Variability and Trends in Physical and Biogeochemical Parameters of the Mediterranean Sea during a Cruise with RV MARIA S. MERIAN in March 2018

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Abstract

The last decades have seen dramatic changes in the hydrography and biogeochemistry of the Mediterranean Sea. The complex bathymetry, highly variable spatial and temporal scales of atmospheric forcing, convective and ventilation processes contribute to generate complex and unsteady circulation patterns and significant variability in biogeochemical systems. Part of the variability of this system can be influenced by anthropogenic contributions. Consequently, it is necessary to document details and to understand trends in place to better relate the observed processes and to possibly predict the consequences of these changes. In this context we report data from an oceanographic cruise in the Mediterranean Sea on the German research vessel MARIA S. MERIAN (MSM72) in March 2018. The main objective of the cruise was to contribute to the understanding of long-term changes and trends in physical and biogeochemical parameters, such as the anthropogenic carbon uptake and to further assess the hydrographical situation after the major climatological shifts in the eastern and western part of the basin, known as the Eastern and Western Mediterranean Transients. During the cruise, multidisciplinary measurements were conducted on a predominantly zonal section throughout the Mediterranean Sea, contributing to the global GO-SHIP repeat hydrography program, and particularly to its Mediterranean Sea component, Med-SHIP, and adhering to the GO-SHIP requirements.

Data coverage and parameter measured

Repository-Reference (table 1a and table 1b):

Table 1a. List of physical parameters from MARIA S. MERIAN cruise MSM72 as seen in the PANGAEA database. PI: Dagmar Hainbucher

Parameter Name	Short name	Unit	Method	Comments
DATE/TIME	Date/Time			Geocode
LATITUDE	Latitude			Geocode
LONGITUDE	Longitude			Geocode
Pressure, water	Press	dbar	CTD, SEA_BIRD SBE 911plus	
Temperature, water	Temp	°C	CTD, SEA_BIRD SBE 911plus	
Salinity	Sal		CTD, SEA_BIRD SBE 911plus	PSU
Oxygen	O2	µmol/kg	CTD with attached oxygen sensor (SBE43) calibrated, corrected using Winkler titration	
Pressure, water	Press	dbar	Underway CTD (UCTD), Oceanscience	
Temperature, water	Temp	°C	Underway CTD (UCTD), Oceanscience	
Salinity	Sal		Underway CTD (UCTD), Oceanscience	PSU
DEPTH, water	Depth	m		
Current velocity east-west	UC	m/s	Shipboard Acoustic Doppler Current Profiling (SADCP)	
Current velocity north-south	VC	m/s	Shipboard Acoustic Doppler Current Profiling (SADCP)	
DEPTH, water	Depth	m		
Current velocity east-west	UC	m/s	lowered Acoustic Doppler Current Profiling (lADCP)	
Current velocity north-south	VC	m/s	lowered Acoustic Doppler Current Profiling (lADCP)	

Table 1b. List of biogeochemical parameters from MARIA S. MERIAN cruise MSM72 as seen in the CCHDO database. PI: Toste Tanhua

Variable	**Unit**
Dissolved Oxygen (O_2)	µmol kg^{-1}
Sulphurhexafluorid (SF_6)	fmol kg^{-1}
CCl_2F_2 (CFC-12)	pmol kg^{-1}
Nitrate (NO_3^-)	µmol kg^{-1}
Nitrite (NO_2^-)	µmol kg^{-1}
Phosphate (PO_4^{2-})	µmol kg^{-1}
Silicate (Si)	µmol kg^{-1}
Dissolved Inorganic Carbon (DIC)	µmol kg^{-1}
Total Alkalinity (TA)	µmol kg^{-1}
pH	Total scale @ 25°C
Carbonate (CO_3^{2-})	µmol kg^{-1}
$\delta^{13}C$ of DIC	Per mille
Total Dissolved Nitrogen (TDN)	µmol kg^{-1}
Total Dissolve Phosphorus (TDP)	µmol kg^{-1}
$CHClF_2$ (HCFC-22)	pmol kg^{-1}
$C_2H_3Cl_2F$ (HCFC-141b)	pmol kg^{-1}
$C_2H_3ClF_2$ (HCFC-142b)	pmol kg^{-1}
CH_2FCF_3 (HFC-134a)	pmol kg^{-1}
C_2HF_5 (HFC-125)	pmol kg^{-1}
CHF_3 (HFC-23)	pmol kg^{-1}

https://doi.pangaea.de/10.1594/PANGAEA.905902 (for CTD)

https://doi.pangaea.de/10.1594/PANGAEA.913512 (for UCTD)

https://doi.pangaea.de/10.1594/PANGAEA.913608 (for ADCP)

https://doi.pangaea.de/10.1594/PANGAEA.913505 (for lADCP)

https://doi.pangaea.de/10.1594/PANGAEA.905887 (for chemical data)

https://doi.org/10.25921/z7en-hn85 (for pCO_2)

A link to the summary page of the cruise MSM72 can be found in the PANGAEA data base under: https://www.pangaea.de/?q=msm72&f.campaign%5B%5D=MSM72

Coverage: 34°N-41°N, 6°W-28°E

Location Name: The Mediterranean Sea

Date/Time Start: 2. March 2018

Date/Time End: 3. April 2018

1. Introduction

Contrary to earlier ideas that the Mediterranean Sea is always in a steady state, we now know in the light of new research that the Mediterranean Sea is not and it is potentially sensitive to climatic changes (Malanotte-Rizzoli, 2014). Proof of this are the drastic changes that the eastern Mediterranean (EMed) has undergone in the past. The largest climatic event, named Eastern Mediterranean Transient (EMT), occurred in the EMed between the late 1980's and early 1990's, where deep-water formation switched from the Adriatic to the Aegean Sea. This episode modified the thermohaline characteristics of the outflow through the Sicily Channel, advecting anomalously salty and warm Levantine Intermediate Water (LIW) to the western Mediterranean Sea (WMed) and leading to a significant increase in temperature and salt in the intermediate and deep layers of the WMed. Additionally, strong deep convection induced by extreme atmospheric events during winter time 2004-2006 (low precipitation, cold, persistent winds) was also enhancing salt and temperature in the entire basin up to about 1600 m (Schroeder et al., 2006, Schroeder et al., 2008). This abrupt climate shift is referred to as Western Mediterranean Transient (WMT) and the physical changes are comparable to the EMT, both in terms of intensity and observed effects (Schroeder et al., 2008). The existence of both transients contradicts the hypothesis of a steady state. On the other hand, it has also been proven that an EMT has never been observed before (Roether et al., 2013).

The characteristic of the Mediterranean Sea is also such that it has the potential to sequester large amounts of anthropogenic CO_2, Cant, since the Mediterranean Sea has high alkalinity and temperature, which can be rapidly transported to deep by the overturning circulation (e.g. Schneider et al., 2010). The column inventories of Cant in the Mediterranean are among the highest found in the world oceans; the Mediterranean Sea thus stores a significant portion of the global anthropogenic emissions of Cant despite its relatively small volume.

Furthermore, marine dissolved organic carbon (DOC) represents the largest reservoir of reduced carbon ($662 \cdot 10^{15}$ g C) on Earth (Hansell, 2009), it therefore plays a major role in the global carbon cycle. Its role in the functioning of marine ecosystems is equally crucial since DOC is released at all the levels of the food web, as a byproduct of many trophic interactions and/or metabolic processes and is the main source of energy for the heterotrophic prokaryotes (Carlson and Hansell, 2015). Although most of DOC is produced in-situ, external sources (atmosphere, rivers, sediments) may affect its concentration and distribution. Physical processes, such as deep-water formation, thermohaline circulation, vertical stratification and mesoscale activities have been reported to be the main drivers of DOC distribution in the Mediterranean Sea (Santinelli, 2015, Santinelli et al., 2015, Santinelli et al., 2013, Santinelli, 2010).

The main scientific objective of the cruise reported here was to add knowledge to the different scales and magnitudes of variability and trends in circulation, hydrography, and biogeochemistry of the Mediterranean Sea. Key variables were measured in strategic regions in order to understand changes, the reason for occurrence, and the drivers. In this context, this cruise is part of the Med-SHIP and GO-SHIP long-term repeat cruise section that is conducted at regular intervals in the Mediterranean Sea to observe changes and impacts on physical and biogeochemical variables.

The following science questions were addressed:

1. What are the long-term changes and/or trends in physics and biochemistry in the Mediterranean Sea, including all the sub-basins?

2. How is the hydrographic situation in the Mediterranean developing further after the EMT and WMT? Is there still a tendency of the system to return to the pre-EMT situation and is there a similar trend in the WMed?

3. How are eddies distributed in the EMed and WMed during the cruise? Do they differ in the sub basins? To what extent is heat and salt transferred into the vertical by eddies in the

WMed and EMed during the cruise period?

4. What is the uptake rate of the anthropogenic carbon in the Mediterranean and is this changing over time?

5. What is the extent of the variability and trends in the inventory of biogeochemical variables (including oxygen, nutrients and dissolved organic carbon)?

6. What are the baseline values of rarely measured Essential Ocean Variables (EOVs) such as dissolved organic carbon (DOC)?

2. Data Provenance

The survey was carried out on the German RV Maria S. MERIAN from 2nd of March to 3rd of April 2018. The cruise started on Iraklion, Greece and ended in Cadiz, Spain. The main focus of the cruise was on an east-west transect across the Western and Eastern Mediterranean Sea (figure 1) starting east of Crete and ending near the Strait of Gibraltar, which is a repeating hydrographic line in GO-SHIP (MED1). Difficulties with diplomatic authorizations for Marine Scientific Research (MSR) in the disputed EEZ between Greek and Turkey made it impossible for us to carry out measurements in this area, so that no data were obtained east of Kasos Strait.

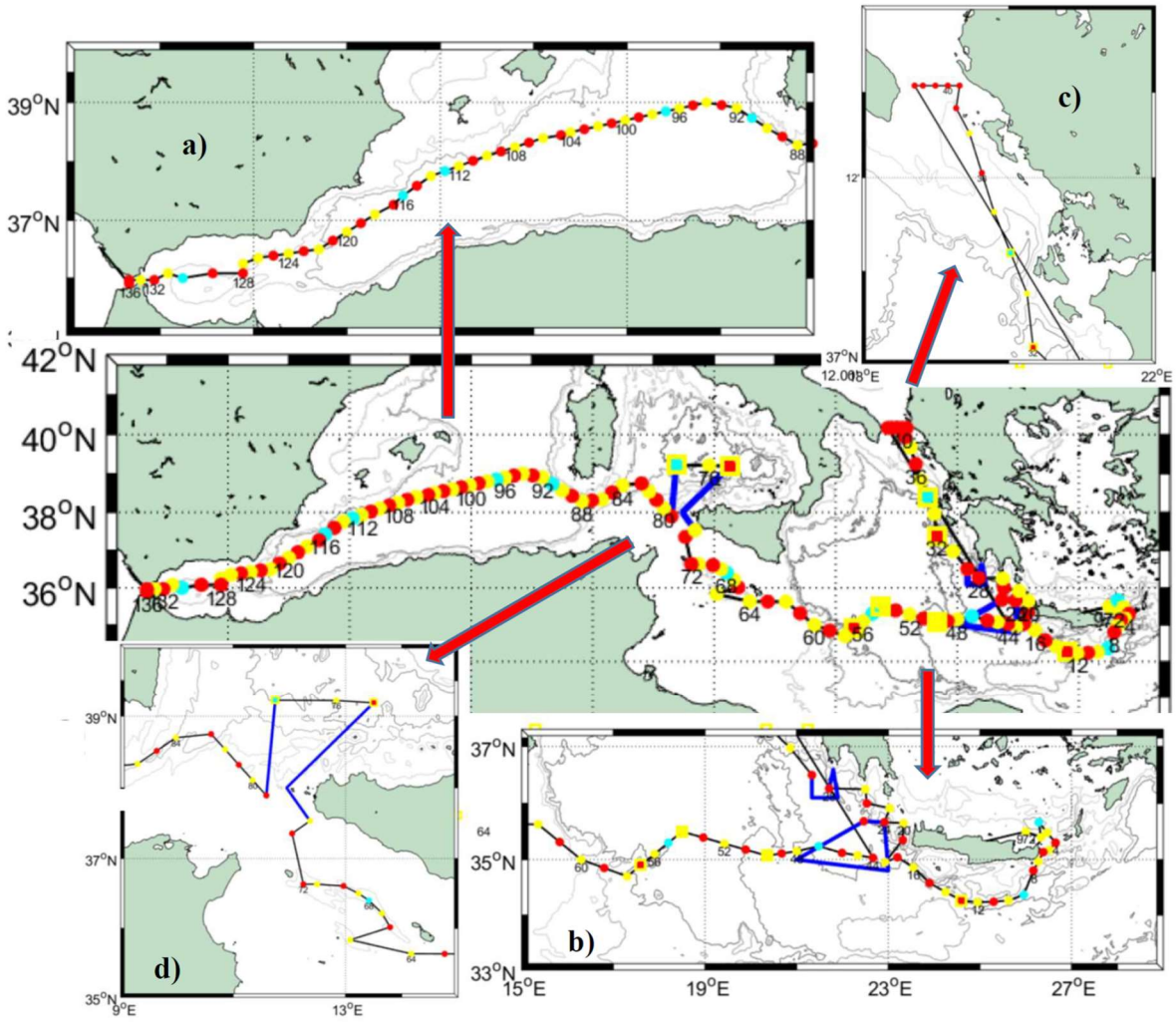

Figure 1: Station Map. Yellow dots: CTD without any chemical sampling, red dots: CTD with chemical sampling, cyan dots: CTD with chemical and additional sampling of isotopes, yellow squares: deployment of drifter and floats, blue lines: fine resolved uCTD and ADCP tracks. Black lines: Track with uCTD casts between CTD stations. a) Detail of the central map: Western Mediterranean Sea. b) Detail of the central map: Eastern Mediterranean Sea. c) Detail of the central map: Otranto Strait and northern Ionian Sea. d) Detail of the central map: Tyrrhenian Sea and Strait of Sicily.

During the thirty-three days of the cruise we carried out measurements of hydrographic and biogeochemical variables along-track with the classical approach i.e. CTD, lADCP, uCTD instrumentation and bottle samples on highly resolved sections across the Mediterranean Sea. The high resolution of CTD stations, enhanced for the physical parameters by additional uCTD measurements, allowed us to resolve the eddy field on the sections, the analysis was also supported and complemented by satellite data.

Most sections and CTD-positions follow previous sampling strategies (cruise M84 and other along the GO-SHIP line MED-01, i.e. Tanhua et al., 2013) to allow long-term trend analyses. Along the different sections, CTD stations including sampling of chemical parameters were conducted approximately every 30 nm, CTD without sampling about every 15-20 nm and with even smaller spacing in the Straits. In addition, underway CTD measurements and ADCP measurements were performed between CTD stations.

The water sampling program included measurements of all level 1 variables as defined by GO-SHIP (i.e. oxygen, macronutrients, transient tracers and the carbonate system, http://www.go-ship.org/DatReq.html) and measurements of the biogeochemical EOVs ^{13}C, nitrous oxide (N_2O) and dissolved organic carbon (DOC). These data were used to quantify trends and variability of ventilation and biogeochemical cycles, in particular uptake of anthropogenic carbon.

Sections were additionally conducted through the important passages: The Strait of Otranto, Kasos Strait, Antikythera Strait, Strait of Sicily and Strait of Gibraltar, in order to characterize the incoming and outgoing flows. CTD stations in the Eastern Ionian Sea were carried out to quantify the flow of the Levantine Surface Water (LSW) into the Adriatic Sea and to track the outflow of the Adriatic Deep Water (AdDW) into the Ionian Sea.

3. Methods

3.1 CTD/rosette

Altogether 136 CTD cast were performed from which 18 catalogued as isotopic (a full suite of observations in Table 1a and b), 65 as chemical (i.e. GO-SHIP level 1 variables), and 59 as physical (i.e. only sampling for salinity). Due to the water amount needed, 2 casts were performed on most of the isotopic stations, the first cast was a full profile and the second a shallow one. During the physical stations water samples at 3 levels were taken for salinity analysis. The samples were then analyzed on board using a Guildline Autosal Salinometer. A total of 162 samples in 59 stations were taken during the cruise with an offset with respect to standard water varying from 0.0002 to 0.0030 depending on the laboratory temperature. The samples were taken at depth with a constant salinity gradient to ensure that no natural changes in salinity affect the comparison between sample and sensor.

The primary CTD system (specifications see table 2) initially used on board was a Seabird SBE9plus + CTD s/n 0285 from the University of Hamburg connected to a SBE11 deck unit,

configured with a 24- position SBE-32 pylon (from GEOMAR) with 10-liter Niskin bottles. Position of bottles #23 and #24 was occupied by the lADCP (specifications see table 3). Initially, the CTD was set up with two sensors for temperature and conductivity, an oxygen sensor, a fluorometer and an altimeter. To test the configuration and performance of the instrument a station was carried out on the Cretan Sea at the start of the cruise. Unfortunately, we had countless problems with instruments, sensors, cables and rosette during most of the campaign which forced us to change them very often with others available on board resulting in a continuous change of system configuration. Thus, all different configurations were carefully considered when post-processing the CTD data.

Temperature, salinity and pressure data were post-processed by applying Seabird software and MATLAB® routines. At this stage, spikes were removed, 1 dbar averages calculated. A first attempt to assess the performance of the conductivity sensors installed on the CTD-Rosette was done by comparing the salinity data with the bottle samples analyzed with the salinometer. The different hardware setups and configurations are taken carefully into account during post-processing. Overall accuracies are within the expected range of salinity (0.003).

Table 2: Used CTD instrument and sensors. Owner of instruments are either the University of Hamburg, Germany (IfM-HH), the National Institute of Oceanography and Geophysics (OGS), Italy or the property of the vessel MERIAN (MSM).

Instrument/Sensor	***Serial Number (owner)***	***Calibration Date***
SBE 911plus / 917plus CTD	285 (IfM-HH) 806 (MSM) 807 (MSM)	03-Dec-14 27-Jan-16 08-Sep-15
Temperature 1: SBE-3-02/F	1717 (OGS) 5716 (MSM)	22-Nov-17 15-Jul-17
Conductivity 1: SBE-4-02/2	3442 (OGS) 4152 (MSM)	22-Nov-17 14-Jul-17
Temperature 2: SBE-3-02/F	1294 (IfM-HH) 5719 (MSM)	11-Apr-17 15-Jul-17
Conductivity 2: SBE-4-02/2	1106 (IfM-HH) 4156 (MSM)	12-Apr-17 14-Jul-17
Oxygen 1 SBE 43	3392 (OGS) 2417 (MSM) 0951 (MSM)	19-Dec-17 16-Aug-17 01-Dec-17
Oxygen 2 SBE 43	1761 (IfM-HH) 2418 (MSM) 0881 (MSM)	11-Apr-17 15-Aug-17 23-Dec-17

Fluorometer WETLAB	1755 (MSM)	18-Apr-17
	1754 (MSM)	21-Dec-17
SeaPoint (used on 1 station)	SCF2874	unknown
SPAR		10-Mar-16
PAR Chelsea		17-Oct-16

3.2 Underway-CTD

Underway CTD measurements (uCTD, specifications see table 4) provide high-resolution profiles of temperature, conductivity and depth, which allow to characterize the upper ocean properties and to identify the position and characteristics of mesoscale structures. The advantage of this type of measurements is that it is not required to stop the vessel, but only to maintain lower velocities (about 3 kn) during the deployments to reach greater depths. These measurements were made with an Ocean Science uCTD system.

The first uCTD deployment was done on March 5th, between CTD 015 and 016 stations, and we continued with this type of sampling between each CTD station to increase the sampling resolution. Unfortunately, several deployments were cancelled due to severe weather conditions and no uCTD cast was performed when the depth was shallower than 500m. Altogether 176 casts were taken with depths ranging from 557 to 864 m.

Two probes were used during the cruise with a no time limit mode configuration (apart from the first cast configured to stop recording after 600 seconds, reaching 616 m depth) in order to get longer records. The probe tail spools were attached to the winch through a rope loop that was made new every day in the morning. Despite the probes can record several casts, data were downloaded right after each cast using a SBE software in order to avoid losing the data in case the probe was lost, and to free the memory. The probes were exchanged when the battery was running low (around 3.8V). In three occasions, no data were recorded because the magnet was taken off twice before deployment.

For calibration purposes, some additional casts were done right after the CTD cast in order to compare the data sets. The probes were also sent down with the starboard CTD in station 130.

Data files were processed using a set of MATLAB® routines. After extracting the downcast data, a first correction was done for removing inaccuracies in the descend rate based on the work of Ullmann and Hebert (2013). Additionally, the data were aligned to the comparable CTD data sets.

Table 3: Used uCTD sensors.

Probe 1	*Device Type*	*Serial Number (owner)*
0289	90745 uCTD /SBE49 FastCat CTD	702-0289 (IfM-HH)
0183	90745 uCTD /SBE 49 FastCat CTD	702-0183 (IfM-HH)

3.3 lADCP Measurements

Ocean currents were studied by means of vertical profiles made with a lADCP-2 system (Workhorse RD Instruments type, table 3) which included two ADCPs operating at a frequency of 300 kHz, one looking upward and the other one looking downward. The system was placed in the rosette occupying the position of Niskin bottles 23 and 24. During the cruise, the lADCP batteries were changed twice: the first time on March 17th in Station 58 and the second time on March 27th in Station 105. Except for three stations (station 73, 74, 80) with water depths less than 500 m, lADCP measurements were done at all CTD. For these stations, the currents were observed by the ship mounted ADCP. At isotope stations, lADCP profiles were only recorded from the deep cast. The gained data were processed with LDEO MATLAB® lADCP-processing system Version 10.15 (Turnherr, 2014). This software uses the raw lADCP data, processed CTD data and navigational data from the CTD. The resulting data are the u- and v-velocities at the depth. The bin size was set to 8m.

Table 4: Used lADCP.

Device Type	Serial Number (owner)
WHM300	Master s/n #22762 (IfM-HH)
WHM300	Slave s/n #22763 (IfM-HH)

Shipborne ADCP

During the whole campaign, underway current measurements were taken with two vessel-mounted VM-ADCPs Ocean Surveyor (ADCP) manufactured by RDI. The first, with work frequency of 75 kHz, covered approximately the top 500-700m of the water column. The number of bins was set to 100 with bin size of 8 m. The second, with work frequency of 38 kHz, has a depth range of about 1600 m, set with the same bin number as the previous one and bin size of 16 m. Both instruments run in narrowband mode and were controlled by computers using the conventional RDI VMDAS software under a MS Windows system with a pinging set to fast as possible. No interferences with other used acoustical instruments were observed. The

ADCP data was afterwards post-processed with the CODAS3 Software System (https://currents.soest.hawaii.edu/docs/adcp_doc/), which allows extracting data, assigning coordinates, editing and correcting velocity data. Moreover, the data were corrected for errors in the value of sound velocity in water, and misalignment of the instrument with respect to the axis of the ship (about -2.8 degrees for 75 kHz ADCP and about -0.15 degrees for 38 kHz ADCP).

3.5 Underway CO_2 and O_2 Measurements

Underway (UW) measurements of partial pressure of CO_2 (pCO_2), and dissolved oxygen partial pressure (pO_2, the corresponding data set in Table 1b only contains pCO2) in seawater were carried out by means of a Contros HydroC pCO_2 analyzer for pCO_2 and an Aanderaa optode for oxygen.

The instruments were placed in a cooling box in the hangar. Seawater was drawn from the ship's centrifugal pump for clean seawater that was continuously flowing through the cooling box with the inlet close to the instruments. Water was pumped through a SeaBird 5 salinity and temperature sensor and on to the HydroC instrument (Gerke et al., 2020).

The system operated reliably throughout the cruise, except when data acquisition was interrupted for the pCO_2 instrument for 2 days directly after the ship's centrifugal pump was switched off. This led to a gap 5-days period without data between March 5th and 10th. During the cruise, 13 samples were taken from the cooling box for discrete measurements of pH and total alkalinity. The UW measurements started on March 2nd at 20:20 and stopped on April 1st, 2018, at 14:00 (UTC).

The underway oxygen measurements were calibrated by comparing to the Winkler measurements taken for surface samples at the chemical CTD stations.

3.6 Dissolved Oxygen

Dissolved oxygen in seawater was not only measured with the CTD, but samples were also taken at every station and depth along the cruise and reported in µmol/kg. GO-SHIP guidelines recommend Winkler measurements on all samples, in addition to sensor measurements on the CTD-package, and we largely followed those recommendations. Unfortunately, we had to mark large numbers of oxygen values determined with the CTD as questionable due to the several technical problems with the CTDs and sensors. Usually, samples were taken at standard depths but specially at the surface and at the bottom the depths were varied according to the requirements of the other biogeochemical parameters. Oxygen was measured following the automatic Winkler potentiometric method modified after Langdon (2010). Titrations were done within the sampling calibrated flasks using an Automatic Titrator Mettler Toledo T50 with a platinum combined electrode.

Reagents blank and Thiosulphate standardization were done daily by means of Potassium Iodate Standard 1.667 millimolar by OSIL, UK. About 1400 samples were analyzed on board. The precision of dissolved oxygen measurements was determined on five replicates, at the beginning and at the end of the cruise (table 5).

In addition, during the cruise 46 duplicates were analyzed. The results are given in table 6.

Table 5: Precision of dissolved oxygen. (STD = standard deviation, CV = Coefficient of Variation)

Parameter	*Beginning of the cruise*			*End of the cruise*		
	Mean µM	STD µM	CV%	Mean µM	STD µM	CV%
DISSOLVED OXYGEN	196.07	0.13	0.07	198.84	0.14	0.07

Table 6: Results of duplicates. [1]AD=|duplicate #1 – duplicate #2|; [2] RPD%=Absolute Difference *100/mean (dupl. #1, #2).

Parameter	Range µM	mean Absolute Difference [1] µM	mean Relative Percentage Difference [2]
DISSOLVED OXYGEN	179-240	0.18	0.09

3.7 Nutrients (nitrite, nitrate, phosphate, and silicate), Total Dissolved Nitrogen (TDN) and Total Dissolved Phosphorus (TDP).

Nutrients

Analyses were performed at 40 °C on a four-channel, Quaatro SEAL Analytical Continuous Flow Analyzer s/n 8014549; https://www.seal-analytical.com/Products/SegmentedFlowAnalyzers/QuAAtro39AutoAnalyzer/tabid/814/language/en-US/Default.aspx, according to Hansen and Koroleff (1999). Nitrite was determined through the formation of a reddish-purple azo dye, and measured at 520 nm (SEAL Method No. Q-030-04 Rev. 2). Nitrate was reduced to nitrite in a copperized cadmium reduction coil and then determined as described for nitrite (SEAL Method No. Q-035-04 Rev. 4). The determination of phosphate was based on the reduced blue phospho-molybdenum complex, and then measured at 880 nm (SEAL Method No. Q-031-04 Rev. 1). Silicate was determined by means of acidic reduction of silicomolybdate to molybdenum blue, then measured at 820 nm (SEAL Method No. Q-038-04 Rev. 0).

About 1400 nutrient samples were analyzed on board. The onboard precision of nutrient measurements was determined on five replicates, at the beginning and at the end of the cruise. The results are shown in table 7.

In addition, during the cruise 140 duplicates were analyzed. The results are shown in table 8.

An internal quality check was daily performed by means of analyses of QUASIMEME samples, which provided results within the already certified ranges.

Table 7: On board precision of nutrient measurements

Parameter	Beginning of the cruise			End of the cruise		
	Mean µM	STD µM	CV%	Mean µM	STD µM	CV%
NITRITE (1)	0.01	0.01	100	0.03	0.01	56.5
NITRITE + NITRATE	4.94	0.01	0.2	9.01	0.02	0.2
PHOSPHATE	0.18	0.01	5.5	0.41	0.01	3.1
SILICATE	8.34	0.03	0.3	9.55	0.04	0.5

Table 8: Analysis of duplicates. (1)AD=|duplicate #1 – duplicate #2|; (2) RPD%=Absolute Difference *100/mean (dupl. #1, #2); (3) Nitrite statistics was given just for completeness, since the concentration levels recorded were too low, often below the detection limit.

Parameter	Range µM	mean Absolute Difference (1) µM	mean Relative Percentage Difference (2)
NITRITE (3)	0-0.19	0.01	48.77
NITRITE+NITRATE	0.33-9.86	0.02	0.42
PHOSPHATE	0-0.47	0.01	5.13
SILICATE	0.93-11.00	0.04	0.72

TDN and TDP

About 550 samples for Total Dissolved Nitrogen and Total Dissolved Phosphorus (TDN and TDP) on land-based laboratory analyses were collected and frozen at -20°C after filtration on pre-combusted GF/F filter. The dissolved organic components, Dissolved Organic Nitrogen (DON) and Dissolved Organic Phosphorus (DOP) were subsequently calculated by subtracting their mineral constituents (NO_3+NO_2) and PO_4, respectively.

3.8 Discrete CO_2 System Measurements

Discrete CO_2 variables were measured on board, being Dissolved Inorganic Carbon (DIC), pH, Total Alkalinity (TA) and carbonate ion (CO_3^{2-}) at selected stations and depths (table 9). In addition, discrete samples for DIC, pH and TA were analyzed specifically from surface Niskin bottles to be compared with the continuous water supply feeding the pCO_2 system in determined stations. For further details, see Hainbucher et al. (2018).

Table 9**:** Total number of CO_2 system samples analyzed during the MSM72 cruise. Total number of fired bottles 1723.

	DIC	**pH**	**TA**	**CO_3^{2-}**	**Surface**
Samples	479	1160	949	391	22

DIC

Samples for DIC were collected following transient tracers and dissolved oxygen, in 500 ml borosilicate bottles following standard procedures. No poison was added. Samples were left at room temperature in the dark until analysis, maximum 48 hours after collection. DIC samples were analyzed with a MARIANDA VINDTA 3D system coupled with a UIC 5011 coulometer. This analysis overall consists of extracting seawater CO_2 from a known volume of sample by adding phosphoric acid, followed by coulometric detection (Johnson et al., 1993). No calibration unit was available for the system. A new coulometric cell was prepared for every batch of analysis and the accuracy of the DIC measurements was assessed by using Certified Reference Material (CRM #158 & #170 provided by Prof. Dickson, UCSD). The calibration factor obtained from the CRM was used for adjusting the final DIC of each sample measured in the corresponding batch of analysis. In addition, substandard seawater (stabilized seawater from the Cretan Sea 700m salinity minimum, stored in the dark in a 30 L container) was analysed at the beginning and end of the batch analysis as a secondary quality control. The

precision of the DIC measurements was checked by: 1) double analysis from the same sample and 2) replicate analysis from 4 to 5 samples collected from the same Niskin bottle. The precision is estimated to be 1 μmol kg^{-1} and the accuracy 2 μmol kg^{-1}.

pH

Seawater spectrophotometric pH was measured following Clayton and Byrne (1993) at almost all depths in the chemical and isotope stations during the MSM72 cruise (Table 1). This method consists on adding a volume of indicator solution to the seawater sample, so that measuring the absorbance of the sample at different wavelengths and obtaining the ratio between two of the wavelength's absorbance is proportional to the sample pH. The indicator was a 2 mM solution of unpurified *m*-cresol purple (Sigma Aldrich®) prepared in seawater and maintained at dark, with no air contact (Absorbance Ratio 1.30). Samples were taken following standard procedures immediately after DIC and directly into cylindrical 10 cm path length optical glass cells. The cells were thermostatized at 25 ± 0.2ºC during one hour before analysis. Absorbance measurements were obtained in the thermostated chamber of a double beam UV 2600 Shimadzu spectrophotometer. The equipment was checked before the cruise for the absorbance and wavelength accuracy using holmium standards. pH values on the total scale were calculated and referred at 25°C by using the formula by Clayton and Byrne (1993). The injection of the indicator in the sample slightly changes the sample pH. Following standard operating procedures, double additions of the indicator were performed over a pH gradient in order to obtain the corresponding correction (Hainbucher et al., 2018). The pH accuracy was controlled measuring TRIS buffer solution samples (batch #72, provided by Prof. Dickson, UCSD). TRIS samples were stabilized at three different temperatures covering the pH range found during the MSM72 cruise. Differences between measured and theoretical TRIS pH varied between 0.009 to 0.005. The pH precision was checked by replicate analysis from cells collected at the same Niskin from surface and deep waters. The precision is estimated to be 0.0004 pH units and the accuracy 0.005 pH units. During the cruise, some samples were also analyzed with purified *m*-cresol purple provided by Prof. Byrne (USC).

TA

TA was analyzed following a double end point potentiometric technique by Pérez and Fraga (1987) further improved by Pérez et al. (2000). This technique is faster than the whole curve titration, with comparable results (Mintrop et al., 2000). TA was measured at most stations and

depths (Table 1). Seawater samples for TA were collected after pH samples in 600 ml borosilicate bottles following standard procedures. Samples were left at room temperature in the dark until analysis, maximum 48 hours after collection. TA was measured by titration with 0.1 N hydrochloric acid dispensed with an automatic potentiometric titrator, Titrando Metrohm®, provided with a combination glass electrode coupled with a temperature probe. The electrode was standardized using a 4.41 pH ftatalate buffer made in CO_2 free seawater. The TA accuracy was assessed with CO_2 CRM (batch #170, provided by Prof. Dickson, UCSD) In addition to the CRM calibration, a drift control was conducted by analyzing substandard seawater (big volume of seawater stored in the dark, as for DIC) at the beginning and at the end of the analysis session. Each sample was measured twice and the mean value is reported, with the mean standard deviation of all duplicate differences being 0.6 μmol kg^{-1}. In addition, typical reproducibility analysis were performed from samples collected from the same niskin bottle at different stations along the cruise. The TA precision is estimated to be 1 μmol kg^{-1} and the accuracy 2 μmol kg^{-1}.

CO_3^{2-}

The CO_3^{2-} ion concentration was determined spectrophotometrically following Byrne and Yao (2008) incorporating the recent improvements by Patsavas et al. (2015), at selected stations and depths (Table 1) Samples for CO_3^{2-} were collected after TA following the same procedure as for pH but within cylindrical optical quartz 10 cm path length cuvettes. The cells were stabilized at 25°C for one hour before the analysis, maximum 24 hours after collection. A solution of 0.022 M of Pb $(ClO_4)_2$ was added to the seawater sample and the $PbCO_3$ complex formed afterwards was detected spectrophotometrically in the UV spectra. Absorbance measurements were obtained in the thermostated chamber of a double beam UV 2600 Shimadzu spectrophotometer. The equipment was checked before the cruise for the absorbance and wavelength accuracy width using holmium standards. The CO_3^{2-} in μmol kg^{-1} is the concentration of ion carbonate at 25ºC calculated using the formula by Patsavas et al. (2015). The CO_3^{2-} precision was checked by replicate analysis from cells collected at the same niskin from surface and deep waters. It is estimated to be 1 μmol kg^{-1}.

3.9 Measurements of CFC-12 and SF_6

During the cruise, one gas chromatograph purge-and-trap (GC/PT) system was used for the measurements of the transient tracers CFC-12 and SF_6. The system is modified versions of the set-up normally used for the analysis of CFCs (Bullister and Weiss, 1988). All samples were

collected in 250 mL ground glass syringes, of which an aliquot about 200 mL was injected to the purge-and-trap system, normally within 5 hours from sampling.

The traps consisted of 100 cm 1/16" tubing packed with 70cm Heysep D kept at temperatures between -70 and -75°C during trapping. The traps were desorbed by heating to 120°C and passed onto the pre-column. The pre-column consisted of 20 cm Porasil C followed by 20 cm Molsieve 5A in a 1/8" stainless steel column. The main column was a 1/8" packed column consisting of 180 cm Carbograph 1AC (60-80 mesh) and a 50 cm Molsieve 5A post-column. Both columns were kept isothermal at 60°C. Detection was performed on an Electron Capture Detector (ECD).

Standardization was performed by injecting small volumes of gaseous standard containing CFC-12 and SF_6. This working standard was prepared by the company Dueste-Steiniger (DS1,). The CFC-12 and SF_6 concentrations in the working-standard has been calibrated vs. a reference standard obtained from R.F Weiss group at SIO, and the CFC-12 data are reported on the SIO98 scale. Calibration curves were measured roughly once a week in order to characterize the non-linearity of the system, depending on workload and system performance. Point calibrations were always performed between stations to determine the short-term drift in the detector. Replicate measurements were taken except for near coastal stations due to high workload. To assess the reproducibility of the set-up, 50 replicates samples were run, and resulted in a reproducibility of 1.0 % or 0.01 pmol kg^{-1} for CFC-12 and 2.3% or 0.03 fmol kg^{-1} for SF_6. In total, we successfully measured 1084 samples on 68 stations for transient tracers. The results are discussed in Li and Tanhua (2020).

In addition to the on-board analysis, on three stations (#52, #84, and #106) 1500 ml glass ampoules were flame sealed for later analysis in the lab in Kiel for the detection of novel halogenated tracers such as HFC134a and HCFC22 (Li and Tanhua, 2019).

3.10 Dissolved Organic Carbon (DOC)

Seawater samples for DOC were collected from the CTD-Rosette into 250 ml Polycarbonate Nalgene bottles. Samples were filtered through a 0.2 µm Nylon filter under high-purity air pressure. Filtered samples were collected in 60 ml Nalgene bottles, acidified and stored at 4°C and in the dark.

DOC measurements were carried out with a Shimadzu Total Organic Carbon analyzer (TOC-Vcsn), by high temperature catalytic oxidation. Samples were acidified with HCl 2N and

sparged for 3 minutes with CO_2-free pure air, in order to remove inorganic carbon. From 3 to 5 replicate injections were performed until the analytical precision was lower than 1% (± 1µM). A five-point calibration curve was done by injecting standard solutions of potassium hydrogen phthalate in the expected concentration range of the samples. At the beginning and end of each analytical day the system blank was measured using low carbon water (LCW) and the reliability of measurements was controlled by comparison of data with a DOC reference (CRM) seawater sample kindly provided by Prof. D.A. Hansell of the University of Miami (http://yyy.rsmas.miami.edu/groups/biogeochem/CRM.html).

In total 650 samples were collected in 38 stations. Samples were collected at the following depths: 10, 25, 50, 75, 100, 150, 200, 300, 400, 500, 750, 1000 and every 250 m until the bottom.

3.11 Chromophoric dissolved organic matter (CDOM)

Chromophoric dissolved organic matter (CDOM) is the fraction of DOM that absorbs light at visible and ultraviolet (UV) wavelengths. It plays a key role in the marine ecosystem by regulating light penetration into the water column (Nelson and Siegel, 2013) and preventing cellular DNA damage (Herndl et al., 1993; Häder and Sinha, 2005). A fraction of CDOM re-emit part of the absorbed light and is called fluorescent DOM (FDOM). The study of the absorption properties of CDOM, together with the analysis of the excitation-emission matrixes (EEMs) through the parallel factorial analysis (PARAFAC) can give qualitative information on the different groups of chromophores (protein-like, humic-like and PAH-like) present in the DOM pool, their changes due to photodegradation and/or microbial transformation, the main sources of CDOM and an indirect estimation of its molecular weight and aromaticity degree (Stedmon and Nelson, 2015, Retelletti et al., 2015, Gonelli et al., 2016, Margolin et al., 2018). The CDOM data collected during the MSM72 cruise will represent an unique opportunity to: (i) Compare CDOM optical properties in the different water masses of the Mediterranean Sea with those collected in the GEOTRACES cruise (Spring-summer 2013) and to relate them to the different trophic conditions of the basin; (ii) Study the relationship between DOC and CDOM in the surface, intermediate and deep waters.

3.12 Sampling for Measurements of Stable Carbon Isotopes on Dissolved Inorganic Carbon (DIC)

Samples for the determination of stable carbon isotopes ($\delta^{13}C$) of Dissolved Inorganic Carbon (DIC) were taken on 11 stations (the "isotope stations", normally performed as a double cast) in the various basins along the cruise-track. In total 214 samples were taken in 100 ml dark glass bottles immediately poisoned with 100 µL saturated mercury chloride. The samples were measured off-line during fall of 2018 at the Centre for Isotope Research (CIO), Energy and Sustainability Research Institute Groningen (ESRIG), University of Groningen.

3.13 NO_3^- isotopes ($\delta^{15}N$ & $\delta^{18}O$)

Samples for nitrogen (N) and oxygen (O) isotopes in nitrate (NO_3^-) and nitrate+nitrite ($NO_3^- + NO_2^-$) analysis were collected at 44 stations evenly distributed along the transect. In total, 790 samples have been collected. High-resolution NO_3^- $\delta^{15}N$ and $\delta^{18}O$ measurements represent a powerful tool to unravel the sources and sinks of reactive (i.e., fixed) N at the scale of the Mediterranean Sea. Complemented with coral-bound $\delta^{15}N$ records covering the last centuries, these measurements may also shed light on the contribution of industrially fixed N to the reactive N budget, by revealing the large-scale systematics required to interpret the records back in time.

Unfiltered samples for N and O isotopic composition of NO_3^- were collected in 60 mL plastic bottles and stored frozen (-20°C) until analysis. $NO_3^-+NO_2^-$ $\delta^{15}N$ and $\delta^{18}O$ will be measured (2019-2020) at the Max Planck Institute using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Briefly, 3-20 nmol of $NO_3^-+NO_2^-$ is quantitatively converted to N_2O gas by denitrifying bacteria (*Pseudomonas aureofaciens*) that lack an active N_2O reductase. The N_2O is then analyzed by gas chromatography-isotope ratio mass spectrometer (GC-IRMS; MAT253, Thermo) with on-line cryo-trapping (Weigand et al., 2016). Measurements are referenced to air N_2 for $\delta^{15}N$ and VSMOW for $\delta^{18}O$ using the nitrate reference materials IAEA-NO_3 and USGS-34. For NO_3^- $\delta^{15}N$ and $\delta^{18}O$ analysis, NO_2^- is removed with the sulfamic acid method prior to the isotopic analysis (Granger and Sigman, 2009). The reproducibility is generally better than 0.1‰ for $\delta^{15}N$ and $\delta^{18}O$, respectively.

3.14 LISST – DEEP

The LISST-Deep instrument obtains in-situ measurements of particle size distribution, optical transmission, and the optical volume scattering function (VSF) at depths down to 3,000 meters.

It is manufactured by Sequoia Inc., and owned by the Hellenic Centre for Marine Research (HCMR) – Greece.

Using a red 670nm diode laser and a custom silicon detector, small-angle scattering from suspended particles is sensed at 32 specific log-spaced angle ranges. This primary measurement is post-processed to obtain sediment size distribution, volume concentration, optical transmission, and volume scattering function. The LISST-Deep s/n 4004 is categorized as a type B instrument, which means that the range of particles it measures ranges from 1.25 μm to 250 μm. The LISST-Deep must be powered externally at all times. This is typically achieved by connecting it to a rosette, getting power from the main CTD unit.

Parameters measured during the cruise were:

- Particle size distribution from 1.25-250μm or 2.5-500μm
- Depth (3000 m max depth @ 0.8 m resolution)
- Optical transmission @ 0.1 % resolution
- Beam attenuation Coefficient @ 0.1 m^{-1} resolution
- Volume concentration @ 0.1 μl/l resolution
- Volume scattering function (VSF)

The measurement of these parameters provided important information on the number, size and quality (phytoplankton, sediment, etc.) of the suspended matter in the water column. Further information for the determination of water masses was provided by the estimation of the intrinsic optical properties. Finally, for the first ~ 100m we estimated the color of the sea and compared this estimation with satellite images, providing valuable information for the calibration of satellite algorithms.

For the cruise MSM72 the sampling of these optical estimates is in itself an important achievement because, for the first time LISST – DEEP was used to record data in a transect over the full length of the Mediterranean Sea. Furthermore, the estimation of these parameters combined with POC - PON estimation, and other physical and chemical parameters, improve the study of the dynamics of the Mediterranean Sea.

In general, the use of LISST – DEEP during the cruise follows the standard methods, which are provided by Sequoia Inc., but with one important difference. For the estimation of the above parameters the use of a background file is required for normalization purposes. This file is normally produced in laboratory conditions with MilliQ 2 filtered water. However, experience

until now has proved that especially in the eastern Mediterranean Sea (which is characterized as ultra-oligotrophic) the use of this background file leads us to an overestimation of the parameters and especially of the beam attenuation coefficient. Therefore, during this cruise we used a sampled in situ background file chosen as the minimum of the sum of the digital counts in the 32 rings and where the LaserPower to LaserReference (Lp/Lr) ratio is maximum.

The main problem, which we faced, was the frequent change of the CTD main unit and the different cables that we had to use for the instrument connection to the CTD. Fortunately, with the most valuable help of the cruise technician we managed to deploy the LISST – DEEP as much as possible. Additionally, the maximum depth limitation of the instrument (3000m) enforced us to remove it in deep casts achieving a total of 54 stations.

4. Discussion and Conclusion

Discussion and conclusion will focus in this publication on the quality of the data of MSM72 cruise. We will concentrate here on the basic physical and biogeochemical parameters, as selected examples, to show the relevance of the sampled data and so as to be able to answer the questions on the scale and variability of the circulation and biogeochemical cycle in the Mediterranean Sea (see Introduction).

4.1 Physical parameters

The west east section (figure 2) is a typical example for the distribution of temperature and salinity in the Mediterranean Sea showing the different heat and salt content between the western and eastern basin. A clear intrusion of the salty Levantine Intermediate Water (LIW) from east to west in the first 500m is depicted while the low salinity Atlantic Water (AW) protrudes eastwards creating a front at about 20-22°E.

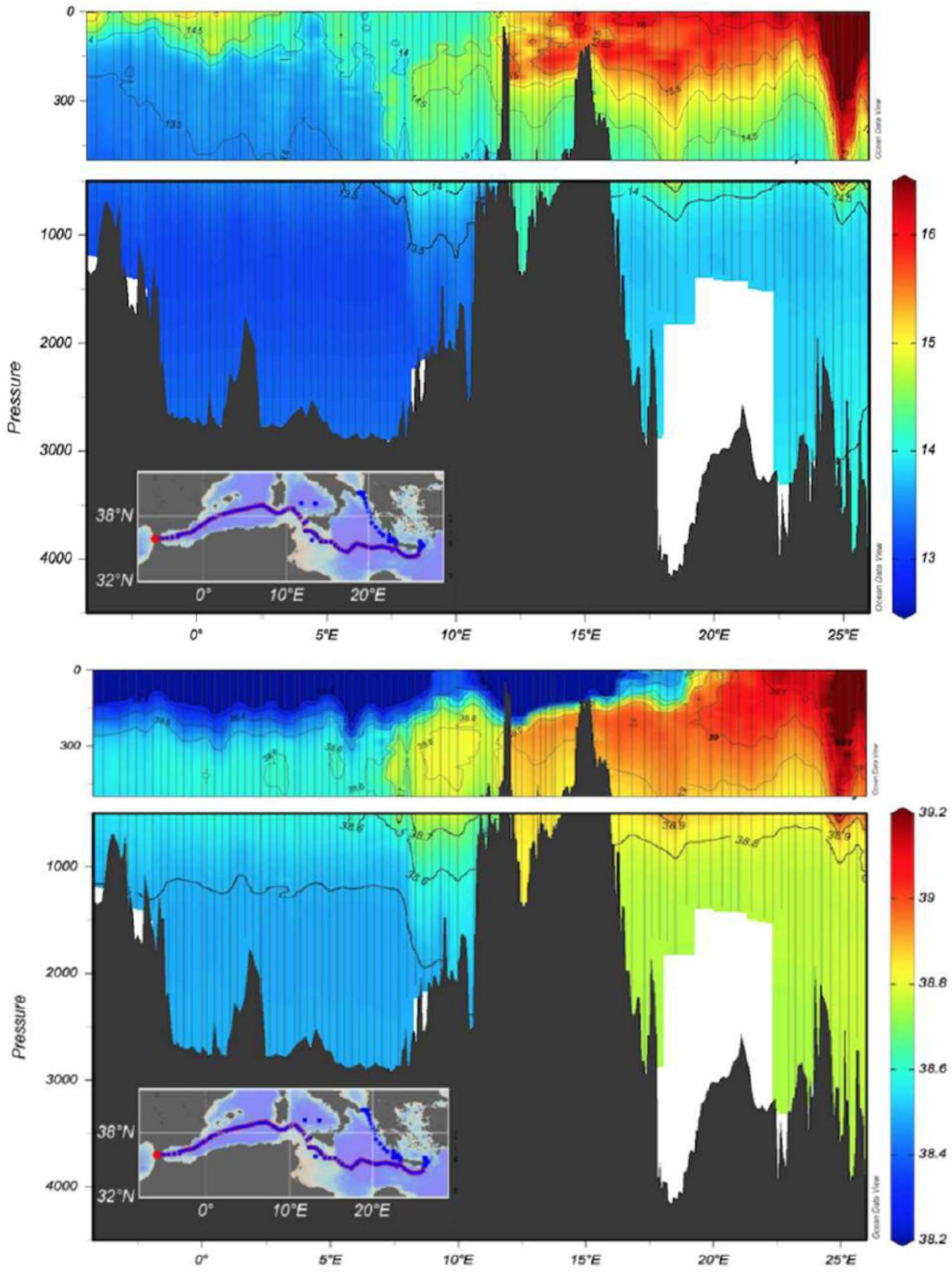

Figure 2: West-east temperature (top) and salinity (below) sections through the Mediterranean Sea.

The underway CTD data are a valuable addition to the classical CTD data. They enhance the resolution of data in the horizontal scale and give insight in eddy activity. Although the data do not reach to the bottom, the vertical resolution with about 1000 m is useful to characterize scales relevant for the LIW transport.

The uCTD stations along the easternmost part of the northward transit in the Ionian Sea are taken in average every 5 nm. Larger gaps in the line were essentially caused by the deployment of CTD stations. The uCTD salinity distribution of figure 3 shows that the Pelops gyre is well resolved.

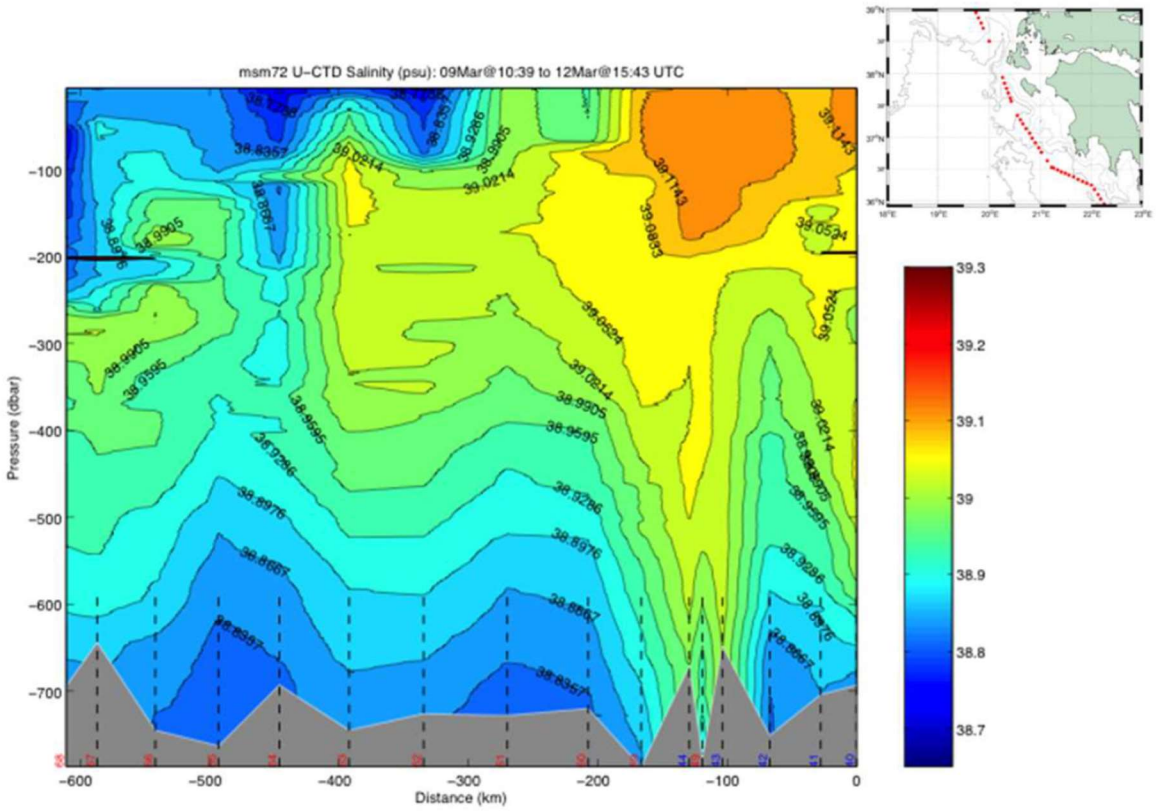

Figure 3: uCTD salinity transect. Location is shown in the upper right panel.

Considering the route of the ship during the cruise, it was possible to identify different ADCP transects that correspond to areas with the most important water mass dynamics. In particular the most important sections were: gyre activity in the area west of Crete and south of Peloponnese, the west Cretan, Otranto (figure 4) and Sicily Straits, the east boundary of the Ionian Sea and the west-east Mediterranean transect. The north-south current component (figure 4) in the Strait of Otranto clearly shows the outflow of the Adriatic Deep Water (AdDW) along the western part while in the upper and intermediate layer of the central part the inflow of the Levantine Intermediate Water (LIW) proceeds.

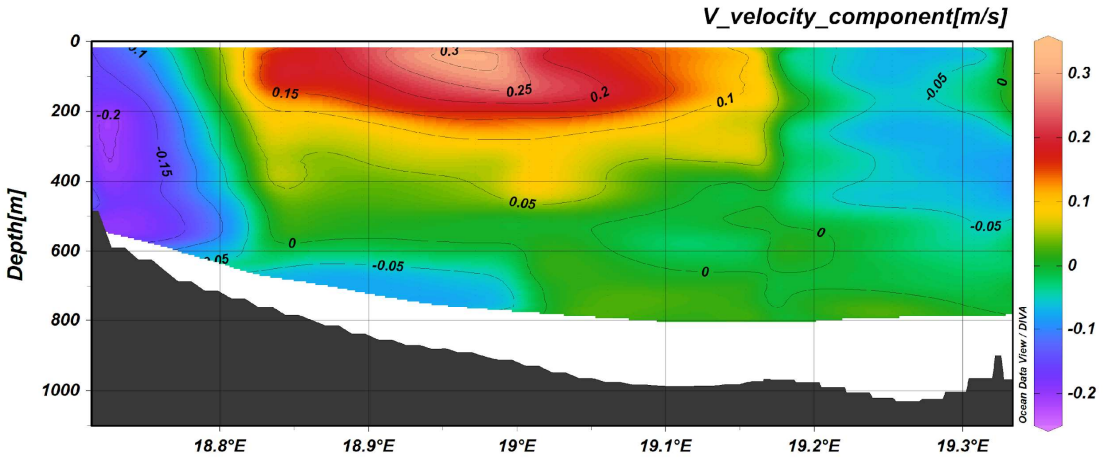

Figure 4: Transect across the Strait of Otranto from ADCP 38, positive numbers correspond to northward currents.

4.2 Biogeochemical parameters

The vertical distribution of dissolved oxygen along a section from the Cretan Sea to Gibraltar, including part of the Cretan Passage and the southern Ionian is shown in figure 5. This section shows the Oxygen Minimum Layer (<180 μmoles/kg) which occupies the layer 500-1500m. Increased oxygen towards the bottom indicate the ventilation of deep water in the Mediterranean. The western part of the Ionian Sea appears to be better oxygenated than the eastern part due to the spreading of newly ventilated dense water from the Adriatic Sea via the Otranto Strait – a feature that is observed in the transient tracer section as well.

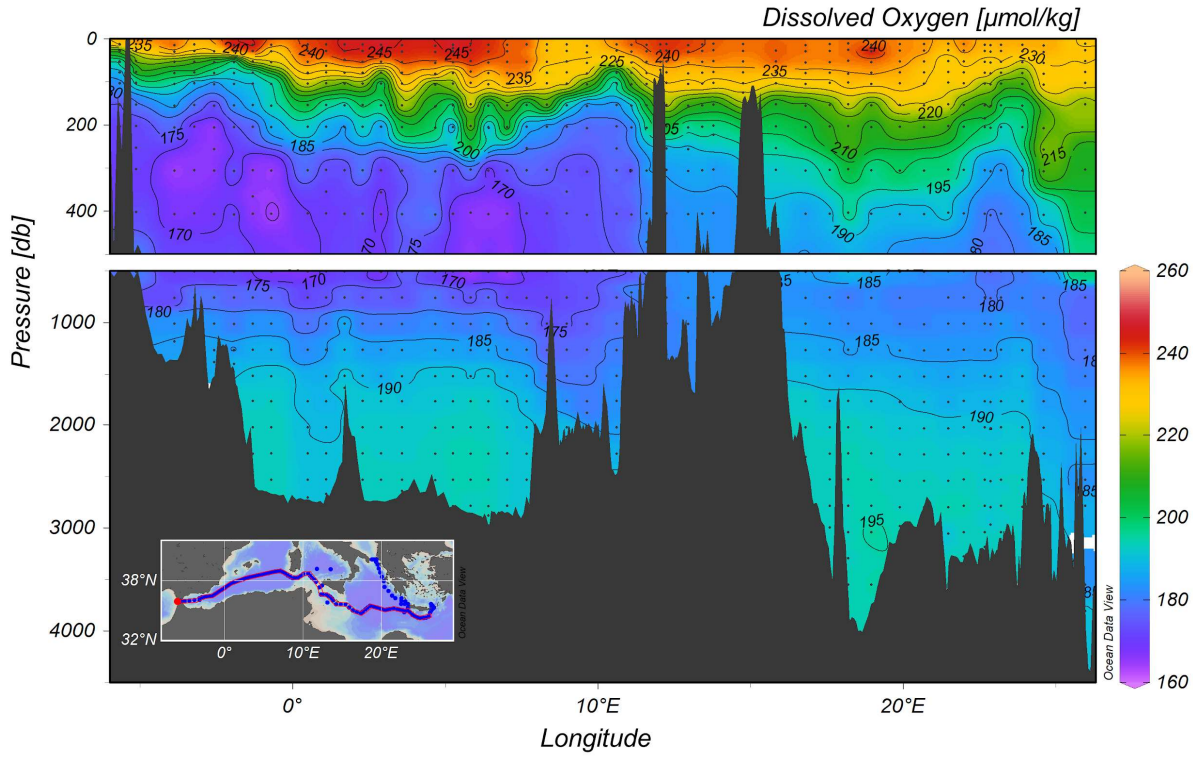

Figure 5: Distribution of dissolved oxygen along the trans-Mediterranean section.

Figure 6 illustrates the distribution of nitrate along the quasi-zonal section. Interesting features include: the maximum nutrient layer in the range of depth of 500-1500 m which is co-located to the minimum of transient tracers; the deepest layer shows an homogeneous distribution of nutrients and the nutrient impoverished upper layer is, not yet completely depleted of nutrients, likely do to subject to mesoscale dynamics (as, for example, south of Crete).

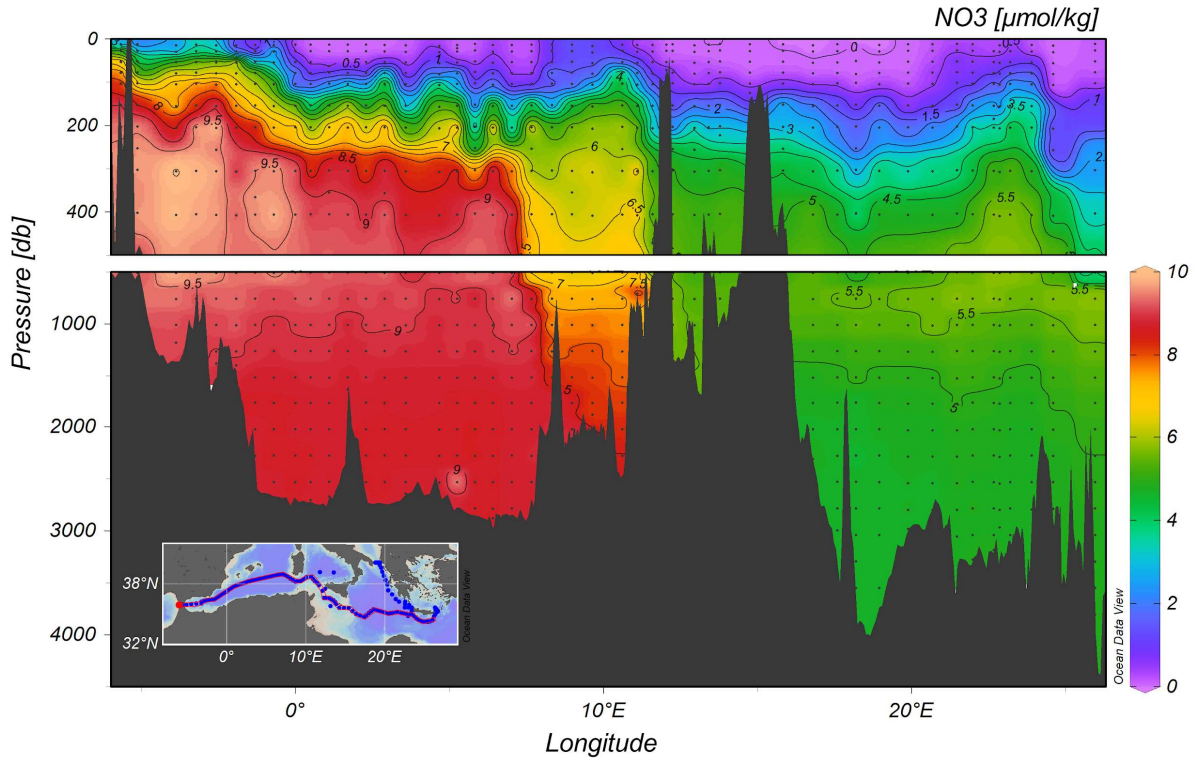

Figure 6: Distribution of nitrate along the trans-Mediterranean section.

The DOC data collected during the MSM72 cruise represents an unique opportunity to (i) investigate the long-term variation in DOC distribution in intermediate and deep waters on a basin scale; (ii) quantify the role of DOC in C export and sequestration in the Mediterranean Sea; (iv) estimate DOC mineralization rates; (v) asses the functioning of microbial loop in the different areas of the Mediterranean Sea.

DOC concentrations range between 34 and 80 µM (figure 7). The highest values (> 50 µM) were observed in the upper 200 m, with a marked increase moving eastward. The lowest concentrations (< 40 µM) are between 1000 and 2000 m, in the bottom waters a slight increase in DOC can be observed. This feature, already reported for the Mediterranean Sea, can be explained by the export of the DOC accumulated in the surface layer by deep water formation (Santinelli, 2015 and references herein). The high stratification, occurring in the easternmost stations, makes DOC accumulation there more visible. A different functioning of the microbial loop has been reported for the western and eastern Mediterranean Sea and these data support that DOC dynamics in the surface layer of the two sub-basins is different.

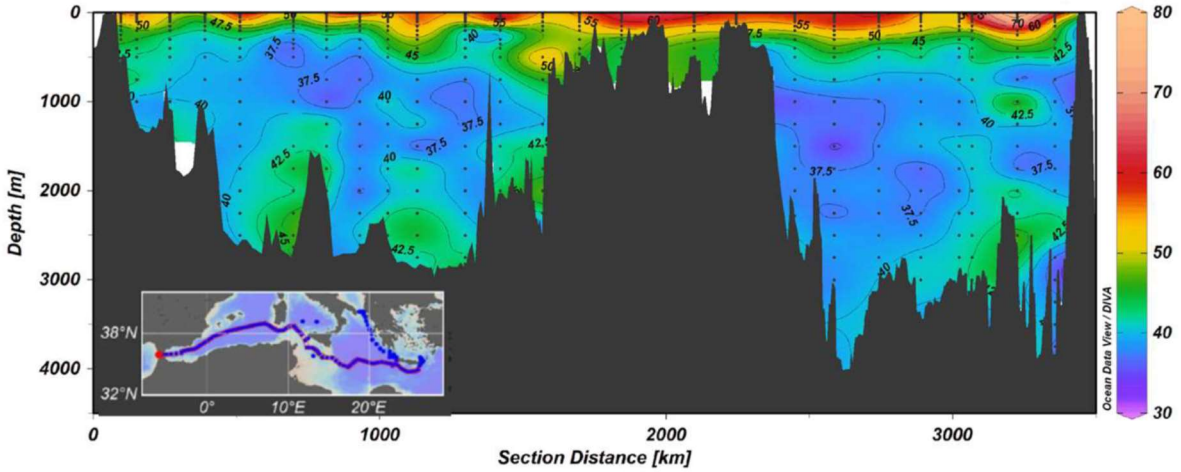

Figure 7: DOC vertical distribution along the trans-Mediterranean section

5. Data access

Data are published at the information system PANGAEA and CCHDO;

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