rd Edition, Wiley-VCH, Weinheim, 600 pp.

Hassoun A.E.R., Guglielmi V., Gemayel E., Goyet C., Abboud-Abi Saab M., Giani M., Ziveri P., Ingrosso G., and Touratier F., 2015 a. Is the Mediterranean Sea Circulation in a Steady State. *Journal of Water Resources and Ocean Science*, **4** (1), 6–17, doi: 10.11648/j.wros.20150401.12.

Hassoun A.E.R., Gemayel E., Krasakopoulou E., Goyet C., Abboud-Abi Saab M., Ziveri P., Touratier F., Guglielmi V. and Falco C., 2015 b. Modeling of the Total Alkalinity and the Total Inorganic Carbon in the Mediterranean Sea. *Journal of Water Resources and Ocean Science*, **4** (1), 24–32, doi: 10.11648/j.wros.20150401.14.

Hassoun, A.E.R., Gemayel, E., Krasakopoulou, E., Goyet, C., Abboud-Abi Saab, M., Guglielmi, V., Touratier, F., Falco, C., 2015a. Acidification of the Mediterranean Sea from anthropogenic carbon penetration. *Deep Sea Research Part I Oceanogr. Res. Pap.*, **102** (0), 1-15. http://dx.doi.org/10.1016/j.dsr.2015.04.005

Hopkins T.S., 1978. Physical Processes in the Mediterranean basins. In: Kjerfve, B. (Ed.), *Estuarine Transport Processes*. Univ. of South Carolina Press, Columbia, SC. 269–310.

Huertas I.E., Ríos A.F., García-Lafuente J., Makaoui A., Rodríguez-Gálvez S., Sánchez-Román A., Orbi A., Ruíz J., and Pérez F.F., 2009. Anthropogenic and natural CO2 exchange through the Strait of Gibraltar. *Biogeosciences Discuss.*, 6, 1021–1067.

IOC, SCOR and IAPSO, 2010. The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp.

Klein B., Roether W., Manca B., Bregant D., Beitzel V., Kovacevic V., Luchetta A., 1999. The large deep transient in the Eastern Mediterranean. *Deep-Sea Research, Part 1, Oceanographic Research Papers*, 46, 371–414.

Kovačević V., Manca B.B., Burca M., Arsella L., Mauri E., Deponte D., 2009. Water masses and dynamical conditions during the Transmed cruise in the Eastern Mediterranean in June 2007. 2nd annual Workshop VECTOR, Roma, February 25–26, 2009 (http://vector-conisma.geo.unimib.it).

Lacombe H. and Tchernia P., 1960. Quelques traits généraux de l’hydrologie Méditerranéenne. *Cahiers Océanographiques XII*, (8), 527–547.

Lacombe H. and Tchernia P., 1972. Caractères hydrologiques et circulation des eaux en Méditerranée, Mediterranean Sea, edited by: Stanley, D., Dowden, Hutchinson and Ross, Stroudsburg, 25–36.

Lacombe H., Tchernia P., Gamberoni L., 1985. Variable bottom water in the Western Mediterranean basin. *Progress in Oceanography*. 14, 319–338.

La Ferla R., Azzaro M., Civitarese G., and Ribera d'Alcalà M., 2003. Distribution patterns of carbon oxidation in the eastern Mediterranean Sea: Evidence of changes in the remineralization processes. *Journal of Geophysical Research*, 108, 8111, doi:10.1029/2002JC001602, C9.

Lascaratos A., Roether W., Nittis K., Klein B., 1999. Recent changes in deep water formation and spreading in the eastern Mediterranean Sea: a review. *Progress in Oceanography*, 44, (1–3), 5–36.

Lee, K., Tong L.T., Millero F.J., Sabine C.L., Dickson A.G., Goyet C., Park G.-H., Wanninkhof R., Feely R. A., and Key R. M., 2006. Global relationships of total alkalinity with salinity and temperature in surface waters of the world's oceans, *Geophysical Research Letters*, 33, L19605, doi:10.1029/2006GL027207.

Le Quéré C., Takahashi T., Buitenhuis E. T., Rodenbeck C., et Sutherland S. C., 2010. Impact of climate change and variability on the global oceanic sink of CO2. *Global Biogeochemical Cycles*, 24.

Manca B., Burca M., Giorgetti A., Coatanoan C., Garcia M.-J., Iona A., 2004. Physical and biochemical averaged vertical profiles in the Mediterranean regions: an important tool to trace the climatology of water masses and to validate incoming data from operational oceanography. *Journal of Marine Systems*, 48, 83–116.

Mariotti A., Struglia M.V., Zeng N., Lau K.-M., 2002. The Hydrological Cycle in the Mediterranean Region and Implications for the Water Budget of the Mediterranean Sea. *Journal of Climate*, 15, 1674–1690.

Mattia, G., Zavatarelli M., Vichi M., and Oddo P., 2013. The Eastern Mediterranean Sea biogeochemical dynamics in the 1990s: A numerical study. Journal of Geophysical Research: Oceans, 118, 2231–2248, doi:10.1002/jgrc.20160.

Mikaloff Fletcher S. E., Gruber N., Jacobson A. R., Doney S. C., Dutkiewicz S., Gerber M., Follows M., Joos F., Lindsay K., Menemenlis D., Mouchet A., Müller S.A., Sarmiento J.L., 2006. Inverse estimates of anthropogenic CO2 uptake, transport, and storage by the ocean. *Global Biogeochemical Cycles*, 20, GB2002, doi:10.1029/2005GB002530, 2006

Millero F.J., Morse J., Chen C.-T.,1979. The carbonate system in the western Mediterranean Sea. *Deep-Sea Research*, 26A, 1395–1404.

Millot C., Candela J., Jean-Luc F., Youssef T., 2006. Large warming and salinification of the Mediterranean outflow due to changes in its composition. *Deep-Sea Research I*. 53, 656–666.

Millot C, 2013. Levantine Intermediate Water characteristics: an astounding general misunderstanding! *Sciencia Marina*, doi : 10.3989/scimar.03518.13A.

Outdot C., Gerard R., Morin P., 1988. Precise shipboard determination of dissolved oxygen (Winkler procedure) for productivity studies with commercial system. *Limnology and Oceanography*, 33, 146-150. Edition, Wiley-VCH, Weinheim, 600 pp.

Oviedo A.M., Ziveri P., Álvarez M., and Tanhua T., 2014. Is coccolithophore distribution in the Mediterranean Sea related to seawater carbonate chemistry?, *Ocean Science Discuss.*, 11, 613-653, doi:10.5194/osd-11-613-2014.

Özsoy E., Hecht A., Unluata U., Brenner S., Sur H.I., Bishop J., Latif M.A., Rozentraub Z., Oguz T., 1993. A synthesis of the Levantine Basin circulation and hydrography, 1985– 1990. *Deep-Sea Research*, Part 2, Top. Stud. Oceanogr, 40, 1075– 1119.

Parrilla G., Kinder T.H., Preller R.H., 1986. Deep and intermediate Mediterranean water in the western Alboran Sea. *Deep-Sea Research I*, 33, 55–88.

Pierrot D., Lewis E., and Wallace D.W.R., 2006. MS Excel Program Developed for CO2 System Calculations. ORNL/CDIAC-105a. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tennessee. doi: 10.3334/CDIAC/otg.CO2SYS_XLS_CDIAC105a

Pollak M. I., 1951. The sources of deep water of the eastern Mediterranean Sea. *Deep-Sea Research*. 10, 128–52.

Raven *et al.*, 2005 Ocean acidification due to increasing atmospheric carbon dioxide. *The Royal Society Policy Document* 12/05, London.

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

Robinson A.R., Leslie W., Theocharis A., Lascaratos A., 2001. Mediterranean Sea circulation. *Encyclopedia of Ocean Science*, vol. 3. Academic Press, San Diego, CA, pp. 1689– 1705.

Roether W., Manca B.B., Klein B., Bregant D., Georgopoulos D., Beitzel V., Kovačević V., Luchetta A., 1996. Recent Changes in Eastern Mediterranean Deep Waters. *Science*. 271, 333-335, doi: 10.1126/science.271.5247.333.

Rohling E. J., Abu-Zied R. H., Casford J.S.L., Hayes A., and Hoogakker B.A.A., 2009. The marine environment: present and past, in J. C.Woodward (ed.), *The Physical Geography of the Mediterranean.* Oxford University Press, Oxford, 33–67.

Sabine, C. L., Key R. M., Feely R. A., and Greeley D., 2002. Inorganic carbon in the Indian Ocean: Distribution and dissolution processes. *Global Biogeochem. Cycles*, 16 (4), 1067, doi:10.1029/2002GB001869

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

Sempéré R., Charrière B., Van Wambeke F., and Cauwet G., 2000. Carbon inputs of the rhone river to the mediterranean sea: Biogeochemical implications. *Global Biogeochemical Cycles*, 14, 669-681.

Schneider A., Wallace D.W.R., and Körtzinger A., 2007. Alkalinity of the Mediterranean Sea. *Geophysical Research Letters*, 34, L15608, doi:10.1029/2006GL028842.

Schneider A., Tanhua T., Körtzinger A., Wallace D.W.R., 2010. High anthropogenic carbon content in the eastern Mediterranean. *Journal of Geophysical Research*, 115, C12050, doi:10.1029/2010JC006171.

Skliris N. and Lascaratos A., 2004. Impacts of the Nile river damming on the thermohaline circulation and water mass characteristics of the Mediterranean sea. *Journal of Marine Systems*, 52, pp. 121-143.

Skliris N., Sofianos S., Gkanasos A., Mantziafou A., Vervatis V., Axaopoulos P. and Lascaratos A., 2011. Decadal scale variability of sea surface temperature in the Mediterranean Sea in relation to atmospheric variability. Ocean Dynamics. DOI 10.1007/s10236-011-0493-5

Souvermezoglou E., Krasakopoulou E. and Goyet C., 2010. Total Inorganic Carbon and Total Alkalinity Distribution in the Aegean Sea. CIESM. Rapp. Comm. int. Mer Médit., 39, 2010.

Sparnocchia S., Gasparini G.P., Astraldi M., Borghini M., Pistek P., 1999. Dynamics and mixing of the Eastern Mediterranean outflow in the Tyrrhenian Sea. *Journal of Marine Systems*, 20, 301–317.

Theocharis A., Lascaratos A., Sofianos S., 2002. Variability of sea water properties in the Ionian, Cretan and Levantine seas during the last century. In: Briand, F. (Ed.), Tracking long-term hydrological change in the Mediterranean Sea. CIESM Workshop Series, 16, 73– 76.

Touratier F. and Goyet C., 2009. Decadal evolution of anthropogenic CO_2 in the northwestern Mediterranean Sea from the mid-1990s to the mid-2000s. *Deep Sea Research Part I: Oceanographic Research Papers*. 56, (10), 1708–1716.

Touratier, F., Goyet, C., 2011. Impact of the Eastern Mediterranean Transient on the distribution of anthropogenic CO_2 and first estimate of acidification for the Mediterranean Sea. *Deep-Sea Research I*, 58,1–15.

Tsimplis M.N., and Rixen M., 2002. Sea level in the Mediterranean Sea -The contribution of temperature and salinity changes. *Geophysical Research Letters*, 0094-8276.

UNEP/MAP-Plan Bleu, 2009. State of the Environment and Development in the Mediterranean, UNEP/MAP-Plan Bleu, Athens.

Uppström, L. R., 1974. The boron/chloronity ratio of deep-sea water from the Pacific Ocean. *Deep-Sea Research*, 21:161-162.

Vargas-Yáñez M., Moya F., García-Martínez M.C., Tel E., Zunino P., Plaza F., Salat J., Pascual J., López-Jurado J. L., and Serra M., 2010. Climate change in the Western Mediterranean Sea 1900–2008. *Journal of Marine Systems*, 82, 171–176.

Wüst G., 1961. On the vertical circulation of the Mediterranean Sea, *Journal of Geophysical Research*. 66, 3261–71.

Zenetos A., Siokou-Frangou I., Gotsis-Skretas O., Groom S., 2002. Europe's biodiversity - biogeographical regions and seas. Seas around Europe : The Mediterranean sea -the blue oxygen-rich, nutrient-poor waters. EEA report, Copenhagen, 2002.

Ziveri P., and Grelaud M., 2013a. Continuous thermosalinograph oceanography along Ángeles Alvariño cruise track MedSeA2013. Universitat Autònoma de Barcelona, doi:10.1594/PANGAEA.822153.

Ziveri P., and Grelaud M., 2013b. Physical oceanography during Ángeles Alvariño cruise MedSeA2013. Universitat Autònoma de Barcelona, doi:10.1594/PANGAEA.822162.

Ziveri P., and Grelaud M., 2013c. Physical oceanography measured on water bottle samples during Ángeles Alvariño cruise MedSeA2013. Universitat Autònoma de Barcelona, doi:10.1594/PANGAEA.822163.

http://www.ifremer.fr/lobtln/OTHER/Terminology.html

http://medsea-project.eu/

http://medseaoceancruise.wordpress.com/