Seasonal and interannual variability of the CO_2 system in the eastern Mediterranean Sea: a case study in the North Western Levantine Basin - Supplementary Material

The following supplementary materials provided more details on the quality control procedure applied to the PERLE dataset (1). Analytical procedure explanation, processing and corrections of the pH measurements are also detailed (2).

(1) A_T and C_T Quality control procedure

Without any apparent reason identifiable, raw A_T and C_T values measured during PERLE2 appeared incorrect. To attribute quality flag value and overcome this issue, a quality control procedure has been implemented. The following steps have been done:

(1) For samples collected in duplicate (A_T and C_T), when the difference was higher than 10 $\mu mol.kg^{-1}$ the values were flagged as "Bad".

(2) Between 500 dbars and the bottom, A_T and C_T values outside a range defined by the mean value $\pm$ 2 $\times$ the standard deviation were flagged as "Bad".

(3) Based on the comparison between calculated pH (from A_T and C_T values – see section 2.4) and the measured pH, A_T and C_T values were flagged as "Bad" if the ΔpH ($pH^{measured}$ - $pH^{calculated}$) was higher than 0.02.

(2) pH measurements and corrections

The pH measurement method performed in this study is based on the absorbance spectra of a pH-sensitive indicator dye added to the seawater sample. Within the current seawater pH-range, the purified pH-sensititve dye (McP) has a pK value centered in the expected oceanic pH. The absorbance ratio can be calculated as the relative absorbance contributions of colored protonated and unprotonated species in the sample of interest. Then, the pH can be calculated using equations proposed by Liu et al. (2011).

In order to estimate the potential perturbation induced by the addition of the dye on the seawater acid-base system, the following steps have been done:

(1) Three standard addition of dye were made for one sample on each cast measured.

(2) Based on the standard addition curve, the effect of dye addition on the absorbance ratio was estimated for each cast as the difference between the ratio measured and the slope coefficient of the standard addition curve.

(3) This difference was plotted according to each cast. A linear regression was done.

(4) The measured ratio was systematically corrected from the addition of dye by subtracting it according to the equation previously obtained.

The effect of this correction on the pH measurements is marginal with an average change on pH_T values ranging between 0.002 (PERLE1) and 0.001 (PERLE2).

Figures and Tables of the Supplementary Material

Supplementary Material - Table 1: General description of the casts sampled for carbonate chemistry parameters during the three PERLE cruises. SHAL stands for casts up to 1000 dbars, INT stands for casts up to 2000 dbars, DEEP stands for the deep cast and REPRO stands for the cast with reproducibility measurements. PERLE2 casts with an asterisk are where all the vertical profile was flagged as bad data after the quality control procedure. PERLE2 cast with a double asterisk is the one where only pH and O_2 measurements were done for reproducibility.

Cruise	Cast	Station	Longitude [°E]	Latitude [°N]	Time (UTC)	Max. Press. [dbars]	Type
PERLE0	006	003	26.0025	34.3980	14/06/2018 06:51:00	1632	INT
PERLE1	002	002	26.5157	34.8155	10/10/2018 20:39:00	2425	DEEP
	005	004	26.5110	34.2930	11/10/2018 10:36:00	3507	DEEP
	012	008	26.4892	33.3202	12/10/2018 08:43:00	2563	DEEP
	015	009	25.3492	34.2053	15/10/2018 03:11:00	3832	DEEP
	016	010	25.6513	34.2087	15/10/2018 08:38:00	3044	DEEP
	025	011	26.0537	34.2080	19/10/2018 01:29:00	2626	DEEP
	019	013	27.8190	33.8150	20/10/2018 08:10:00	3307	DEEP
	020	014	27.0980	34.2090	16/10/2018 04:40:00	2634	DEEP
	023	017	26.6407	33.9022	16/10/2018 17:09:00	2789	DEEP
	027	018	27.0918	33.8303	19/10/2018 23:08:00	2478	DEEP
	030	019	27.8190	33.8150	20/10/2018 08:10:00	2595	DEEP
PERLE2	002	001	25.2963	35.8555	27/02/2019 11:00:00	1879	INT
	013*	009	23.5360	35.6215	28/02/2019 17:01:00	822	SHAL
	014	004	23.7585	35.9500	28/02/2019 20:29:00	1087	INT
	021	014	22.8188	34.4357	02/03/2019 03:22:00	2786	DEEP
	025	017	23.7348	34.4428	02/03/2019 18:28:00	2506	DEEP

034	024	24.5197	34.3267	03/03/2019 22:35:00	2555	DEEP
043	030	24.3847	33.6345	04/03/2019 23:56:00	1989	INT
049	034	25.3003	34.3198	05/03/2019 21:39:00	2482	DEEP
059	042	26.0937	34.2903	07/03/2019 08:01:00	2978	DEEP
068*	049	28.8052	33.5927	08/03/2019 20:50:00	2965	DEEP
074	053	27.9878	33.8612	09/03/2019 18:41:00	2582	DEEP
079	056	27.3215	33.9648	10/03/2019 11:58:00	2551	DEEP
089	063	26.8968	34.6813	11/03/2019 18:14:00	2445	DEEP
093	066	26.7388	34.9382	12/03/2019 09:28:00	823	SHAL
104	076	26.6580	35.3702	13/03/2019 06:32:00	937	SHAL
108	080	27.4285	35.8375	13/03/2019 17:14:00	956	SHAL
112**	084	27.2577	34.0715	14/03/2019 17:14:00	1004	REPRO
124	095	26.2742	35.6418	16/03/2019 03:19:00	2317	DEEP

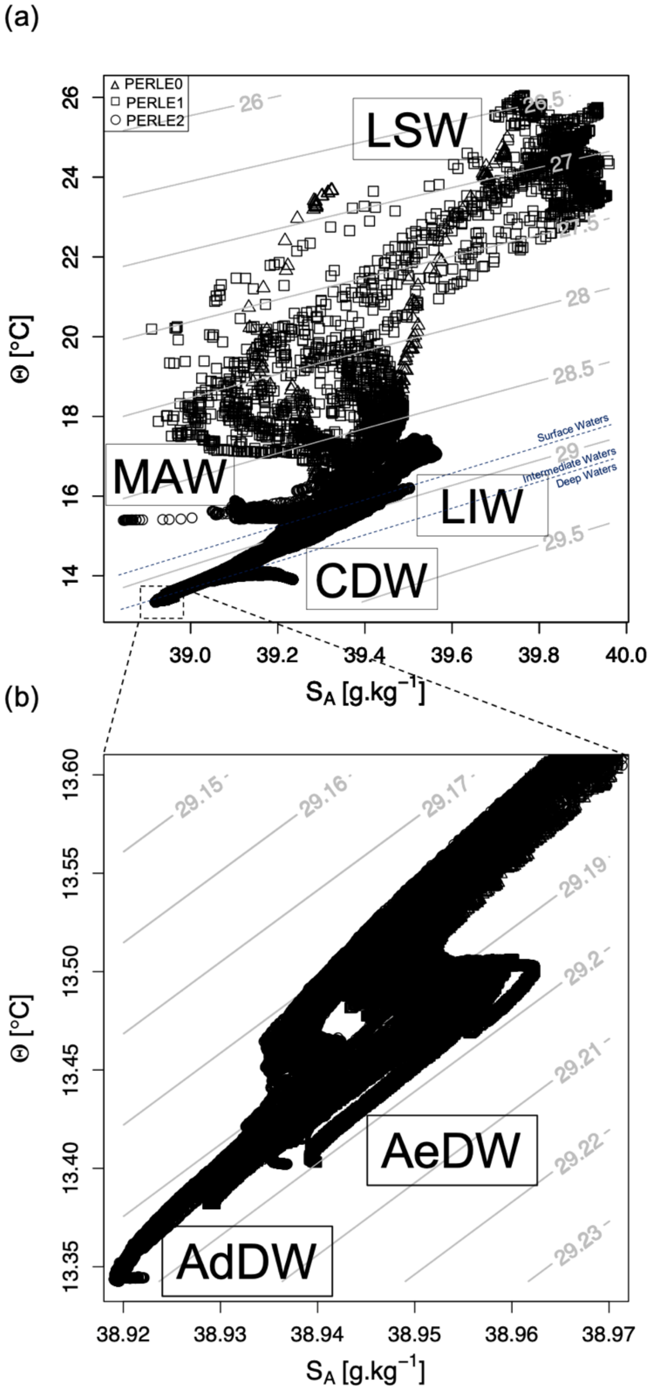
Supplementary Material - Table 2: Temperature (°C), Salinity, total alkalinity (A_T - µmol.kg^{-1}), total inorganic carbon (C_T - µmol.kg^{-1}) and pH_T^{25} mean values ± standard deviation in the Levantine basin from different cruises (Meteor 51/2, TRANSMED, BOUM, Meteor 84/3, MedSeA, HOTMIX and MSM72). Salinity-normalised changes in A_T ($NA_T^{39.3}$) and C_T ($NC_T^{39.3}$) were calculated by dividing by in situ salinity and multiplying by 39.3. Surface depth corresponds to the layer between the surface and 50 dbars, and bottom depth represents the layer between 500 dbars and the bottom.

Region	Cruise	Depth	*Geographical parameters*		*Hydrological parameters*		*Carbonate parameters*					Reference
			Latitude [°N]	Longitude [°E]	Temp. [°C]	Salinity	A_T [µmol.kg^{-1}]	$NA_T^{39.3}$ [µmol.kg^{-1}]	C_T [µmol.kg^{-1}]	$NC_T^{39.3}$ [µmol.kg^{-1}]	pH_T^{25}	
Levantine basin	M51/2 cruise (October 2001)	Surface	34.24 ± 0.64	25.25 ± 1.87	22.52 ± 1.35	39.04 ± 0.22	2602 ± 13[a]	2610 ± 5[a]	2240 ± 8[a]	2252 ± 4[a]	8.050 ± 0.004*	Schneider et al. (2007, 2010)
		Deep	34.12 ± 0.68	25.47 ± 1.94	13.92 ± 0.17	38.78 ± 0.05	2610 ± 5[a]	2646 ± 5[a]	2310 ± 3[a]	2341 ± 3[a]	7.956 ± 0.008*	
Levantine basin	TRANSMED (June 2007)	Surface	34.64 ± 0.24	24.33 ± 1.91	21.30 ± 2.58	38.80 ± 0.48	2601 ± 40	2635 ± 8	/	/	8.017 ± 0.027	Rivaro et al. (2010)
		Deep	34.63 ± 0.23	24.40 ± 1.78	14.02 ± 0.38	38.78 ± 0.07	2609 ± 3	2643 ± 3	/	/	7.960 ± 0.012	
Levantine basin	BOUM cruise (June 2008)	Surface	34.02 ± 0.13	24.86 ± 2.15	21.57 ± 2.49	38.95 ± 0.32	2598 ± 24[b]	2621 ± 7[b]	2266 ± 16[b]	2286 ± 7[b]	8.003 ± 0.007*	Touratier et al. (2012)
		Deep	34.00 ± 0.12	25.20 ± 1.99	13.89 ± 0.19	38.78 ± 0.05	2607 ± 5[b]	2642 ± 6[b]	2310 ± 4[b]	2341 ± 4[b]	7.947 ± 0.007*	
Levantine basin & Cretan Sea	M84/3 cruise (April 2011)	Surface	34.59 ± 0.54	25.67 ± 2.17	17.18 ± 0.34	38.93 ± 0.26	2603 ± 20	2626 ± 5	2270 ± 15	2289 ± 7	8.011 ± 0.008	Álvarez et al. (2014)
		Deep	34.32 ± 0.56	26.36 ± 2.16	13.98 ± 0.24	38.80 ± 0.08	2615 ± 5	2649 ± 2	2308 ± 6	2338 ± 3	7.967 ± 0.004	
Levantine basin	MedSeA cruise (May 2013)	Surface	33.62 ± 0.16	26.57 ± 1.97	19.93 ± 0.69	38.83 ± 0.09	2612 ± 8	2644 ± 14	2266 ± 3	2293 ± 4	8.027 ± 0.014*	Hassoun et al. (2015b)
		Deep	33.61 ± 0.15	26.69 ± 1.77	13.91 ± 0.11	38.77 ± 0.03	2612 ± 6	2648 ± 5	2302 ± 10	2333 ± 10	7.972 ± 0.012*	
Levantine basin	HOTMIX (May 2014)	Surface	34.07 ± 0.00	24.90 ± 1.71	18.38 ± 0.77	38.81 ± 0.10	2593 ± 12	2625 ± 6	2255 ± 10	2287 ± 8	7.999 ± 0.021	/
		Deep	34.07 ± 0.00	25.24 ± 1.58	13.89 ± 0.13	38.77 ± 0.04	2613 ± 2	2649 ± 2	2306 ± 17	2337 ± 17	7.965 ± 0.007	
	MSM72 (March 2018)	Surface	34.80 ± 0.32	24.42 ± 1.53	16.78 ± 0.59	39.18 ± 0.14	2625 ± 10	2633 ± 5	2295 ± 10	2302 ± 13	7.991 ± 0.009	

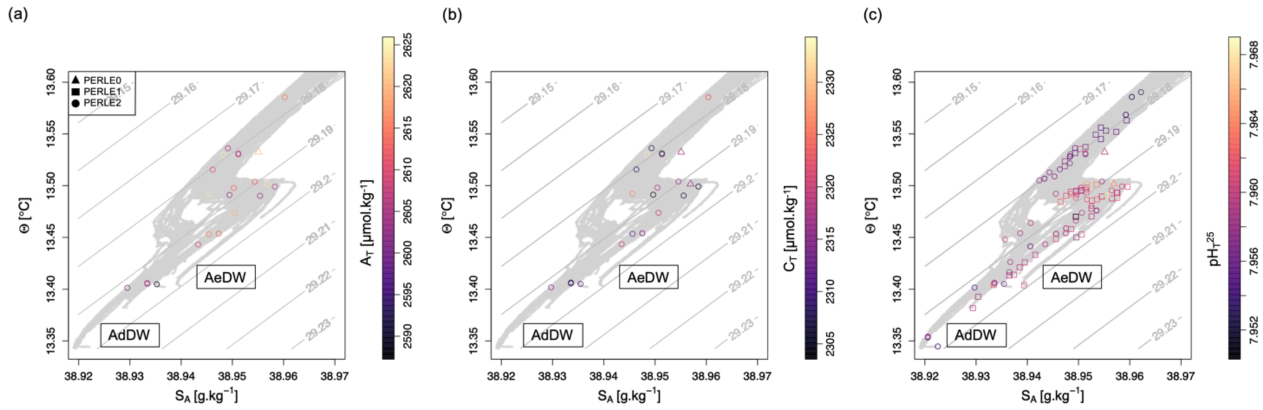
Levantine basin & Cretan Sea		Deep	34.63 ± 0.34	24.50 ± 1.35	13.95 ± 0.20	38.78 ± 0.06	2613 ± 4	2648 ± 3	2311 ± 7	2342 ± 5	7.958 ± 0.007	Hainbucher et al. (2019)
Levantine basin	PERLE0 (June 2018)	Surface	34.46 ± 0.10	25.11 ± 1.35	23.09 ± 1.96	39.33 ± 0.22	2655 ± 10	2646 ± 1	2303 ± 5	2296 ± 3	8.021 ± 0.004*	This study
		Deep	34.44 ± 0.09	25.47 ± 1.21	13.84 ± 0.08	38.79 ± 0.03	2623 ± 2	2658 ± 2	2322 ± 5	2352 ± 4	7.956 ± 0.007*	
Levantine basin	PERLE1 (October 2018)	Surface	34.13 ± 0.44	26.63 ± 0.56	24.55 ± 1.08	39.67 ± 0.11	2685 ± 10**	2660 ± 2**	2305 ± 9**	2286 ± 4**	8.050 ± 0.010	This study
		Deep	34.05 ± 0.34	26.61 + 0.55	13.94 ± 0.15	38.79 ± 0.05	/	/	/	/	7.956 ± 0.007	
Levantine basin & Cretan Sea	PERLE2 (March 2019)	Surface	34.25 ± 0.41	25.83 ± 1.84	16.02 ± 0.42	39.12 ± 0.16	2628 ± 12	2642 ± 10	2319 ± 14	2331 ± 14	7.979 ± 0.010	This study
		Deep	34.24 ± 0.38	25.84 ± 1.87	13.89 ± 0.14	38.78 ± 0.04	2616 ± 8	2646 ± 8	2316 ± 8	2347 ± 8	7.955 ± 0.006	

[*] pH_T^{25} values calculated with the A_T/C_T couple.
[**] A_T values deduced from the A_T-S relationship proposed by (Hassoun et al., 2015a – see section 3.2.2.). C_T values were calculated with the A_T/pH_T^{25} couple.
[a] Offsets of +6 and +5 were applied to A_T and C_T, respectively (M.Álvarez, Pers. Comm.).
[b] Offsets of -11 and -12 were applied to A_T and C_T, respectively (M.Álvarez, Pers. Comm.).

Supplementary Material - Figure 1: Θ - S_A diagrams during the three PERLE cruises with the name of the main water masses described in the literature for the entire water column (Fig.1a) and the deep waters (Fig.1b). Isopycnal horizons based on potential density referenced to a pressure of 0 dbar (σ_θ) are represented by grey contour lines. Different dots have been used for each PERLE cruise.



Supplementary Material - Figure 2: Θ - S_A diagrams for the three PERLE cruises with the name of the main water masses end members for the deep waters. Colored points correspond to A_T on Fig.2a, to C_T on Fig.2b and to pH_T^{25}on Fig.2c. The colour scale has been modified in comparison to Fig.2. Isopycnal horizons based on potential density referenced to a pressure of 0 dbar (σ_θ) are represented by grey contour lines. Different dots have been used for each PERLE cruise. Because no A_T and C_T data were available for PERLE1 cruise, only pH_T^{25} data have been represented (Fig.2a and b).



Supplementary Material - Figure 3: Longitudinal variations in (Fig.3a) absolute salinity (S_A) and (Fig.3b) conservative temperature (Θ) along a transect realised during PERLE1 cruise between the surface and 2000 dbar depth. This transect has been chosen as crossing the Ierapetra Eddy. Black contour lines represent the isopycnal horizons based on potential density referenced to a pressure of 0 dbar.