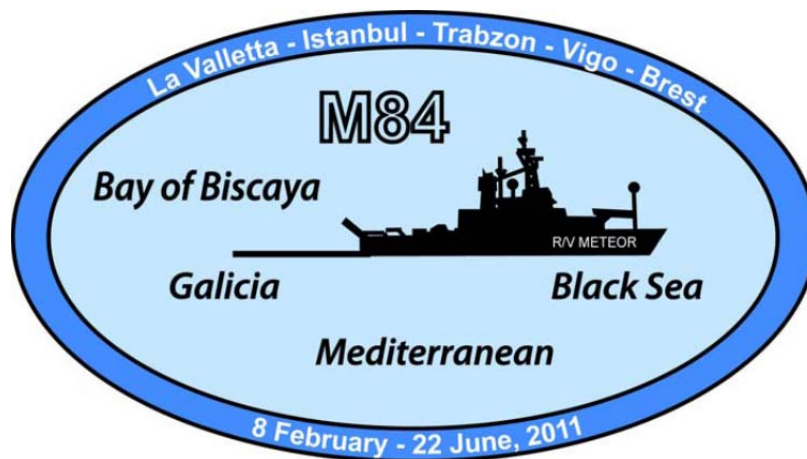


METEOR-Berichte

Repeat hydrography in the Mediterranean Sea

Cruise No. M84/3

April 5 – April 28, 2011
Istanbul (Turkey) – Vigo (Spain)



T. Tanhua

Editorial Assistance:

DFG-Senatskommission für Ozeanographie
MARUM – Zentrum für Marine Umweltwissenschaften der Universität Bremen

2013

The METEOR-Berichte are published at irregular intervals. They are working papers for people who are occupied with the respective expedition and are intended as reports for the funding institutions. The opinions expressed in the METEOR-Berichte are only those of the authors.

The METEOR expeditions are funded by the *Deutsche Forschungsgemeinschaft (DFG)* and the *Bundesministerium für Bildung und Forschung (BMBF)*.

Editor:

DFG-Senatskommission für Ozeanographie
c/o MARUM – Zentrum für Marine Umweltwissenschaften
Universität Bremen
Leobener Strasse
28359 Bremen

Author:

Dr. Toste Tanhua
Marine Biogeochemie
GEOMAR
Düsternbrooker Weg. 20
D-24105 Kiel / Germany

Telefon: +49 (0)431 600 4219
Telefax: +49 (0)431 600 4202
e-mail: ttanhua@geomar.de

Citation: T. Tanhua (2013) Repeat hydrography in the Mediterranean Sea - Cruise No. M84/3 - April 5 - April 28, 2011, Istanbul (Turkey) - Vigo (Spain). METEOR-Berichte, M84/3, 48 pp., DFG-Senatskommission für Ozeanographie, DOI:10.2312/cr_m84_3

ISSN 2195-8475

Table of Content	Page
1 Summary	3
2 Participants M84/3	4
3 Research Program	6
4 Narrative of the Cruise	7
5 Preliminary Results	8
5.1 CTD/Rosetta and hydrographic sampling	8
5.1.1 Preliminary Hydrographic Results	9
5.2 Current Measurements	12
5.3 Underway Measurements	12
5.4 Determination of dissolved Oxygen	13
5.5 The Carbonate System	16
5.5.1 Dissolved Inorganic Carbon	16
5.5.2 Determination of pH	18
5.5.3 Determination of Alkalinity	20
5.5.4 Internal Consistency Analysis of the Carbonate System	22
5.6 Measurements of CFC-12 and SF ₆	25
5.7 Determination of Nutrients	26
5.8 Sampling for Helium Isotopes and Tritium	28
5.9 Sampling for Carbon Isotopes	28
5.10 Sampling for Barium	28
5.11 Coccolithophores Assemblages in the Mediterranean Sea	29
5.12 Prokaryotic Community Composition	30
5.12.1 Instituto Español de Oceanografía Centro Oceanográfico de A Coruña	30
5.12.2 Molecular Microbial Ecology Unit at DiSTAM, University of Milan	31
5.13 N ₂ Fixation Experiments and Aerosol Sampling	32
5.14 Persistent Organic Pollutants (POPs)	33
5.15 Perfluorinated Substances	34
5.16 Trace Metals and Methylmercury	35
5.17 Radium Isotopes	37
5.18 Neodymium Isotopes	38
6 Ship's Meteorological Station	39
7 Station List M84/3	41
8 Data and Sample Storage and Availability	44
9 Acknowledgement	45
10 References	45

1 Summary

The main objectives of this cruise was to conduct measurements of physical, chemical and biological variables on a section across the Mediterranean Sea with the goal of producing a synoptic picture of the distribution of relevant properties and to compare those to historic data sets. During the cruise we were able to collect a comprehensive data set of relevant variables following the guide lines for repeat hydrography outlined by the GO-SHIP group (<http://www.go-ship.org/>). The measurements include salinity and temperature (CTD), the carbonate system, nutrients, oxygen, transient tracers (CFC-12, SF₆), Helium isotopes and tritium, carbon isotopes, barium, Radium isotopes, Neodymium isotopes, POPs, PFOS, trace metals and Methyl Mercury. Also measurements of prokaryotic community composition, were carried out and determination of coccolithophores assembles were made. In addition nitrogen fixation experiments were carried out and aerosol sampling was conducted.

The cruise sampled all major basins of the Mediterranean Sea following roughly an east-to-west section from the coast of Lebanon to through the Strait of Gibraltar and to the coast of Portugal. Also a south-to-north section from the Ionian Sea to the Adriatic Sea was carried out. We were also able to carry out sampling in the Aegean, Adriatic and Tyrrhenian Seas. The sections roughly followed lines that have been sampled previously during other programs, thus providing the opportunity for comparative investigations of the temporal development of various parameters.

Zusammenfassung

Die Reise diente dazu, Messungen physikalischer, chemischer und biologischer Parameter auf einem Schnitt durch das gesamte Mittelmeer auszuführen. Ziel dieser Messungen war, ein synoptisches Bild der Verteilung der relevanten Eigenschaften zu erhalten und diese mit historischen Daten zu vergleichen. Es gelang uns, während der Reise einen umfassenden Datensatz zu erstellen, der die Richtlinien der GO-SHIP Gruppe (<http://www.go-ship.org/>) für die Wiederholung von hydrographischen Messungen erfüllt. Die Messungen umfassen Salzgehalt und Temperatur (CTD), das Kohlenstoff System, Nährstoffe, Sauerstoff, Tracer (CFC-12, SF₆), Helium Isotope und Tritium, Kohlenstoff Isotope, Barium, Radium Isotope, Neodymium Isotope, POPs, PFOS, Spurenmetalle und Methyl Quecksilber. Weiterhin wurde die Zusammensetzung von prokaryotischen Gemeinschaften und von Coccolithophoren bestimmt und es wurden Stickstoff-Fixations-Experimente sowie Aerosol Messungen durchgeführt.

Während der Reise wurde in allen Hauptbecken des Mittelmeers gemessen. Dabei wurde ein Schnitt in Ost-West Richtung von der libanesischen Küste bis zur Straße von Gibraltar und der Küste Portugals gefahren. In der Ionischen See und der Adria wurde auf einem Süd-Nord Schnitt gemessen. Weitere Messungen erfolgten in der Ägäis, der Adria und dem Tyrrhenischen Meer. Die Schnitte folgten in etwa den Messprogrammen früherer Fahrten, um so die Möglichkeit zu Vergleichsuntersuchungen der zeitlichen Entwicklung der verschiedenen Parameter zu erhalten.

2 Participants

Toste Tanhua, Dr.	Fahrtleiter	IFM-GEOMAR
Dagmar Hainbucher	CTD/ADCP	IfM-ZMAW
Vanessa Cardin, Dr.	CTD	OGS
Andreas Welsch	CTD	IfM-ZMAW
Udo Hübner	CTD	IfM-ZMAW
Ilse Büns	O ₂ , nutrients	IfM-ZMAW
Fernando Rozada	O ₂ , nutrients	IEO
Giuseppe Civitarece, Dr.	O ₂ , nutrients	OGS
Marta Álvarez; Dr.	Carbon/bacterial DNA	IEO
Inigo Hueso	Carbon	IEO
Ludger Mintrop, Dr.	Carbon	Marianda
Carlos Colmenero	Carbon	IEO
Gaston Schaller	Carbon isotopes	CAU
Boie Bogner	Tracers	IFM-GEOMAR
Tim Stöven	Tracers	IFM-GEOMAR
Henner Bieligk	Tracers	IFM-GEOMAR
Rolf Schneider	POPs	IOW
Eike Hümpel	³ He/ ³ H sampling	IFM-GEOMAR
Eleni Stathopoulou	Mercury/TM	LEC-NKUA
Valenti Rodellas	Radium Isotopes	UAB
Mor Feldman	Radium Isotopes	BIU
Paolo Montagna, Dr.	Nd-Isotopes	LDEO
Ángela Oviedo Sabogal	Coccolithophores	UAB
Francesca Mapelli	Microbiology	DISTAM
Giuseppe Merlino	Microbiology	DISTAM
Eyal Rahav	Aerosol/N ₂ fixation	IOLR
Adi Levi	Aerosol/N ₂ fixation	IOLR
Robert Brünjes	Tracers / Barium	IFM-GEOMAR
Andreas Raeke	Weather technician	DWD
Harald Rentsch	Meteorology	DWD

Participating Institutions:

IFM-GEOMAR	Leibniz Institute of Marine Sciences Marine Biogeochemistry Kiel, Germany
CAU	Christian-Albrechts-Universität zu Kiel Kiel, Germany
IOW	Leibniz-Institut für Ostseeforschung Warnemünde, Germany
IFM-ZMAW	Institut für Meereskunde Centre for Marine and Atmospheric Sciences University of Hamburg Hamburg, Germany

Marianda	Marine analytics and data Kiel, Germany
OGS	Istituto Nazionale di Oceanografia e di Geofisica Sperimentale Trieste, Italy
IOLR	Israel Oceanographic and Limnological Research Institute, Israel
LDEO	Lamont-Doherty Earth Observatory USA
UAB	Universitat Autònoma de Barcelona Barcelona, Spain
IEO	Instituto Espanol de Oceanografia La Coruna, Spain
DISTAM	Università degli Studi di Milano Dipartimento di Scienze e Tecnologie Alimentari e Microbiologiche Milano, Italy
LEC-NKUA	Laboratory of Environmental Chemistry Faculty of Chemistry National & Kapodistrian University of Athens Athens, Greece
BIU	Bar-Ilan University, Ramat-Gan, Israel
DWD	Deutscher Wetterdienst Hamburg, Germany

3 Research Program

The last few decades has seen dramatic changes in the circulation of the Mediterranean Sea. This is manifested amongst others as a shift of deep water formation from the Adriatic to the Aegean Seas in the Eastern Mediterranean Sea and an intense deep water formation event in the mid 2000's in the Western Mediterranean Sea. The deep water formed from these two sources has different properties of salinity and temperature and different biogeochemical signature. The characteristics of the Mediterranean Sea are such that it has the potential to sequester large amounts of anthropogenic CO₂, C_{ant}, (i.e. high alkalinity and temperature and an active overturning circulation). In fact, the column inventories of C_{ant} are higher in the Mediterranean than anywhere else in the world ocean, and the C_{ant} storage in the Mediterranean is a significant portion of the anthropogenic emissions of CO₂. However, few carbon data exist in the Mediterranean Sea, and very little is known about how the recent changes in circulation has affected the storage rate of C_{ant}.

The principal scientific objectives for M84/3 had two closely-linked components: understanding and documenting the large-scale Mediterranean water property distributions, their changes and drivers of those changes. This will address the questions of a future Mediterranean Sea that will experience increasing concentrations of dissolved inorganic carbon, might become more stratified and experience changes in circulation and ventilation processes as a consequence global warming and increasing CO₂ concentrations.

The main goals of the cruise were to:

- Acquire data for a (nearly) synoptic picture of property distribution across the whole Mediterranean Sea, including all major sub-basins.
- Use these physical and chemical data to determine changes in circulation and ventilation and to quantify changes in inventory and distribution of properties, particularly inorganic carbon, i.e. uptake of anthropogenic carbon.
- Fill in existing gaps in the knowledge of the carbonate system of the Mediterranean Sea, including its sub-basins. More accurate estimates of anthropogenic carbon will be made and the storage rate of carbon will be quantified.

The objectives of the main goals were achieved by measurements of physical parameters with CTD (including oxygen measurements) and by on-board measurements of oxygen by titration, nutrients (nitrate, nitrite, phosphate and silicate), dissolved inorganic carbon (DIC), total alkalinity, pH, and the transient tracers SF₆ and CFC-12. In addition were samples taken for the determination of Helium-3 and tritium, as well as for the carbon isotopes ¹⁴C and ¹³C, for later shore-based analysis.

Several additional and complementary measurement and sampling programs were carried out during the cruise:

- A sampling program for the surface distribution of persistent organic pollutants (POPs), which was augmented by sampling for measurements of Polyfluorooctansulfonate (PFOS) on 6 depth profiles.
- Samples for the determination of dissolved barium were taken at all stations.
- Large volume samples for determination of Ra were taken from surface waters at several stations and extra CTD casts for large volume sampling were taken at 7 stations.
- Samples for determination of microbiological community structure were taken at all stations in surface and bottom waters, for stations in the Ionian/Adriatic area

additional samples in the intermediate waters were taken. The microbiological community structure will be evaluated as tool for characterization of water masses.

- Samples for determination of the isotopic composition, abundance and size of coccolithophores were taken at all stations.
- Aerosol sampling was carried out during the whole cruise; filters were changed once daily.
- Incubation experiments for nitrogen fixation were carried out for 6 positions during the cruise.
- Samples for determination of methyl-mercury were taken on 12 stations.
- Samples for determination of neodymium isotopes were taken on 13 stations.

The cruise was very successful and all measurements were carried out as planned with only slight modifications. The most significant change was the exclusion of any work in the Strait of Sicily due to the conflicts in Libya and Tunisia. A list of the stations (Figure 3.1) shows the large scale sampling and the cruise track.

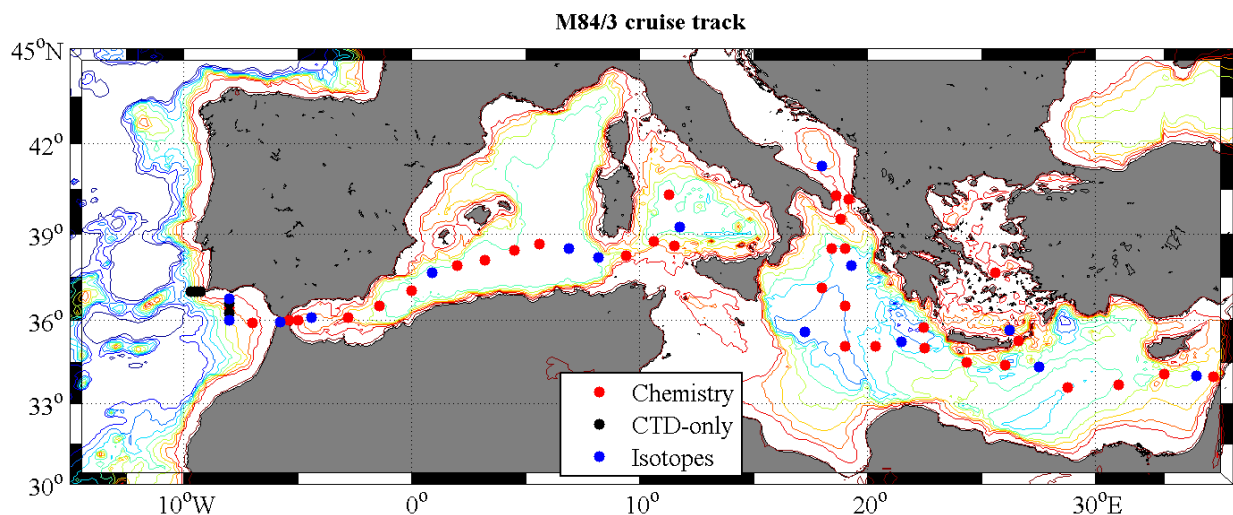


Figure 3.1: Cruise Track of M84/3 with CTD stations marked in different colors based on type of measurements that were carried out.

4 Narrative of the Cruise

The METEOR left the Haydarpacha port in Istanbul in the morning of April 5, 2011. At noon on April 6 a test CTD cast was carried out in the Aegean Sea where several groups took samples to test their instrument performance. The first ordinary station was carried out in the deep Crete basin early morning of April 7.

April 7 – 18, CTD work in the Eastern Mediterranean Sea

From here on the METEOR sailed into the Levantine basin and moved towards the eastern extreme of the Mediterranean Sea with CTD stations at regular intervals. We reached the easternmost stations around noon on April 11 just off the coast of Beirut. The METEOR now worked its way westward, occupying a CTD station roughly every 8 hours. On April 14 we reached our westernmost position in the Eastern Mediterranean, where we occupied a station that was worked during the GEOSECS experiment in 1978. From this position we headed north and occupied a meridional section from the central Ionian Sea into the deep basin of the Adriatic Sea.

On April 13 we sampled a brine lake at position N 35° 13.8' and E 21° 28.8'; this brine lake is known as lake Atalante. The brine started abruptly at 3517 dB and our deepest recording is at 3553 dB, which was approximately 20 meters above the bottom. It thus seems that the brine lake was about 55 meters deep at this position. We measured a salinity of 160 with the salinometer.

Due to the political situation in Tunisia and Libya, we could not continue our track as planned through the Strait of Sicily but instead passed through the strait of Messina on April 18. We used the long transit time between stations to have a BBQ on deck; this time was roughly half-time of the cruise.

April 19 – 24, CTD work in the Western Mediterranean Sea

On April 19 we resumed the CTD work with four stations in the Tyrrhenian Sea. From here on the METEOR moved along the section towards the Strait of Gibraltar with a full depth CTD roughly every 8 hours. We passed the Strait of Gibraltar on April 25 and then continued our section at roughly 36° N to 8°W. Here we made a short section towards the coast of Portugal. Due to the short distance between stations, the chemistry program sampled only 3 out of 5 stations on this section. Finally, we occupied a zonal section along 37° N from the coast of Portugal (Cabo Sao Vicente). This section consisted of 4 stations at which only measurements from the CTD-sonde were taken as the chemistry groups was running the last samples before packing the instruments in boxes.

5 Preliminary Results

In the following a detailed account of the types of observations, the methods and instrument used as well as some of the early results are given.

5.1 CTD/Rosette and Hydrographic Samples (D. Hainbucher, V. Cardin)

Altogether, 61 standard hydrographic stations were occupied during the cruise, employing a SeaBird SBE911 plus CTD-O₂ sonde, attached to a SeaBird carousel 24 bottle water sampler. The CTD was equipped with 2 TEMPERATURE SENSORS, 2 CONDUCTIVITY SENSORS, 2 O₂ SENSORS, a FLUOROMETER and an ALTIMETER. Additionally, a DIGITAL REVERSING THERMOMETER was attached to the sonde for calibration purposes. All sensible sensors (which are owned by IfMHH) are sent to the factory once a year for calibration. The serial numbers and calibration dates are listed in Table 5.1.

At almost all stations water samples were taken from 24 depth levels within the water column from the surface to the bottom. From three depth levels, depending on the vertical profile of the stations, samples were taken for salinity analysis. During sampling the CTD/Rosette worked without any major problems. At the beginning of the cruise we got some spiky profiles of CONDUCTIVITY SENSOR 1. After cleaning all plugs and changing the cable between the CTD and CONDUCTIVITY SENSOR 1, this problem vanished.

Instrument	Type	Ser. No.	Cal. Date	Institute
SBE 1	9plus 6800m	09P6395-0285		IfMHH
ROSETTE	SBE 9plus 6800m	09P6395-0285		RV METEOR
DECK UNIT	11plus V2	791		RV METEOR
1 ST TEMPERATURE SENSOR	SBE 3-02/F	031294	23.02.10	IfMHH
2 ND TEMPERATURE SENSOR	SBE 3plus	034324	03.03.10	IfMHH
1 ST CONDUCTIVITY SENSOR	SBE 4-02/0	041106	23.02.10	IfMHH
2 ND CONDUCTIVITY SENSOR	SBE 4-02/0	041329	23.02.10	IfMHH
1 ST OXYGEN SENSOR	SBE 43	1761	12.03.10	IfMHH
2 ND OXYGEN SENSOR	ARO-CAV	54	15.06.10	IfM Geomar
1 ST PUMP	SBE 5T	050749 3K	18.01.02	IfMHH
2 ND PUMP	SBE 5T	050931 3K	15.03.94	IfMHH
PRESSURE SENSOR	SBE 410K-105	050633	2006	IfMHH
ALTIMETER	PSA 916D	885		IfMHH
FLUOROMETER	Seapoint	SFC2874		IfMHH
DIGITAL REVERSING THERMOMETER	SBE 35RT	0065	04.04.10	RV METEOR

Table 5.1: A list of CTD sensors and instruments that were used during the cruise.

The salinity samples were analyzed using a GUILDLINE AUTOSAL SALINOMETER (Model 8300A, Serial No. 49.904). The batch-no. of the standard seawater samples is 38H11 which have a K15-factor of 1.07631 (24°C). 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, and temperature, salinity were corrected with a regression analysis which fits the downcast profiles with the temperature and salinity. Since corrections to these parameters were small, the data quality was excellent. Overall accuracies are within expected ranges: 0.002°C for temperature and 0.003 for salinity.

5.1.1 Preliminary Hydrographic Results (D. Hainbucher, V. Cardin)

The lack of stations in the Sicily Channel prevents us to have a continuous transect (Figure 5.1). However, the signal of the water flowing from the eastern to the western part of the basin is clearly evident.

The easternmost part of the East Mediterranean transect, i.e. the Levantine basin was characterized by the presence of the Levantine Surface Water (LSW), which occupies the first 50m showing high temperatures ($\theta > 18^\circ\text{C}$) and salinities ($S > 39$). Beneath the Levantine Intermediate Water (LIW) protrudes to the west with salinities higher than 38.9.

Towards the west the permanent Rhodes Gyre breaks the main LSW/LIW tongue with the outcrops of the isohalines. The well-known oxygen minimum layer is clearly present between 35°E and 30°E, in accordance with the salinity minimum in the area

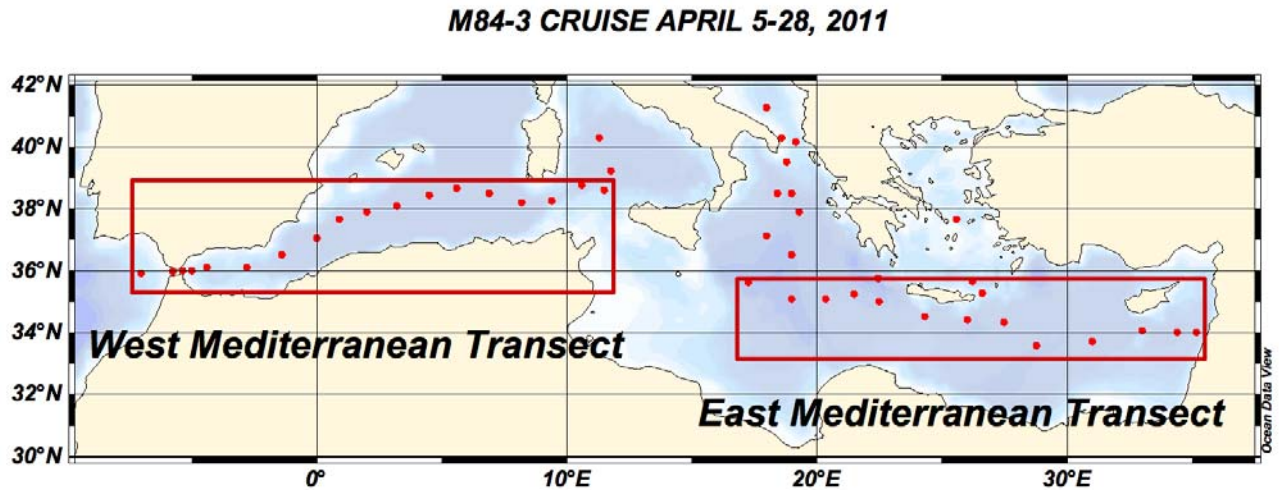


Figure 5.1: A station map with boxes indicating the position of the sections showed in Figures 5.2 and 5.3.

At the western part of the Eastern Mediterranean transect no signature of the LSW is shown in the Ionian, where the surface layer is now occupied by the Ionian Surface Water (ISW). The Cretan Cyclonic Gyre influence is confined to the upper thermocline – intermediate layer (first 400m) seen by the deepening of the isotherms.

A core of ADW is present in the bottom layer (below 2000m) as shown by the minima in temperature, $\theta < 13.4$ °C, and salinity, $S < 38.73$, and corresponding maxima in oxygen of > 204 μ M. The influence of this water seems to divide to layer below 1500m into two parts. It extends from the Central Ionian Sea to the deepest part of the Eastern Hellenic Trench.

The major LIW pathway is westward directly to the Sicilian Straits. However, a secondary important pathway is towards the north following the western shelf-break of Greece and enters the Otranto Strait. Unfortunately, the lack of stations in the Sicily Channel avoids the determination of its pathway through the Strait on its way to the Western Mediterranean. We find the core of the LIW in the northernmost part of the Strait of Sicily protruding westwards, where its characteristics are modified, occupying the layer between 300 and 800m (Figure 5.3). Near the Gibraltar Strait the LIW outflows below 200m; the upper layer of the Gibraltar strait is occupied by the inflow of the Atlantic Water (AW) into the Mediterranean Sea. The LIW tongue coincides with the oxygen minimum layer

The deepest part of the western basin (below 1000m) is filled by homogenized water with almost constant θ , S , and oxygen. The last showing high values if compared with the overlying layer.

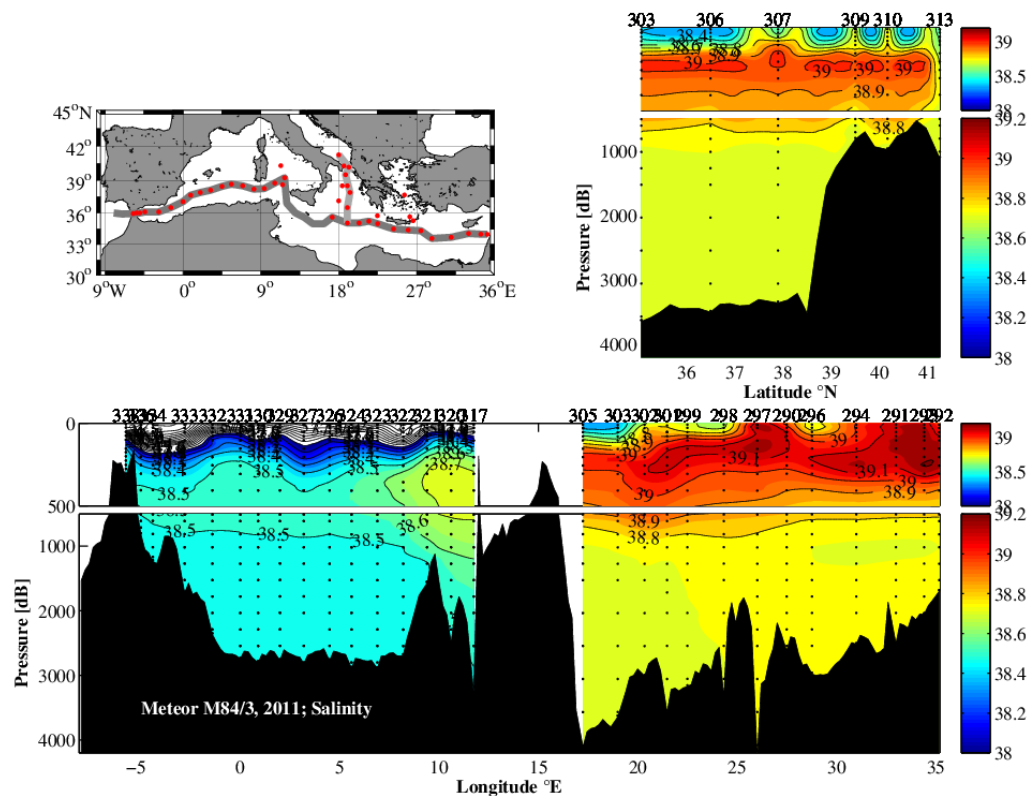


Fig. 5.2 Section of Salinity across the Mediterranean Sea. Top section is a meridional section from the Adriatic Sea to the Ionian Sea, the two bottom sections are zonal sections in the Eastern and Western Mediterranean Sea, respectively, (figure from Tanhua et al., 2013 submitted to Ocean Science).

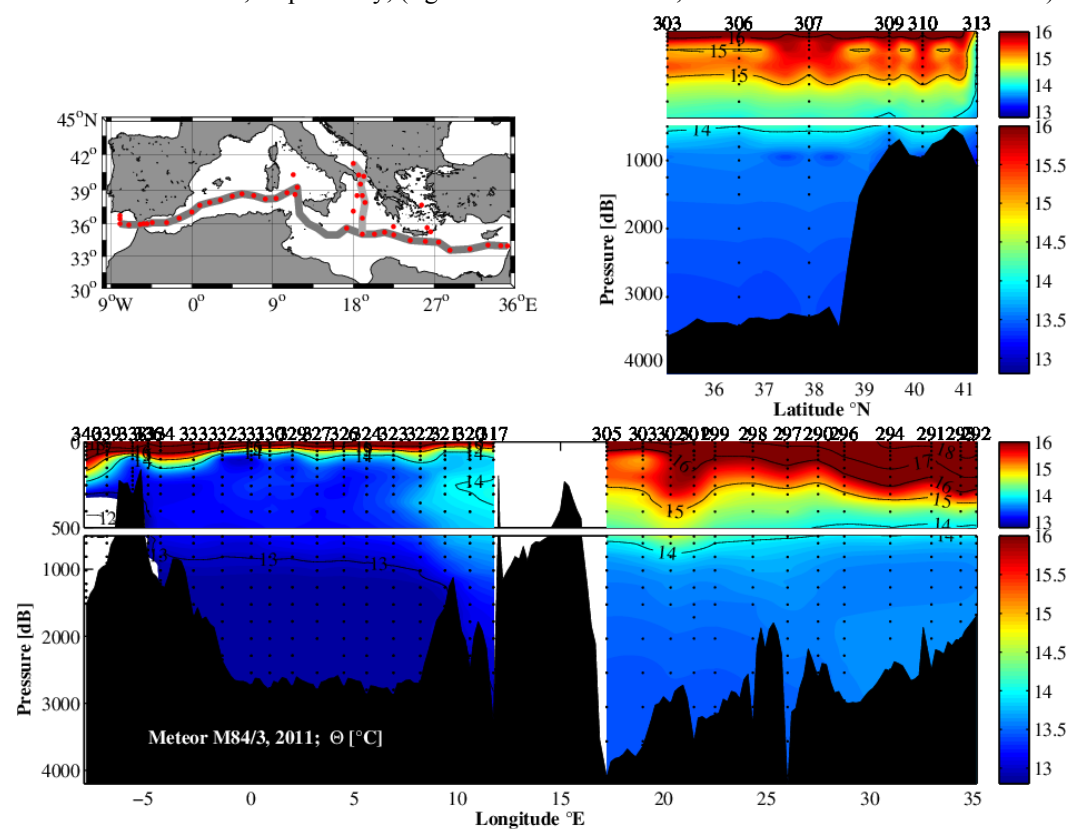


Fig. 5.3 Section of Potential Temperature across the Mediterranean Sea. Top section is a meridional section from the Adriatic Sea to the Ionian Sea, the two bottom sections are zonal sections in the

Eastern and Western Mediterranean Sea, respectively, (figure from Tanhua et al., 2013 submitted to Ocean Science).

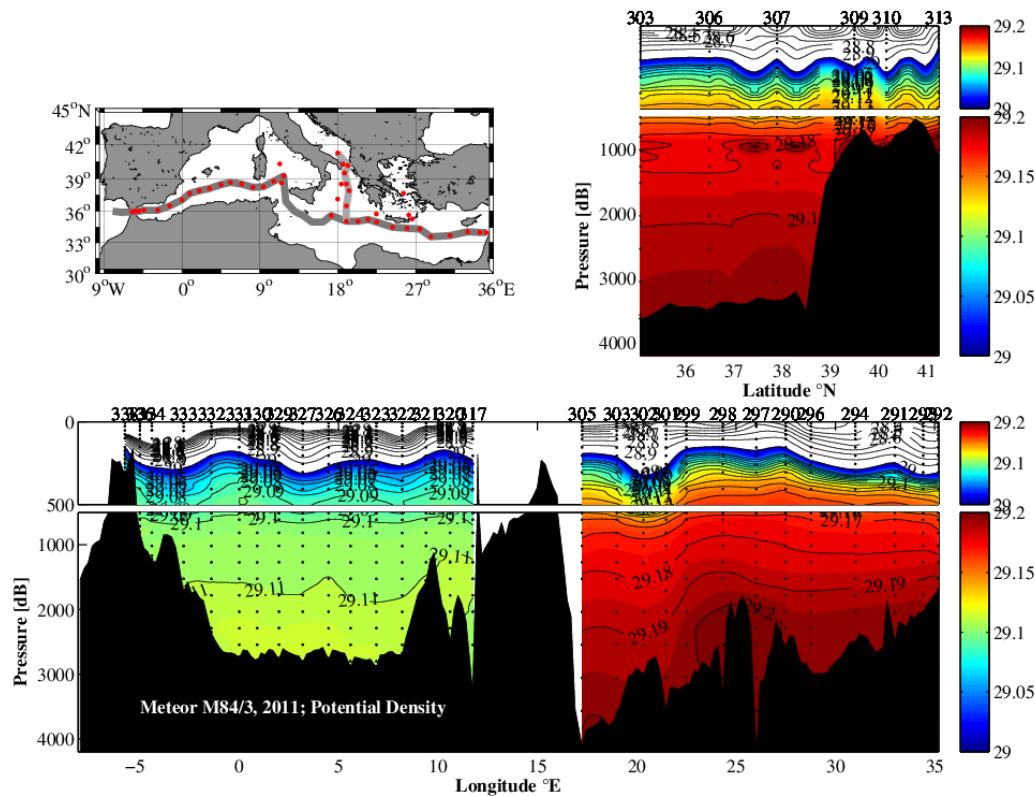


Fig 5.4 Section of Potential Density across the Mediterranean Sea. Top section is a meridional section from the Adriatic Sea to the Ionian Sea, the two bottom sections are zonal sections in the Eastern and Western Mediterranean Sea, respectively, (figure from Tanhua et al., 2013 submitted to Ocean Science).

5.2 Current Measurements (D. Hainbucher, V. Cardin)

Vertical profiles of horizontal currents were made with a LADCP-2 system attached to the ROSETTE WATER SAMPLER. The system consists of two ADCPs of the WORKHORSE type WHM300, Sentinel (serial no. 14109, 14411) manufactured by RD instruments and operating at a frequency of 300 kHz. During the cruise MSM13-2 in 2010 we already experienced several problems with the LADCP system and the LADCPs were sent back to RDI to fix the problems and repair the instruments prior to cruise M84-3. During cruise M84-3 the instruments were used after repair for the first time. However, the system continued to cause severe problems. This time, the two APCP units were not pinging synchronously, presumably due to hardware difficulties as the command files of both ADCPs should have forced them to ping synchronously. Furthermore, for almost all stations, the data stored on the internal RAMs were stored in several small files that had to be un-fragmented afterwards. We assume that this problem might have been caused by voltage drops during operation. In the end, results for some stations were totally unreliable even after post-processing them with the standard software LDEO (Turnherr et al., 2010). We suggest that we experienced interferences with the ALTIMETER of the CTD. Unfortunately, the quality of the LADCP data are therefore questionable.

5.3 Underway Measurements (D. Hainbucher, V. Cardin)

Underway temperature and salinity measurements were made with a SEABIRD THERMOSALINOGRAPH SBE21 (see METEOR Handbuch) installed in the ship's port well. For calibration purposes we took salinity samples during the first days of the cruise. Furthermore, the data were compared at stations with the results of the CTD.

It was planned to take underway current measurements with the vessel-mounted 75 kHz and 38 kHz OCEAN SURVEYORS (ADCPs). The specifications of the ADCPs can be found in the METEOR Handbuch. Unfortunately, the data of the first two days showed strange results when both ADCPs were running simultaneously. We decided to try only operate the 38 kHz ADCP, and from that time on we got reasonable results. In order to lose no more data, we waived to find out which reasons caused this difficulty and instead we were using just the 38 kHz ADCP alone during the whole cruise as our track led us to very deep waters, mostly deeper than the approximately 1000m range of the ADCP. We suggested that the 38 kHz and 75 kHz ADCPs were interfering each other or with other instruments, but other explanations like wrong or missing navigational data, wrong installation of the 38 kHz ADCP or ship's vibrations may add to the problem.

The bin size of the 38 kHz ADCP was set to 32m, the ADCP run in narrowband mode. The instrument was controlled by computers using the conventional VMDAS software under a MS Windows system. Pinging was set as fast as possible (2 s). The data was afterwards post-processed with the software package ossi14 (OCEAN SURVEYOR SPUTUM INTERPRETER), developed by the Leibniz Institute of Marine Sciences, Kiel, which also corrects for the misalignment angle (Tim Fischer, pers. communication). The misalignment angle was calculated at -3.45 degrees.

Navigational and meteorological data were taken from the ship's data system DAVIS (see METEOR Handbuch). The data were stored every minute. Navigational data like longitude, latitude, heading, pitch, roll, speed and course over ground were taken from different sources (GPS, GYRO, SEAPATH, etc.). Meteorological parameters, which were stored, are: air pressure, wind speed and direction, air temperature, humidity, dew point and radiation.

5.4 Determination of Dissolved Oxygen (M. Alvarez, F. Rozada, G. Civitarese, I. Buns)

Dissolved oxygen in seawater was measured at every station and depth along the METEOR 84/3 cruise and reported in $\mu\text{mol/kg}$. Oxygen was measured following the Winkler potentiometric method modified after Langdon (2010).

Sampling

Dissolved oxygen samples were immediately taken after the tracers, Helium, CFCs and SF_6 , when sampled. The oxygen samples were taken in pyrex "iodine titration" flasks with flared necks and ground glass stoppers, with a nominal volume of about 100 ml. The flasks were provided and calibrated at IFM-Geomar.

Each Niskin bottle was sampled using a flexible silicone tubing placed at the bottom of the flasks, which was filled till overflowing. No bubbles were allowed. The temperature of seawater was measured with a digital thermometer while sampling. The pickling reagents were immediately added afterwards, 1 ml each. The recommendations given in Langdon (2010) were carefully followed in this particular step.

After shaking the fixed samples were stored in the dark till the analysis, which was usually done within maximum 15 hours, minimum 2 hours.

Titration

The reagents used during the cruise were:

Manganous chloride (3M)

Sodium iodide (4M) / sodium hydroxide (8M)

Sulfuric acid (5M)

Thiosulfate (0.05M nominal)

As standard solutions: potassium iodate (0.01N, provided by OSIL (UK) and Wako (Japan)) and potassium hydrogen iodate (0.01N, homemade)

Titrations were done within the sampling calibrated flasks using a 808 TITRANDO METROHM POTENTIOMETRIC TITRATOR with a platinum combined electrode. The Titrand was coupled with a exchangeable unit or burette of 5 ml. Nominal errors reported by the company are 0.1 mV and $\pm 15 \mu\text{L}$. The pickling reagents were dispensed with a high precision bottle-top dispenser VARISPENSER 0.5-2.5 ml (EPPENDORF). The iodate additions were dispensed with a high precision MULTIPETTE PLUS (EPPENDORF).

Reagent blank and standardization of thiosulfate

The titration procedure for each batch of measurements is the following: i) start up the system to withdraw any bubbles in the dosing tubes titrating 2 to 3 faked samples; ii) reagent blank; iii) thiosulfate standardizations; iv) real samples. All the reagents and the samples were stored in the same lab where the temperature varied $20 \pm 1^\circ\text{C}$. The details for the former steps are given in Langdon (2010). In the case of the thiosulfate standardization in the first two batches 10 ml of iodate were used in the others 5 ml due to problems with the dispenser.

Two independent reference materials for the iodate standard were used to follow the thiosulfate evolution: 1) Homemade - a solution of around 0.01N prepared from IFM ampoules of 325 mg of potassium hydrogen iodate dissolved in 1L of distilled water. The temperature of the final solution was recorded and the molarity finally referred to 20°C . 2) Commercial potassium iodate solutions of 0.01N (20°C) provided by OSIL (UK) and a Wako (Japan). The thiosulfate solution and the reagent blank are assessed for each batch of measurements (Table 5.2 and Figure 5.5).

Note that during 19, 20, 23, 24 and 25 April two different iodate standards were used to standardize the thiosulfate concentration yielding practically the same results and assuring the reproducibility of our results with regard to the preparation of the iodate standard and the titration procedure for the standardization.

Batch	Date	Thiosulfate batch	Thiosulfate standardizations	Thiosulfate standardizations	Reagent Blank	Reagent Blank	Reagents	Standards
			Molarity 20°C	CV*100	ml	STD*100	1	IFM 1
1	06-abr	1	0.050222	0.22	0.0162	0.92	1	IFM 1
2	07-abr	1	0.050093	0.16	0.0113	0.22	1	IFM 1
3	08-abr	1	0.049829	0.64	0.0137	0.44	1	IFM 1
4	09-abr	1	0.049960	0.229	0.0106	0.62	2	IFM 1
5	10-abr	1	0.049960	0.29	0.0060	0.23	2	IFM 1
6	11-abr	1	0.049607	0.27	0.0060	0.23	2	IFM 2
7	12-abr	1	0.049680	0.20	0.0039	0.04	2	IFM 2
8	13-abr	1	0.049377	0.27	0.0080	0.04	2	Wako
9	14-abr	1	0.049681	0.05	0.0043	0.09	2	IFM 2
10	15-abr	2	0.049757	0.16	0.0031	0.12	2	IFM 2

11	16-abr	2	0.050389	0.23	0.0216	0.54	2	Wako
12	17-abr	2	0.049995	0.17	0.0152	1.26	2	IFM 2
13	18-abr	2	0.049942	0.11	0.0073	0.74	2	IFM 2
14	19-abr	2	0.049896	0.10	0.0060	0.76	2	OSIL
14	19-abr	2	0.049835	0.10	0.0060	0.76	2	IFM 2
15	20-abr	2	0.049970	0.56	0.0102	0.47	2	OSIL
15	20-abr	2	0.049961	0.20	0.0102	0.47	2	IFM 2
16	21-abr	2	0.049854	0.19	0.0080	0.15	2	IFM 3
17	22-abr	2	0.049585	0.38	0.0023	0.15	2	IFM 3
18	23-abr	2	0.049879	0.03	0.0040	0.16	2	OSIL
18	23-abr	2	0.049640	0.07	0.0040	0.16	2	IFM 3
19	24-abr	2	0.049877	0.27	0.0068	0.37	2	OSIL
19	24-abr	2	0.049821	0.23	0.0068	0.37	2	IFM 3
20	25-abr	3	0.050099	0.42	0.0072	0.47	2	Wako
20	25-abr	3	0.050157	0.05	0.0072	0.47	2	IFM 3
21	26-abr	3	0.049825	0.05	0.0059	0.58	2	IFM 3

Table 5.2: Temporal evolution of the thiosulfate concentration and reagent blank along the cruise. CV stands for Coefficient of Variation and STD for standard deviation.

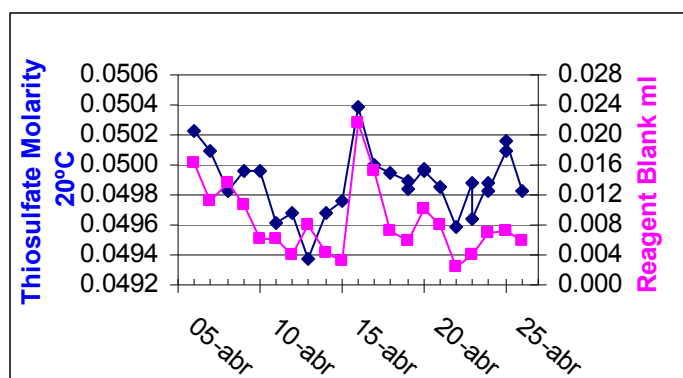


Fig. 5.5: Temporal evolution of the Thiosulfate Molarity at 20°C and the Reagent Blank (ml) along the cruise.

Reproducibility

Three reproducibility exercises were performed along the cruise. Several samples were taken from the same Niskin bottle and analysed afterwards. The results are shown in Table 5.3. These results allow us to tell that the precision for the dissolved oxygen measurements during the METEOR 84/3 cruise was $\pm 0.6 \mu\text{mol/kg}$ or better.

Station	Niskin	Bedford	Depth (m)	Salinity	O ₂ ($\mu\text{mol/kg}$)	STD	N
290	20	209705	51.6	39.124	219.7	0.57	5
311	1	212134	124.4	38.292	240.6	0.40	5
316	3	212224	1648.1	38.510	187.0	0.41	6

Table 5.3: Results from the reproducibility exercises for the dissolved oxygen samples withdrawn from the same Niskin bottle.

First quality control

A first visual inspection of the vertical distribution of the CTD and winkler oxygen data allowed us to identify some questionable data, which was considered during the final quality control of the data (Table 5.4). Note that for most of the questionable numbers correspond to Niskin bottle N°8 we have no clear explanation for as most other chemical measurements do not present any association between Niskin bottle 8 and questionable measurement. Only two

different persons sampled the Niskin bottles for oxygen, and only one was operating the titrating device.

Station	Niskin	Pressure (dbar)	Bedford	Comments
290	8	1267	209693	
292	3	1678	209736	Software error
292	8	608	209741	
293	8	1014	209765	
296	6	1777	209811	
296	8	1268	209813	
298	8	1267	209862	
301	8	1268	209930	
303	8	1268	209974	
305	8	1268	212009	
306	10	609	212033	
316	4	1648	212225	Software error
316	12	507	212233	Niskin misfire
323	8	1777	212373	

Table 5.4: Questionable oxygen data identified during the cruise.

5.5 The Carbonate System

5.5.1 Dissolved Inorganic Carbon (L. Mintrop)

A total of 836 samples were analyzed for its DIC content during the METEOR cruise 84-3

Method:

The measurement was carried out with SOMMA # 014 belonging to IfM Geomar Kiel.

The system was modified as follows:

ISA data acquisition boards replaced by LABJACK U12, temperature sensors and level sensor modified accordingly. Shuttle computer set-up to control the system: Windows XP prof. installed, all necessary programs installed. The SOMMA software (in LabVIEW, provided by MARIANDA) was installed on the PC. The software was adjusted to communicate with the respective hardware.

Samples were thermostated at 20 (+/- 0.2) °C. A calibrated thermostated pipette (volume approx. 26 ml) was filled with the sample by gas pressure (nitrogen), the sample was transferred to the stripper, acidified with phosphoric acid (approx. 10% solution) and extracted with nitrogen as carrier gas. Liberated CO₂ was measured with an UIC COULOMETER type 5012.

Since no calibration data were available for the loops of the gas calibration unit mounted to the SOMMA, this was not used. Therefore, no independent method to check the accuracy was available. The results of the CRM measurements were used to estimate the pipette volume.

Technical problems:

At some time during the first half of the cruise, the circulation pump of the thermostat bath ceased working. This led to different temperatures of sample (nominally 20°C) and pipette (room temperature). Therefore, the temperature of the sample in the pipette will have been somewhere in between these two temperatures, most likely varying with changing room temperature. This affects the mass of the sample. A non-calibrated temperature sensor was

attached to the pipette and the software modified to record this temperature. Re-calibration of this sensor after the cruise should give an estimate of the real temperature difference and its variation during the cruise. Since CRMs were run between samples, most of the error will be compensated by calibration with the CRM.

The circulation bath was repaired and worked fine for the rest of the cruise.

Precision:

The precision was controlled by titration of several bottles filled from the same Niskin bottles at two different locations (Table 5.5). From these results, it can be concluded that precision is $\pm 0.6 \mu\text{mol/kg}$ or better.

	n	mean CT [$\mu\text{mol/kg}$]	stddev.
sample A (st 310, Niskin 2)	6	2333.59	0.56 (0.024%)
sample B (st 344, Niskin 6)	6	2198.22	0.30 (0.014%)

Table 5.5: reproducibility of sea water replicates

Accuracy:

Accuracy and system calibration was done by analyzing certified reference material (CRM, Andrew Dickson, Scripps, CA, USA), batch 108; CT of this batch is given as 2022.70 [$\mu\text{mol/kg}$].

The accuracy was checked by running a total of 42 bottles of certified reference material (CRM, batch 108). Standards were run occasionally (18 times) in duplicate from the same bottle (if the first value differed by more than $1 \mu\text{mol/kg}$ from the certified value). However, only the first result was taken, since it cannot be excluded, that the bottle was affected by contact with lab air between first and second measurement. The second only had the purpose to flag the bottle questionable, should the second measurement deviate by more than $1 \mu\text{mol/kg}$ from the first measurement (this was not the case).

The certified value is given with a standard deviation of $\pm 0.7 \mu\text{mol/kg}$. Using the result of the first (worse) reproducibility test ($0.56 \mu\text{mol/kg}$) the maximum error by using the CRMs to calibrate the system can be estimated as $2.52 \mu\text{mol/kg}$ (sum of all errors).

Sample measurement:

Samples were collected from the Niskin bottles at every station in borosilicate bottles according to standard operation protocol. A small headspace ($<1\%$) was adjusted to prevent pressure build-up and loss of CO_2 during storage. Samples were not poisoned and normally measured within 12 hours (maximum storage time less than 24 hours at room temperature).

A new cell was prepared at least every 24 hours. A number of junks were measured before running samples and the blank was determined. Normally CRMs were measured after start-up and before shut-down of a cell, often also in between. 2 to 4 stations were measured with the same cell. Total carbon titrated (TCT) went up to about $60 \mu\text{g C}$ without indication for reduced performance of the cell. Preliminary results were calculated using a correction factor calculated from the CRM measurements of every single cell.

Samples were measured in the order of Bedford numbers, therefore starting with the deep samples.

Post cruise adjustment:

To calculate density of the sample, salinity values from the CTD were used. Since no calibration was needed for the salinity data, density data were not recalculated.

During the cruise, correction factors from CRM measurements were calculated for every coulometer cell, thereby comprising 2-4 stations. After the cruise, results for all CRM measurements were compared. A plot of counts for the CRM versus TCT shows a slight increase of counts with TCT (age of cell). Using the empirical formula: $\text{counts}(\text{CRM}) = 258000 + 16 \cdot \text{TCT}$ to correct for this effect, this trend can be eliminated, see Figure 5.6.

The increase of counts over time could lead to overestimation of CT for samples measured close to the end of the cell lifetime. An equation based on the relation found (see above) was used to slightly reduce counts measured for the samples, depending on TCT at time of measurement:

$$\text{counts} = \text{counts}_0 - (16 \cdot \text{TCT} \cdot \text{CT}_0 / \text{CT}_{\text{CRM}})$$

where counts_0 and CT_0 are the uncorrected values, TCT is in $\mu\text{g C}$ and CT_{CRM} is 2022.7. Only in some cases the correction was up to 2-3 $\mu\text{mol/kg}$, mostly the difference was insignificant.

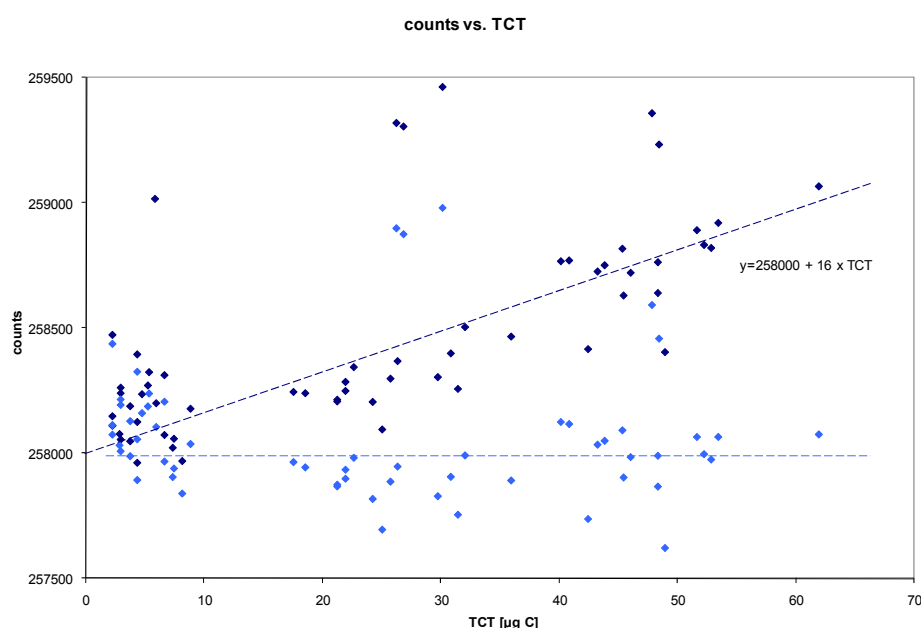


Fig. 5.6: Counts for the CRMs plotted versus total carbon titrated (TCT); dark blue - measured, light blue - equation applied to data

5.5.2

Determination of pH

(M. Álvarez, C. Colmenero Modrón, I. Hueso Zabaleta)

Spectrophotometric pH in seawater was measured following Clayton and Byrne (1993) at every station and depth along the METEOR 84/3 cruise and reported at 25°C and on the Total scale; hereinafter pH_{25T}.

Sampling

pH was sampled after Dissolved Inorganic Carbon (DIC), which was also immediately taken after dissolved oxygen and the tracers, Helium, CFCs and SF₆, when sampled. Samples were collected in cylindrical optical glass 10-cm path-length cells, which were filled to overflowing and immediately stoppered. After sampling the cells are immediately stabilised at 25°C.

Analytical method.

Seawater pH was measured using a double-wavelength spectrophotometric procedure (Byrne, 1987). The indicator was a solution of m-cresol purple (Sigma Aldrich) prepared in seawater

(2 mM). All the absorbance measurements were obtained in the thermostated (25 ± 0.2 °C) cell compartment of a BECKAM COULTER DU-800 single beam spectrophotometer. The temperature was controlled with a POLYSCIENCE (12L) thermostatic bath.

After blanking with the sampled seawater without dye, 50 μ l of the dye solution were added to each sample using an adjustable repeater pipette (EPPENDORF MULTIPETTE PLUS). The absorbance was measured at three different fixed wave-lengths (434, 578 and 730 nm). pH on the total hydrogen ion concentration scale was calculated using the following formula (Clayton and Byrne, 1993):

$$\text{pH}_1 = 1245.69/T + 3.8275 + (2.11 \cdot 10^{-3})(35-S) + \log((R-0.0069)/(2.222-R \cdot 0.133))$$

where R is the ratio of the absorbances (A) of the acidic and basic forms of the indicator corrected for baseline absorbance at 730 nm ($R = (578A-730A) / (434A-730A)$), T is temperature in Kelvin scale and S is salinity.

As the injection of the indicator into the seawater perturbs the sample pH slightly, the absorbance ratios measured in the seawater samples (R_m) should be corrected to the R values that would have been observed in an unperturbed analysis (R_{real}). In order to do this, we obtain the correction in the absorbance ratio of every sample as a function of the absorbance ratio measured (R_m). This linear function was calculated from second additions of the indicator over samples with a wide range of pH:

$$R_{\text{real}} = R_m - (-0.012 \pm 0.0016 \cdot R_m + 0.012 \pm 0.0028); \quad r^2 = 0.16, \quad n=289$$

This function also corrects for deviations in the linear relationship between absorbance and the indicator concentration; i.e., deviations from the Beer Law in the spectrophotometer. Figure 5.7 shows the relationship between the first addition ratio (R_1) and the ΔR ($R_2 - R_1$) for the set of double additions over a range of R, equivalent to pH.

All the pH measurements are referred to 25°C and corrected for the addition of the indicator using the former formula. The magnitude of that correction over our range of pH is small ranging from 0.003 to 0.0007 pH units, which are added to the uncorrected pH values.

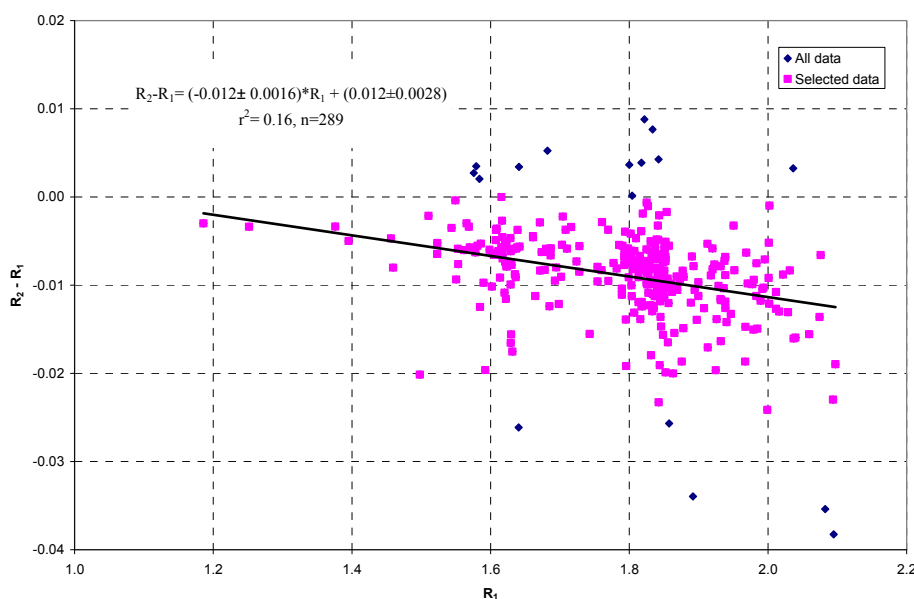


Fig. 5.7: Perturbation of sample pH induced by addition of indicator, expressed as ΔR ($=R_2 - R_1$) as a function of R_1 . R_1 is the first addition and R_2 the double addition. R is the ratio between absorbances $((578A - 730A)/(434A - 730A))$.

Accuracy.

In order to check the precision of the pH measurements, samples of CO₂ reference material (CRM, batch 108, distributed by A.G. Dickson from the Scripps Institution of Oceanography, SIO) were analyzed during the cruise. Once a week, ten to fifteen samples from a CRM bottle (batch 108, certified chemical characteristics for salinity, 33.224; silicate, 2.9 $\mu\text{mol kg}^{-1}$; nitrate, 2.71 $\mu\text{mol kg}^{-1}$; nitrite, 0.00 $\mu\text{mol kg}^{-1}$; phosphate, 0.41 $\mu\text{mol kg}^{-1}$; total alkalinity, 2218.00 \pm 0.60 $\mu\text{mol kg}^{-1}$; and total inorganic carbon, 2022.70 \pm 0.45 $\mu\text{mol kg}^{-1}$) were drawn carefully to avoid bubbles and analysed for pH using the spectrophotometric method. The corresponding theoretical pH_{25T} value for this batch using the dissociation constants from Mehrbach *et al.* (1973) refitted by Dickson & Millero (1987) is 7.8782.

The four series of CRMs measurements analysed for pH are shown in Table 5.6. Our pH measurements are lower than the theoretical value and should be increased in 0.0962 \pm 0.0012 pH units without taking into account the 08/04 values. We will discuss this point at the end of this report.

Date	pH _{25T}	STD	N	pH diff
08/04/2011	7.7891	0.0017	14	-0.0891
17/04/2011	7.7808	0.0028	8	-0.0974
19/04/2011	7.7822	0.0022	10	-0.0960
26/04/2011	7.7831	0.0026	9	-0.0951

Table 5.6: Mean and standard deviation (STD) values for the CRM batch 108 determinations on pH. N stands for the number of measurements and pH diff is the difference with the theoretical value using the Mehrbach *et al.* (1973) refitted by Dickson and Millero (1987) CO₂ constants.

Reproducibility

At three occasions along the cruise-track at stations when enough water and time was available, we analyzed several samples collected from the same Niskin bottle (Table 5.7). The mean of the STD is \pm 0.0012 which could be considered as the reproducibility of pH measurements during the cruise.

Date	Bedford	Station	Niskin	Pressure (dbar)	Salinity	pH _{25T}	STD	N
09/04/2011	209759	293	2	2038	38.788	7.8062	0.0028	7
16/04/2011	212113	310	2	960	38.720	7.9332	0.0009	8
25/04/2011	213203	339	11	202	35.924	7.8575	0.0010	8

Table 5.7: Characteristics of the replicate samples taken along the cruise, the mean and standard deviation (STD) and number of cells collected from each bottle for the pH analysis.

5.5.3

Determination of Alkalinity

(M. Álvarez, C. Colmenero Modrón, I. Hueso Zabaleta)

Total Alkalinity (TA) along the METEOR 84/3 cruise was analyzed following a double end point potentiometric technique by Pérez y Fraga (1987) further improved in Pérez *et al.* (2000). This technique is faster than the whole curve titration but comparable (Mintrop *et al.*, 2000).

Sampling.

Seawater samples for TA were collected in 600 ml borosilicate bottles after pH samples and stored in the laboratory until analysis, usually no later than 1 day after sampling. Samples were filled to overflowing and immediately stopped. All the stations and depths were

sampled for TA, DIC and pH in order to have an over-determined CO₂ system. However due to lack of sampling bottles no TA samples were collected in station 309. Additionally in stations 319, 338, 339 and 340 TA measurements were done from the „left over” water after the DIC measurements.

Analytical method

TA was measured using an automatic potentiometric titrator TITRANDO 808 METROHM, with a METROHM AQUATRODE PLUS 6.302.6150 combination glass electrode and a Pt-100 probe to check the temperature. The system is coupled with a 10 mL burette or exchangeable unit. Potentiometric titrations were carried out with hydrochloric acid ($[HCl] = 0.1\text{ N}$) to a final pH of 4.40 (Pérez and Fraga, 1987). The electrodes were standardised using a phthalate buffer of pH 4.41 made in CO₂ free seawater (Pérez *et al.*, 2002). Concentrations are given in $\mu\text{mol kg}^{-1}$. Table 5.8 shows the value of the asymmetrical pH (pH_{as}), which is the value of the electrode pH after its calibration. The 0.1 N hydrochloric acid solution was prepared by mixing 0.5 mol (18.231 g) of commercially available HCl supplied by Riedel-deHaën® (Fixanal 38285) with distilled water into a graduated 5-L beaker at controlled temperature conditions. The HCl normality is exactly refereed to 20°C. The variation of salinity after the titration is lower than 0.1 units, which is taken into account in the final TA calculation.

Accuracy

CRM analyses were performed in order to control the accuracy of our TA measurements (Figure 5.8). Accordingly, the final pH of every batch of analyses was corrected to obtain the closest mean TA on the CRM analyses to the certified value ($2218.00 \pm 0.60\text{ }\mu\text{mol kg}^{-1}$). Table 5.8 shows the pH (ΔpH) correction applied to each batch and the mean value of the CRM determinations after applying the former correction.

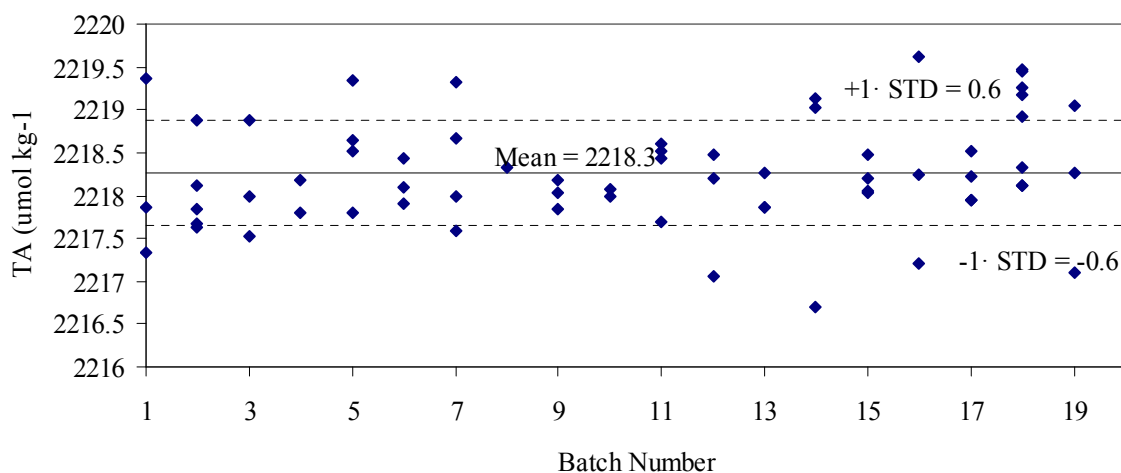


Figure 5.8: Alkalinity ($\mu\text{mol kg}^{-1}$) measurements on the CRM batch 108 during the cruise against station number. The final mean and standard deviation (STD) for the 65 determinations was $2218.3 \pm 0.6\text{ }\mu\text{mol kg}^{-1}$.

Reproducibility

Usually, each sample is analyzed twice for alkalinity. Table 5.8 shows the average standard deviation of the replicates analyzed during each batch of analysis. This difference was about $1.0\text{ }\mu\text{mol kg}^{-1}$. In order to check the precision of the TA measurements, surface seawater was used as a “quasi-steady” seawater substandard (SB). It consists in surface seawater taken from the non-toxic supply and stored in the dark into a large container (25 L) during 2 days before use. This substandard seawater was analyzed at the beginning and at the end of each

batch of analyses to control the drift in the analyses for each batch. The estimated drift for each day was very low.

At three stations along the cruise when enough water and time was available, we analyzed several samples collected from the same Niskin bottle (Table 5.9). Disregarding the first exercise where in fact samples for TA were taken from left-over of several bottles closed at the same depth, the maximum STD is $\pm 0.6 \mu\text{mol kg}^{-1}$ which is considered as the reproducibility of TA measurements during the cruise.

Batch	April 2011	Stations	N _{HCl}	ΔpH	Fitted TA	Av. Dif.
1	06	287-288-289	0.100088	-0.021	2218.2 \pm 1.1 (3)	0.5
2	08	290	0.100088	0.016	2218.0 \pm 0.5 (5)	0.6
3	09	291-292	0.100088	0.001	2218.1 \pm 0.7 (3)	0.4
4	10	293-294	0.100088	0.015	2218.0 \pm 0.3 (2)	0.5
5	11	296	0.100088	0.000	2218.3 \pm 0.5 (4)	0.2
6	12	297-298	0.100088	0.009	2218.1 \pm 0.3 (3)	0.5
7	13	299-300-301	0.100088	0.010	2218.4 \pm 0.8 (4)	0.5
8	14	302-303	0.100088	0.022	2218.3 \pm 0.1 (4)	0.5
9	15	305	0.100088	0.030	2218.0 \pm 0.2 (3)	0.6
10	16	306-307-309	0.100064	0.030	2218.0 \pm 0.1 (2)	0.4
11	17	313-314	0.100064	0.050	2218.3 \pm 0.4 (4)	0.3
12	18	315	0.100064	0.062	2218.1 \pm 0.8 (4)	0.3
13	20	316-317-319	0.100064	0.040	2218.0 \pm 0.2 (3)	0.4
14	21	320-321-322	0.100064	0.022	2218.3 \pm 1.4 (3)	0.6
15	22	323-324-325	0.100064	0.040	2218.2 \pm 0.2 (4)	0.6
16	23	327-329	0.100064	0.055	2218.4 \pm 1.2 (3)	0.5
17	24	330-331-332	0.100071	0.026	2218.0 \pm 0.2 (4)	0.6
18	25	333-334-336-337	0.100071	0.039	2218.2 \pm 0.1 (8)	0.6
19	26	339-338-340-342	0.100071	0.029	2218.1 \pm 0.9 (3)	0.8

Table 5.8: Alkalinity analysis supplementary information for each batch of analysis: N_{HCl} is the normality referred to 20°C of the hydrochloric solution used; ΔpH is the pH correction applied to refer the TA determinations on the CRM to the corresponding nominal value (batch 108 with a certified TA of $2218.00 \pm 0.60 \mu\text{mol kg}^{-1}$). The mean value of the TA measurements on the CRM samples is also shown (Fitted TA \pm standard deviation (number of analysis)). The average of the difference (Av. Dif.) in the duplicate's analyses is shown.

Date	Bedford	Station	Niskin	Pressure (dbar)	Salinity	TA $\mu\text{mol kg}^{-1}$	STD	N
10/04/2011	209759	293	2	2038	38.788	2614.9	2.3	23
16/04/2011	212113	310	2	960	38.720	2614.0	0.3	12
26/04/2011	213520	344	6	698	36.502	2410.0	0.6	12

Table 5.9: Characteristics of the replicate samples taken along the cruise, the mean and standard deviation (STD) and number of analysis performed from each bottle for the TA analysis.

5.5.4 Internal Consistency Analysis of the Carbonate System (M. Álvarez)

The over determination of the CO₂ system during the METEOR 84/3 cruise measuring simultaneously DIC, TA and pH allows performing an internal consistency analysis in order to check for the best CO₂ constants. Using the CO2SYS 1.01 program option 4 using the Mehrbach et al (1973) refit by Dickson and Millero (1987) seems to be our preferred option.

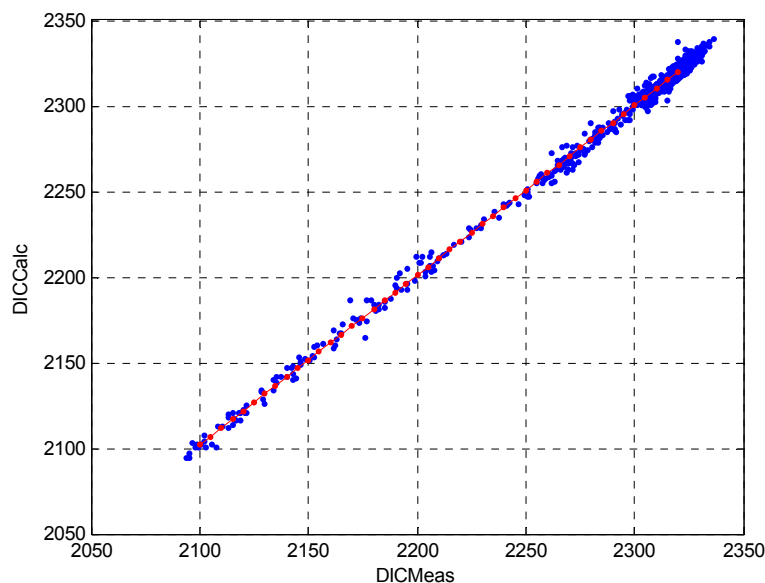


Figure 5.9: Relationship between measured and calculated (from pH and alkalinity) Dissolved Inorganic Carbon (DIC in $\mu\text{mol kg}^{-1}$). Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

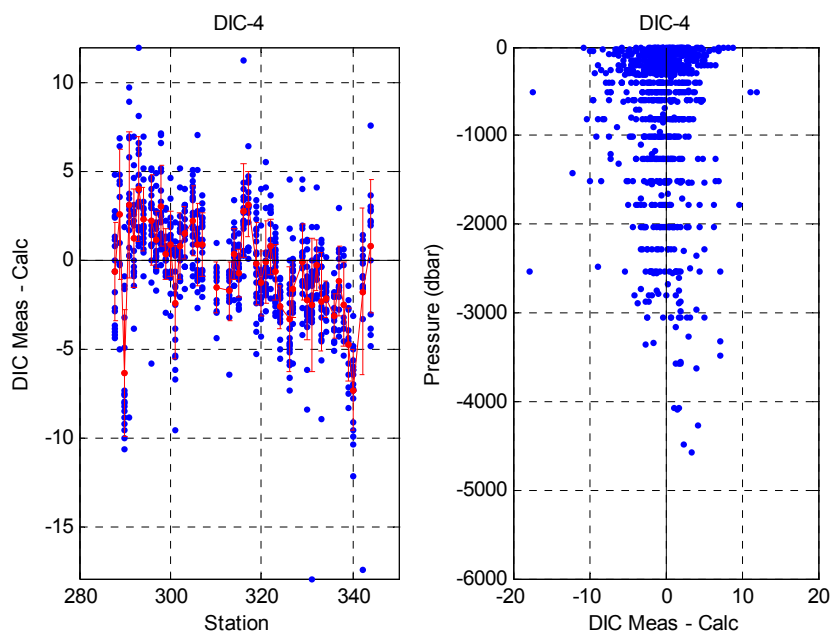


Figure 5.10: Distribution of the residuals between measured and calculated (from pH and alkalinity) Dissolved Inorganic Carbon (DIC in $\mu\text{mol kg}^{-1}$) by station and with pressure. Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

DIC calculated from measured pH25T (error 0.0012) and TA ($1 \mu\text{mol kg}^{-1}$) using option 4 yields an error of about $4 \mu\text{mol kg}^{-1}$. The relationship between DIC calculated and measured is the following: $\text{DIC calc} = 0.992 \pm 0.002 \times \text{DIC meas} + 19.5 \pm 4.7$ ($r^2=0.997$, $n=805$, $-0.3 \pm 3.3 \mu\text{mol kg}^{-1}$, mean \pm STD of the residuals). Figure 5.9 shows this relationship and Figure 5.10 the residuals against station number and pressure. TA calculated from measured pH25T (error 0.0012) and DIC ($0.7 \mu\text{mol kg}^{-1}$) using option 4 of CO2SYS yields an error of about $3 \mu\text{mol kg}^{-1}$. The relationship between TA calculated and measured is the following: $\text{TA calc} = 1.015 \pm 0.002 \times \text{TA meas} - 38 \pm 5$ ($r^2=0.998$, $n=805$, $0.4 \pm 3.7 \mu\text{mol kg}^{-1}$, mean \pm STD of the residuals). Figure 5.11 shows this relationship and Figure 5.12 the residuals against station number and pressure.

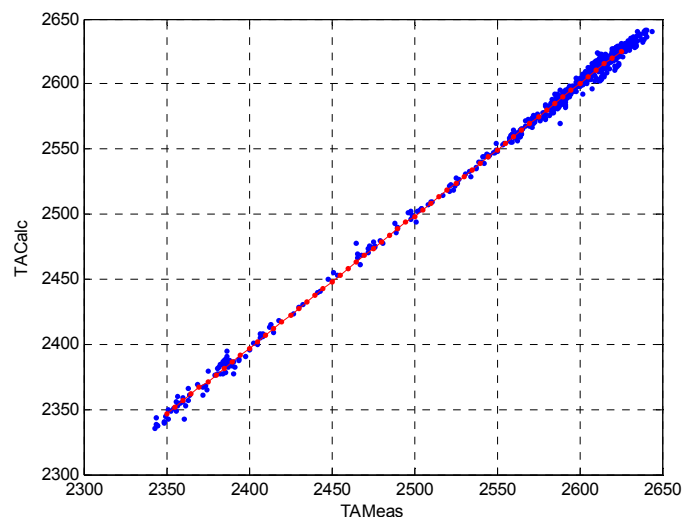


Figure 5.11: Relationship between measured and calculated (from pH and DIC) Dissolved Total Alkalinity (TA in $\mu\text{mol kg}^{-1}$). Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

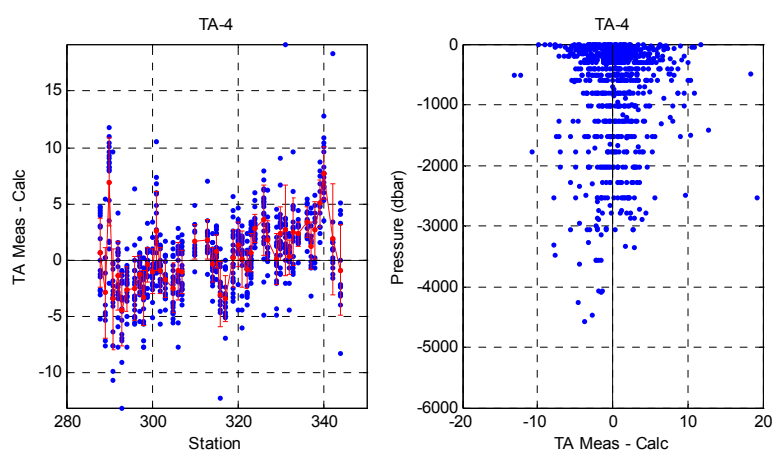


Figure 5.12: Distribution of the residuals between measured and calculated (from pH and DIC) alkalinity (TA in $\mu\text{mol kg}^{-1}$) by station and with pressure. Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

pH_{25T} calculated from measured TA (error $1 \mu\text{mol kg}^{-1}$) and DIC ($0.7 \mu\text{mol kg}^{-1}$) using option 4 yields an error of about $0.003 \mu\text{mol kg}^{-1}$. The relationship between pH_{25T} calculated and measured is the following: $\text{pH}_{25T} \text{ calc} = 0.937 \pm 0.004 \times \text{pH}_{25T} \text{ meas} + 0.49 \pm 0.03$ ($r^2 = 0.987$, $n = 805$, $-0.0008 \pm 0.006 \mu\text{mol kg}^{-1}$, mean \pm STD of the residuals). Figure 5.13 shows this relationship and Figure 5.14 the residuals against station number and pressure.

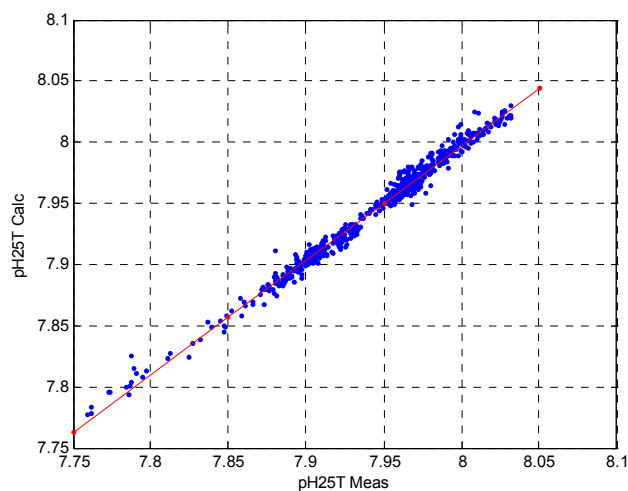


Figure 5.13: Relationship between measured and calculated (from TA and DIC) pH_{25T}. Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

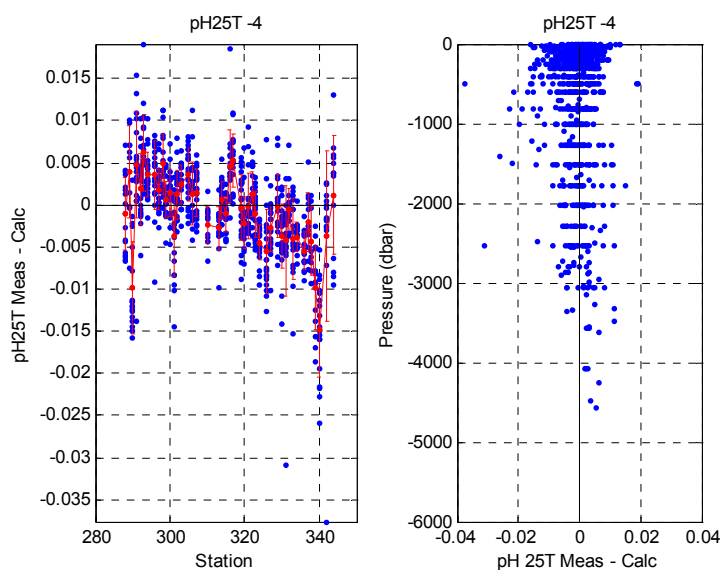


Figure 5.14: Distribution of the residuals between measured and calculated (from TA and DIC) pH25T by station and with pressure. Using the Mehrbach et al (1973) refit by Dickson and Millero (1987) constants.

5.6 Measurements of CFC-12 and SF₆ (T. Stöven, B. Bogner, T. Tanhua)

During the cruise, two GAS CHROMATOGRAPH / PURGE-AND-TRAP (GC/PT) systems were used for the measurements of the transient tracers CFC-12 and SF₆. The systems are modified versions of the set-up normally used for the analysis of CFCs (Bullister and Weiss, 1988). The first section from Istanbul to the middle of the Ionian section the instrument “PT2” was used for measuring SF₆ and CFC-12. Afterwards, in the Tyrrhenian Sea, the instrument “PT3” was used for measuring CFC-12 due to some problems with the ELECTRON-CAPTURE-DETECTOR from PT2 which finally broke down at the beginning of the Adriatic section. The samples of the stations of Adriatic Sea and the second part of the Ionian Sea were flame sealed in ~350 ml ampoules, and was measured onshore at IFM-GEOMAR after the cruise. Due chromatographic difficulties on PT3, we were not able to measure SF₆ on board, but flame sealed samples from selected stations (normally the same as we collected isotopes from) for onshore measurement post-cruise.

The traps for both systems were 100 cm of 1/16” tubing packed with Heysep D. The tracers were trapped at -60 to -68°C; desorption at 125°C. For both systems, the pre-column was a 30 cm long Porasil C 1/8” column, whereas the main column consisted of a 200 cm 1/8” column packed with 180 cm Carbograph 1AC (60-80 mesh) and a 20 cm Molsieve 5A tail end. Detection was performed on an Electron Capture Detector (ECD). This set-up allowed efficient analysis of SF₆ and CFC-12 on the PT2 system (CFC-12 elutes slightly after, but well separated from SF₆). For both systems the column temperature was set to 50°C followed by a temperature program to optimize the measuring time per sample mostly affected by a large area peak at the end of the chromatogram.

For PT3, samples were collected in 250 ml ground glass syringes, and an aliquot of about 200 ml was injected into the analytical system. For PT2, samples were collected in 350 ml glass ampoules, and an aliquot of about 250 ml was injected into the system through a vacuum-sparge technique, similar to that described by (Law et al., 1994).

Standardization was performed by injecting small volumes of gaseous standard containing SF₆ and CFC-12. This working standard was prepared by the company Dueste-Steiniger (Germany). The CFC-12 and SF₆ concentration in the standards 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 and SF₆ on the NOAA-2000 scale. Another calibration of the working

standard took place in the lab after the cruise. Calibration curves were measured every few days to characterize the non-linearity of the system, depending on work load and system performance, to determine the non-linearity of the detector. Point calibrations were always performed between stations to determine the short term drift in the detector. Replicate measurements were only taken on a few stations due to high work load. The determined values for precision and accuracy are listed in Table 5.10.

Compound	System precision	PT2 System PT3 precision
SF ₆	1.0 %	NA
CFC-12	0.65 %	0.34 %

Table 5.10: Precision of tracer measurements determined from replicate measurements and approximate limit of detection.

A detailed account for the CFC-12 and SF₆ measurements and scientific results are available from the diploma-thesis of Stöven (2011).

5.7 Determination of Nutrients

(G. Civitarese, I. Büns, F. Rozada)

Nutrients (nitrate, nitrite, silicate, and phosphate) were measured on-board with a QUAATRO AUTO-ANALYZER from SEAL analytics. The following protocols from SEAL analytics were followed:

Nitrite and Nitrate – (Method No. Q-068-05 Rev. 4):

In the automated procedure for the determination of nitrate and nitrite, nitrate is reduced to nitrite at pH 8 in a copperized cadmium reduction coil. The nitrite reduced from nitrate plus any nitrite is transformed to a diazo compound that then couples with N-1-naphthylethylenediamine dihydrochloride (NEDD) to form a reddish-purple azo dye measured at 520 nm.

Phosphate – (Method No. Q-031-04 Rev. 2):

The blue color is formed by the reaction of phosphate, molybdate ion and antimony ion followed by reduction with ascorbic acid. The reduced blue phospho-molybdenum complex is read at 880 nm.

Silicate – (Method No. Q-066-05 Rev. 3):

The procedure is based on the reduction of a silicomolybdate complex in acid solution to molybdenum blue by ascorbic acid. Oxalic acid is added to minimize interference from phosphate. The absorbance is measured at 820 nm.

About 900 samples were analyzed on board. The precision of the nutrient measurements were determined on 5-7 replicates of samples taken at selected stations. The results, expressed as C_v% (STD*100/AVG) were: Nitrite + Nitrate: ≤ 1.5 %; Phosphate: ≤ 3,6 %; Silicate: ≤ 1.7 %. The precision expressed as in μmol kg⁻¹ was: Nitrate 0.08; Phosphate 0.007; Silicate 0.10.

Preliminary results:

Figure 5.15 provides the vertical distribution of nutrients along the section carried out in the Eastern Mediterranean. Some typical feature are: 1) The maximum nutrient layer (nitrate and phosphate) in the range of depth of 500-1500 m. 2) In the deepest layer nutrient

concentrations decrease due to the presence of EMDW of Adriatic origin, 3) The easternmost part of the basin showed a remarkable oligotrophy, with the surface layer often completely depleted in phosphate and nitrate.

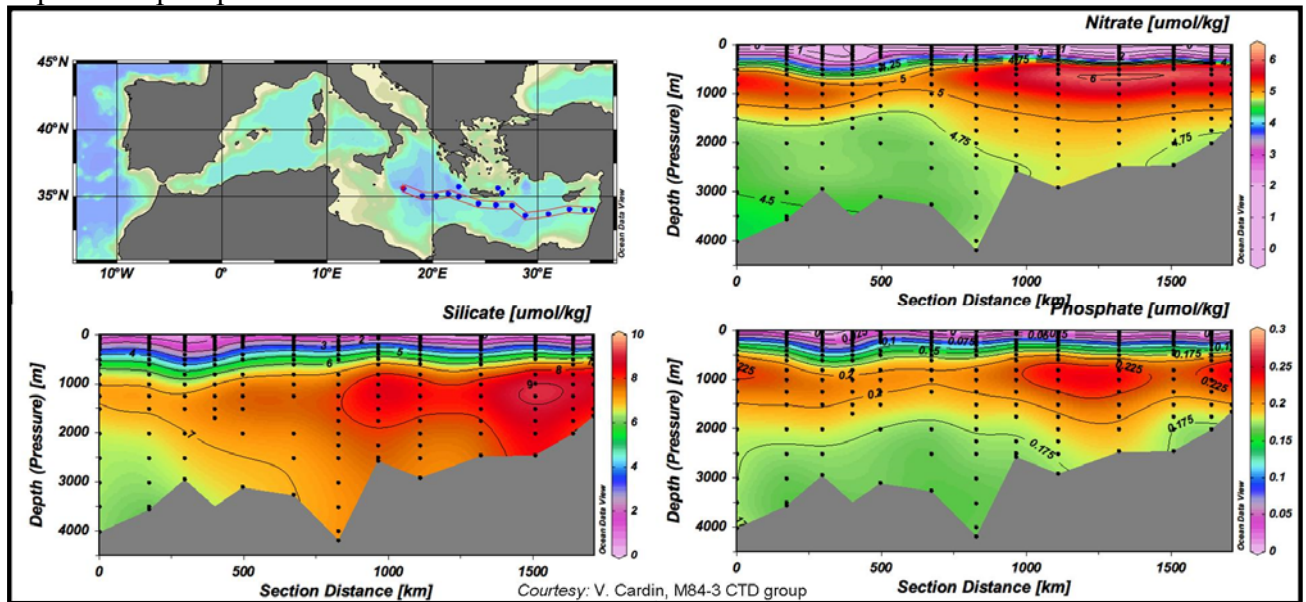


Figure 5.15: Vertical distribution of nutrients along the eastern Mediterranean section.

One of the most intriguing and peculiar feature of the Mediterranean Sea is its deviation from the classical Redfield ratio (N:P ~16). In Figure 5.16 we report the cumulative plot of nitrate vs. phosphate, subdivided into the three investigated areas: the Eastern Mediterranean, the Western Mediterranean, and the Atlantic Ocean. The positive deviation from the Redfield ratio that is larger for the Eastern Med than for the Western Med, As already observed by Ribera d'Alcalà et al. (2003), suggests that there is a source of re-workable nitrogen in compounds that do not contain phosphorus, or contain it in non-Redfieldian ratios. This fraction could derive from the dissolved organic nitrogen, but may also include organic material produced by nitrogen fixers.

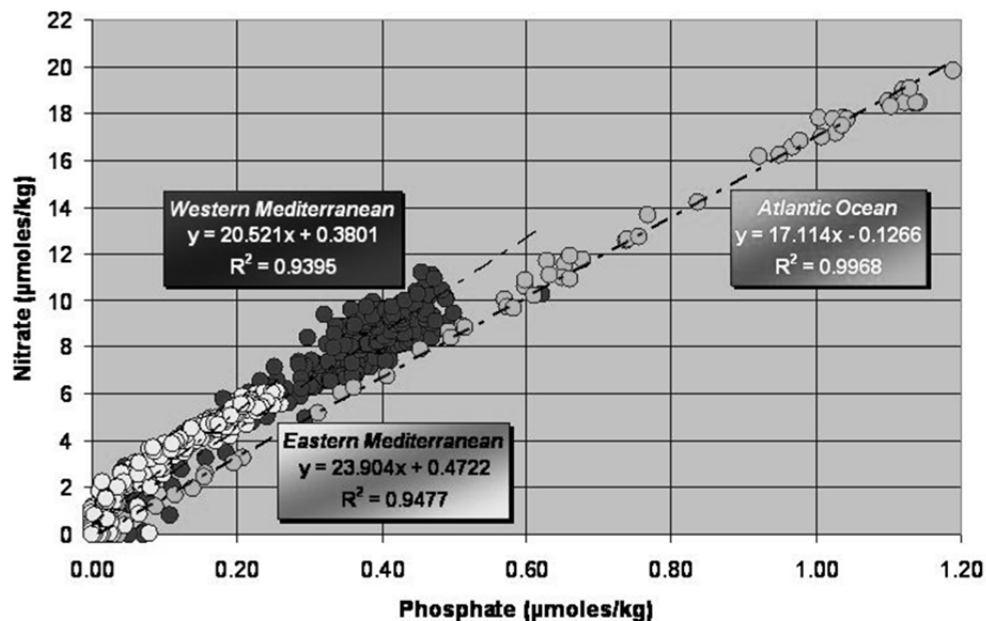


Figure 5.16: Linear regression of nitrate vs. phosphate in the three areas investigated.

5.8 Sampling for Helium isotopes and Tritium

(E. S. Huempel, T. Tanhua)

During the cruise, samples for helium isotope measurements were taken for measurements by two different groups with slightly different focus. At ten station samples were taken along the whole depth profile for the measurement of ^3He and tritium (total amount of samples: 165). One of the aims of this sampling is to use ^3He and tritium as transient tracers of ventilation processes. These samples were measured Institute of Environmental Physics at the University of Bremen Germany (J. Sueltenfuss). At 13 other stations, samples were taken for the analysis of ^3He but not for tritium (240 samples). These samples were measured at Laboratoire de Sciences du Climat in LSCE-CEA Saclay, France (E. Fourré).

Sampling procedures: The samples for the ^3He analysis were always taken first from the Niskin bottles in order to avoid any influence of gas exchange. The water from the Niskin bottles was filled up in copper tubes. After making sure that there are no air bubbles left in the tube, the screws at both ends have been closed properly with a rattle. After finishing, the tubes were cleaned with freshwater and stored in the corresponding boxes. The sample volume was either 40 or 6.4 ml for the two groups, respectively. Samples for tritium analysis were taken after the nutrient samples; 1L of water was filled into plastic bottles and put into zip-lock plastic bags. The sampling was performed by Eike Sophie Huempel.

Contamination issues:

At station 301 the CTD Rosetta was lowered into a brine lake that contained very high concentrations of radiogenic helium. This high concentrations contaminated the Niskin bottles so that values for ^3He had to be flagged as “questionable”, and since the contamination lasted for a while, also stations 303 and 305 was flagged as “questionable” for ^3He .

5.9 Sampling for Carbon Isotopes

(T. Tanhua, G. Schnaller)

During the cruise a total of about 280 samples were taken for the determination of the carbon isotopes ^{14}C and ^{13}C (mostly at the same station as where samples were taken for tritium and ^3He). The samples were taken in 500 ml. bottles and were poisoned with HgCl and were sealed according to standard procedures. The samples were shipped to the National Ocean Sciences AMS Facility at Woods Hole Oceanographic Institution, USA, for analysis after the cruise. The sampling was performed by Gaston Schnaller.

5.10 Sampling for Barium

(R.M. Brünjes, T. Tanhua)

During the M84/3 cruise, a total of 839 seawater samples for dissolved Barium (15 ml each) were taken throughout the water column (about 20 depths per station). The samples will be analyzed post-cruise by Stéphanie Jacquet from the LOPB (Laboratoire d'Océanographie Physique et Biogéochimique) in Marseille. With the data, the saturation index of dissolved Barium and abundance will be calculated and determined for the Mediterranean Sea.

Sampling procedure:

In order to minimize the danger of contamination, the sampling scientist was wearing powder free gloves while sampling. 15µl of 37%-fuming HCl was added to the sample immediately

after sampling in order to conserve the samples. The samples were then sealed with PARAFILM and stored in plastic bags prior to shipping. The sampling was performed by Robert Martin Brünjes.

5.11 Coccolithophores Assemblages in the Mediterranean Sea (A. M. Oviedo, P. Ziveri)

The main goal during the M84/3 of this program was to provide an up-to-date state of the coccolithophores assemblages in relation to the carbonate chemistry and nutrient concentration of the different water masses, covering the main basins of the Mediterranean and analyzing changes in the distribution patterns and the $\delta^{18}\text{O}$ isotopic fractionation in calcite and water. We are interested in these parameters because the column inventories of anthropogenic CO_2 are higher in the Mediterranean than anywhere else in the world ocean and changes in the coccolithophores assemblage composition and its calcification capabilities might bring potential local impacts on the carbonate pump. The samples will be analyzed at ICTA, University Autònoma de Barcelona, after the cruise.

For this purpose we used the following methods:

Taxonomy:

Filtration on Acetate-Cellulose filters of a known volume of seawater. The filters were dried at 40°C . Once at the UAB, cells per sample will be count using a polarized microscope for / SYRACO software

$\delta^{18}\text{O}$ (calcite):

Filtration on PC filters. Mass spectrometer analysis of CO_2 produced after calcite reacts with phosphoric acid. This is comparison with water sample ratios.

$\delta^{18}\text{O}$ (water):

20 ml of water from the Niskin bottles (usually at 5m dept) were placed in amber glass vials with rubber/Teflon septum. Fixation of the samples was done by adding Lugol-iodine solution. Mass spectrometer analysis of CO_2 in water was performed in the lab in Barcelona.

Station	Sample type	$\delta^{18}\text{O}(\text{calcite})$	$\delta^{18}\text{O}(\text{water})$
	Taxonomy-Morphology		
Test	209631,209634,209635,209636	Yes	209636
288	209658, 209661	Yes	209661
290	209709	Yes	209709
291	209716,209729,209730,209733	Yes	209733
293	209780	Yes	209780
294	0m,209799,209801,209802,209805	Yes	209805
296	209825,209827,209829	Yes	209829
297	209851,209853	Yes	209853
298	209876,209878	Yes	209878
299	209900	Yes	209900
302	209961,209963,209964,209966	Yes	209966
305	6m pumped water	Yes	6m pumped
306	212040,212042,212043,212045	Yes	212045
307	0m, 212066,212067	Yes	212067
308	0m, 212084,212085,212087,212089	Yes	212089
309	212105,212107,212108,212111	Yes	212111
311	212154	Yes	212154

313	212170,212173,212174,212177	Yes	212177
314		Yes	212199
316	212242,212245	Yes	212245
317	212263,212267,212269	Yes	212269
319	0m, 212293	Yes	212293
320	212312,212314,212315,212317	Yes	212317
321	212335,212337,212338,212341	Yes	212341
322		Yes	212365
324	212408,212410,212411,212412	Yes	212412
329	0m, 212480,212482,212483,212485	Yes	212485
331	0m,213043,213045,213046,213048	Yes	213048
332	213070,213072	Yes	213072
334	0m, 213120	Yes	213120
337	0m,213160,213164,213165,213168	Yes	213168
338	213184,213192	Yes	213192
342	213514	Yes	213514

Table 5.11: Samples taken during the cruise for investigations of coccolithophores, numbers refer to the sample identification numbers used during the cruise.

5.12 Prokaryotic Community Composition (M. M. Varela, M. Álvarez, F. Mapelli, G. Merlino)

The meso- and bathypelagic ocean is the largest and unexplored aquatic habitat in our planet, and it is inhabited by a wide variety of life. Marine biodiversity is dominated by microscopic organisms, playing an important role in all biogeochemical cycles in the sea. They are responsible for more than 95 % of the respiration in the oceans, and they may regulate climate and food chains as they contribute to the sequestration of carbon dioxide in the deep ocean.

The M84-3 oceanographic cruise did, interestingly enough; cover most of the basins located in the Mediterranean Sea, which was of particular interest. During the cruise samples were collected by two different groups with slightly different focus. The results from the two groups are compared to each other and joint publications are in the work. The sampling programmes of the two groups are described below.

5.12.1 Instituto Español de Oceanografía Centro Oceanográfico de A Coruña (M. M. Varela, M. Álvarez)

The aim of the present study was to determine the spatial patterns of prokaryotic abundance and community composition along the METEOR 84/3 cruise by using catalysed reported deposition in situ fluorescence hybridization (CARD-FISH) and fingerprinting techniques (T-RFLP, terminal restriction fragment length polymorphism). Specifically, we assessed spatial variations of the prokaryotic community composition in relation to the specific water masses identified by their temperature and salinity characteristics.

A) CARD-FISH; 69 samples

Enumeration of *Bacteria* and *Crenarchaeota* by catalyzed reporter deposition fluorescence *in situ* hybridization: Immediately after collecting the samples from the Niskin bottles, 20 to 80 mL of water was fixed with 0.2- μ m filtered paraformaldehyde at a final concentration of 2% and subsequently, the samples were kept in the dark at 4°C for 12-18 h. Thereafter, the samples were filtered through 0.2- μ m polycarbonate filters (Millipore GTTP, 25-mm filter diameter) supported by cellulose nitrate filters (Millipore, HAWP, 0.45- μ m), washed twice

with Milli-Q water, and dried and stored in a microfuge vial at -20°C until further processing in the home laboratory as following Varela et al. (2008).

B) Fingerprinting: 35 samples

A volume of 10L of seawater was filtered through a 0.22 µm Sterivex filter cartridge (Millipore). Thereafter, 1.8 ml of lysis buffer (40mM EDTA, 50 mM Tris HCl, 0.75M sucrose) was added to the filter cartridge and stored at -80°C. DNA will be extracted from the Sterivex filter cartridges by Mega Kit extraction (MoBIO Laboratories) and the DNA extracts will be concentrated (10-fold) with a centricon device. PCR and T-RFLP will be further processing in the home laboratory as described by Moeseneder et al. (2001).

5.12.2 Molecular Microbial Ecology Unit at DiSTAM, University of Milan (F. Mapelli, G. Merlino)

Concerning the Adriatic and Ionian basins the main purpose of the group from DiSTAM on board was the sampling of seawater from stations previously studied in the frame of our collaboration with the groups of Dr. Dagmar Hainbucher and Dr. Vanessa Cardin. In this area the investigation of the microbiota zonation is expected to confirm the oceanographic measurements, helping to determine the pathway of the Adriatic Deep Water outflow from the Otranto strait. However we were also interested in study the whole transect performed along both the Eastern and Western basins, obtaining an overall description of microbial diversity in the Mediterranean Sea.

Description of the work:

The microbiological unit collected deep and superficial seawater from all the station sampled during the M84-3 cruise. From each station, water collected at the bottom layers and at 5m depth has been collected to evaluate microbial community composition and abundance. For those stations located in the Ionian and South Adriatic basins the study of the microbiota through DNA fingerprinting analyses was also applied on additional water samples collected from each sampling sites in correspondence of the variations of parameters, such as salinity and oxygen concentrations, that allow us to recognize water masses of Levantine origin.

For each sample, 5 liters of seawater was immediately filtered on board on sterile 0.22 µm pore-size filters to collect the whole cells for the microbiota composition analyses. After the addition of a sterile lysis buffer the filters was stored at – 20°C. A small volume (50 ml) of the water samples collected from the bottom layer will be used to evaluate the cell concentration through a fluorescent microscopy analysis at the University of Milan, after the staining with diamidino-2-phenylindole (DAPI). The samples have been prepared on board performing a formaldehyde fixation (5 hours) and a subsequent filtration on black polycarbonate filters that were stored at -20°C in sterile Eppendorf vials. Direct counting based on fluorescence microscopy, such as DAPI count, is commonly applied to asses microbial abundance in natural ecosystems and it will be employed with this goal on both deep and surface water samples collected along the whole Mediterranean Sea transect.

From a subset of station, surface seawater samples have been also collected with the purpose to isolate pure or mixed cultures of bacteria displaying interesting catabolic capabilities. Biodegradation experiments were performed in the laboratory of the University of Milan post-cruise.

Expected results:

The water samples were characterized microbiologically at the University of Milan. DNA was extracted from filters and quantified; to investigate the biodiversity of the metagenome extracted a DNA fingerprinting approach was applied using the Automated Ribosomal Intergenic Spacer Analysis (ARISA) method. In the Eastern Mediterranean such information will be then correlated with the salinity and temperature value of the samples to track the circulation of the water masses, and a special focus will be the pathway of Adriatic Deep Water outflow from Otranto strait toward the Ionian basin. Moreover, considering the wide set of stations that have been sampled along the section across the whole Mediterranean Sea a biogeography study will be performed. Nutrient profiles will be integrated to support microbiological observations and to correlate microbial diversity with the fluxes of matter and energy in this oligotrophic marine environment.

5.13 N₂ Fixation Experiments and Aerosol Sampling

(E. Rahav, A. Levi, B. Herut, I. Berman-Frank))

Research Objectives:

- To examine N₂ fixation rates during springtime at different water provinces along the Mediterranean Sea. Measurements were taken using a newly developed methodology described by Mohr et al. (2010).
- To examine the contribution of heterotrophic diazotrophs to N₂ fixation in the Mediterranean Sea. This was tested using dark incubation, giving the heterotrophs community advantage over the autotrophs.
- To examine the interactions and competitions of the natural diazotrophic community (and other natural phytoplankton community) with the cultured unicellular diazotroph *Crocospaera watsonii* (WH 8501) in the ambient seawater under different nutrients and light scenarios.
- To examine the areal changes in expressed *nifH* genes at the major basins.
- To examine the phytoplankton photo-physiology during springtime, after winter mixing. Photo physiology parameters were taken using FIRE (that measures photosynthetic efficiency) 6 times a day along the cruise track (Table 5.12), with aspect to physical-chemical parameters (i.e. nutrients, chlorophyll concentration, POC and FACs).

Experimental approaches:

Along the cruise track of M84/3, a total of 6 N₂-fixation microcosm experiments were performed at different trophic provinces along the Mediterranean Sea covering the main basins: 1) the north Levantine basin, 2) Shikmona Eddy, 3) Ionian Sea, 4) Adriatic Sea, 5) Tyrrhenian Sea and 6) Gibraltar straits. Seawater from each of the experiments were treated (P addition, diazotrophs addition and combined) and incubated for 48 hours at either ambient lighting or dark conditions. A list of the stations sampled and measurements taken is specified in Table 5.12.

Samples of spatial distribution of chlorophyll, PSII photosynthetic efficiency (F_v/F_m) and the effective cross section (θ) of phytoplankton were also taken along the cruise track (6 measurements per day) using a FLUORESCENCE INDUCTION AND RELAXATION SYSTEM (FIRE). Note that the seawater used for all the experiments were taken from 6-8 m depth using the membrane pump of the METEOR.

St. #	Lat. N	Lon. E	Nut.	Magic	DOC N	POC	FACs	TEP	FIRe	N fix.	C fix.	DNA
290	34° 20′	27° 30′	18	18	18	18	36	15	24	24	24	1
294	34° 00′	34° 25′	18	18	18	18	36	15	24	24	24	7
304	35° 36′	17° 15′	18	18	18	18	36	15	24	24	24	7
312	41° 15′	18° 00′	18	18	18	18	36	15	24	24	24	7
316	38° 36′	11° 30′	18	18	18	18	36	15	24	24	24	7
333	36° 06′	-2° 48′	18	18	18	18	36	15	24	24	24	7
Sampling along transect			46	46	0	46	96	0	144	0	0	0
Total samples			154	154	108	154	312	90	288	144	144	36

Table 5.12: – List of parameters taken and number of the total replicates.

Aerosol sampling:

Aerosol and dust were sampled along the cruise track using an AEROSOL SAMPLER (TD 19). The filters (Whatman 41) were changed on a daily basis (every ~24 hours).

Preliminary results

N₂ fixation rates were within previously reported rates for the Mediterranean and exhibited strong zonal gradients from east to west ($R^2 = 0.8$, Figure 5.16). The lowest rates were measured in the eastern basin waters, ranging from 0.10 ± 0.02 nmol N L⁻¹ d⁻¹ in the Ionian Sea to 0.15 ± 0.01 nmol N L⁻¹ d⁻¹ at station 290 (affected by the Rhodes gyre). N₂ fixation rates increased gradually toward the west ranging from 0.22 ± 0.03 in the Tyrrhenian Sea to 2.35 ± 1.12 nmol N L⁻¹ d⁻¹ in the westernmost Gibraltar straits.

The springtime rates of N₂ fixation at all stations were 3-7 folds higher than measurements published previously during summertime (Ibello et al. 2010, Yogev et al. 2011, Bonnet et al. 2011).

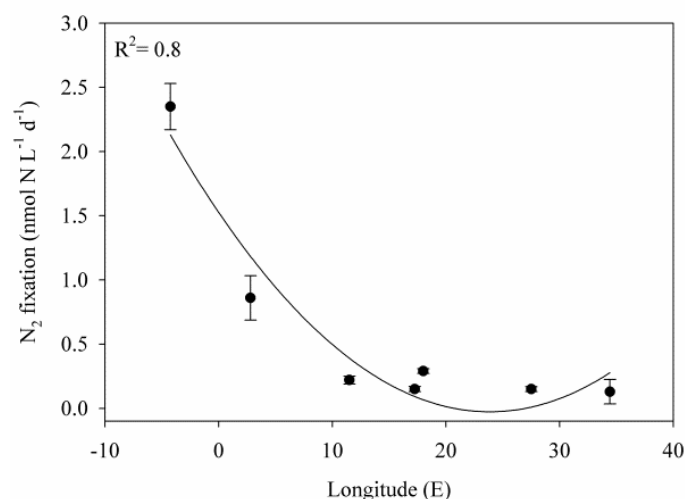


Figure 5.17: Spatial distribution of N₂ fixation in the surface waters of the Mediterranean Sea during springtime.

5.14 Persistent Organic Pollutants (POPs) (R. Schneider)

The occasion of this cruise through the Mediterranean Sea was utilized to conduct repeat sampling for persistent organic pollutants (PAHs, PCBs and DDTs) in the dissolved and particulate phase of seawater, as was carried out in the mid 1980ies and 1990ies. Since the time schedule for the program was limited, only surface seawater pumped by the vessel's

clean seawater supply was used instead of including samples from different water depths, which would have required an extra eight hours per depth using the in-situ pumping system.

The surface seawater was continuously pumped in excess into a pre-cleaned glass bottle, from which it was pumped at an average rate of 1.2 l/min through a Millipore filter (particulate phase) and an XAD-2 column to retain the POPs contained in the dissolved phase. To avoid any ship-bound contamination, all pumping was stopped during sampling stations. The filters and XAD columns were stored and later extracted, worked up and analyzed by HRGC/MS in the IOW organic analytical chemistry lab according to the standard operational procedures applied, e.g., in the institute's Baltic Monitoring Programme. Table 15.13 lists samples taken for POP analysis during the cruise.

Transect	Date	Region	betw. Stations	Volume extracted
1	Apr 06	Aegean Sea	# 1 - # 2	529
2	Apr 07	Cretan Sea	# 3 - # 4	600
3	Apr 08	Central Eastern	# 5 - # 6	510
4	Apr 10	Central Eastern	# 9 - # 5	812
5	Apr 12	SW of Crete	# 12 - # 14	840
6	Apr 14	Ionian Sea	# 16 - # 17	810
7	Apr 16	Otranto / Adriatic	# 21 - # 23	760
8	April 18-19	Tyrrhenian Sea	# -- - # 33	825
9	Apr 20	Tyrrhenian Sea	# 35 - # 37	816
10	Apr 21	Western Med	# 39 - # 40	803
11	Apr 23	Western Med	# 44 - # 46	802
12	Apr 25	Gibraltar into the Gulf of Cadiz	# 50 - # 53	902

Table 5.13: Table over surface samples taken for the determination of POPs.

5.15 Perfluorinated Substances (N. Yamashita, T. Tanhua)

Surface and vertical water samples were collected for the determination of perfluorinated compounds. Both surface and vertical profiles were discussed to understand the possible sources and atmospheric and/or hydrospheric kinetics of PFAS in the Mediterranean Sea in comparison with the Japan Sea and open oceans.

Procedures:

The samples were collected into blank free polypropylene bottles during the cruise and shipped to AIST within one month. PFASs were measured in each 1 L of waters, totally 37 samples. Around 500 to 1000 ml of seawater samples were analyzed by following the modified International Standard Method (ISO25101:2009, published in March 1st) and the Japanese Industrial Standard Method (JIS K0450-70-10:2011, published in March 22nd). Briefly, water samples were extracted using Oasis® WAX cartridges following the Taniyasu et al. (2005, 2008). Separation and determination of target PFCs was performed using HPLC-MS/MS (electrospray ionization in negative mode). For high accuracy, all extracted samples were injected into both RSpak JJ-50 2D column (2.0 mm i.d. × 150 mm length, 5 µm; Shodex, Showa Denko K.K., Kawasaki, Japan) with 50 mM ammonium acetate and methanol as the mobile phase and Keystone Betasil C18 column (2.1 mm i.d. × 50 mm length, 5 µm, 100 Å

pore size, end-capped), with 2 mM ammonium acetate and methanol as the mobile phase. Seven PFASs (PFDS, PFOS, PFHpS, PFHxS, PFBS, PFPrS, PFEtS), fourteen PFCAs (PFOcDA, PFHxDA, PFTeDA, PFTrDA, PFDoDA, PFUnDA, PFDA, PFNA, PFOA, PFHpA, PFHxA, PFPeA, PFBA, PFPrA), FOSA, N-EtFOSA, N-EtFOSAA, unsaturated fluorotelomer carboxylates (8:2, 10:2 FTUCA) and fluorotelomer alcohols (8:2, 10:2 FTOH) were analyzed.

Preliminary results:

Figure 5.17 show some preliminary results of PFAS concentrations in surface waters collected from the Mediterranean Sea. Although PFOA concentrations were lower than the North Atlantic Ocean, concentration of PFOS was generally higher than the North Atlantic Ocean and comparable to the South Atlantic Ocean in 2003. Interestingly, PFOS and PFOA were only part of all PFASs detected and shorter chains such as PFBA and PFPeA also found to be predominant in each location. It's surprising that no clear regional pollution was found in the Mediterranean Sea.

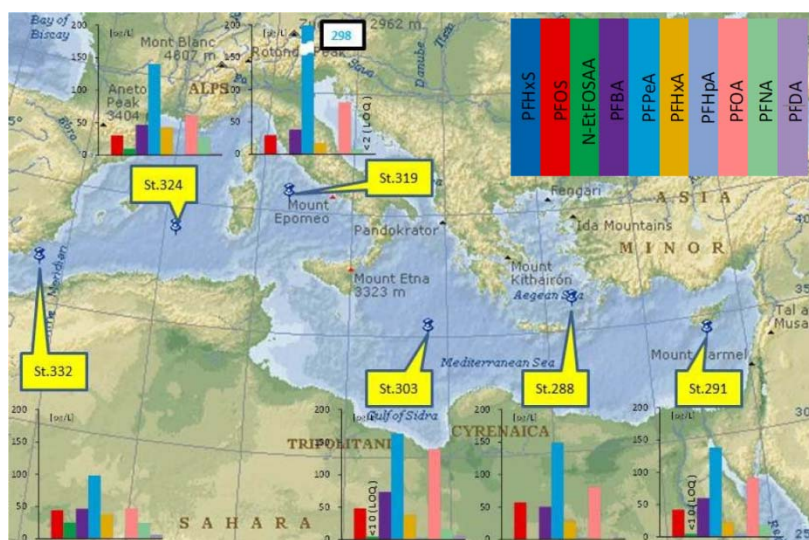


Figure 5:17 Concentrations of PFASs in surface seawaters collected from the M84/3 cruise.

5.16 Trace Metals and Methylmercury

(Lars-Eric Heimbürger, Eleni Stathopoulou, Jeroen E. Sonke, David Point, Daniel Cossa, Bastien Thomas)

Monomethylmercury (MMHg) accumulates to harmful levels along the marine food chain and presents a health risk at a global scale. Determinations of MMHg in sea-water are still scarce mainly due to analytical limitations that did not allow for detecting ultra-trace concentration levels, in the femtomolar range. Three techniques are used today to measure MMHg in sea-water and of which all imply a derivatization step: cryofocussing hydrate generation (Stoichev et al., 2002), ethylation (Bloom, 1989) and propylation (Monperrus et al., 2005). Determination of MMHg in sea-water by species-specific isotope dilution, derivatization by propylation, and detection via gas chromatography–inductively coupled plasma mass spectrometry (ID-GC-ICP-MS) was shown to be most promising (Monperrus et al., 2005). At the GET laboratory we improved the performance of this method by optimizing the coupling between a gas chromatograph and a high resolution sector field inductively coupled plasma mass spectrometry (Element XR). We applied this method to samples from the METEOR cruise M84/3. A total of 160 (estimated) samples were taken in pre-cleaned 250mL Savillex PFA Teflon bottles. Pre-cleaning in a class 100 clean lab involved soaking

the bottles for 24h in concentrated (10N) and diluted (1N) bidistilled HCl at 120°C. Bottles were double bagged and all handling was done in an ultra-trace clean manner. On board, each bottle was rinsed 3 times with the sample from the Niskin bottle, filled to the top, acidified with bidistilled HCl to 0.4% (v:v) and tightly capped. Acidification converts dimethylmercury (DMHg) to MMHg. The measured MMHg is therefore the sum of both species. Sub-samples were double bagged and stored in the dark at 4°C until analysis in the home laboratories. Samples were taken at 11 stations along the East-West transect. The set of samples was split in a way that the samples were analyzed in the 3 partner laboratories: 1) GET laboratory in Toulouse, France, IFREMER, 2) IFREMER Nantes, France and 3) University of Athens, Greece. Triplicates were taken at several stations to provide an intercomparison.

1) MeHg (MMHg+DMHg) was analyzed at the GET laboratory via isotopic dilution gas chromatography sector field inductively coupled plasma mass spectrometry (GC-SF-ICP-MS) after derivatization with propylborate and extraction into hexane. The 8 full depth vertical profiles consist of 84 samples (stations 292, 297, 306, 313, 319, 324, 331, 340). MeHg concentrations show typical profiles (Heimbürger et al., 2010) with very low surface concentration and highest concentration in the oxygen minimum zone and generally higher in the more productive Western Basin (mean=0.202±0.152pM, range=0.011(LOD)-0.723pM, n=84, Fig. 1).

2) MeHg (MMHg+DMHg) was analyzed at the IFREMER Nantes laboratory via cryofocussing hydrate generation followed by cold vapour atomic fluorescence spectrometry (CVAFS) (Stoichev et al., 2002; Cossa et al., 2003). The 4 full depth vertical profiles consist of 47 samples (stations 297, 313, 319, 340; mean=0.143±0.116pM, range=0.040(LOD)-0.467pM, n=47). Those are the same samples that were measured at the GET laboratory and both measurements compare well.

3) Another 4-8 profiles were analyzed at the University of Greece via ethylation followed by CVAFS using a MERX automated analyzer (Brooks Rand).

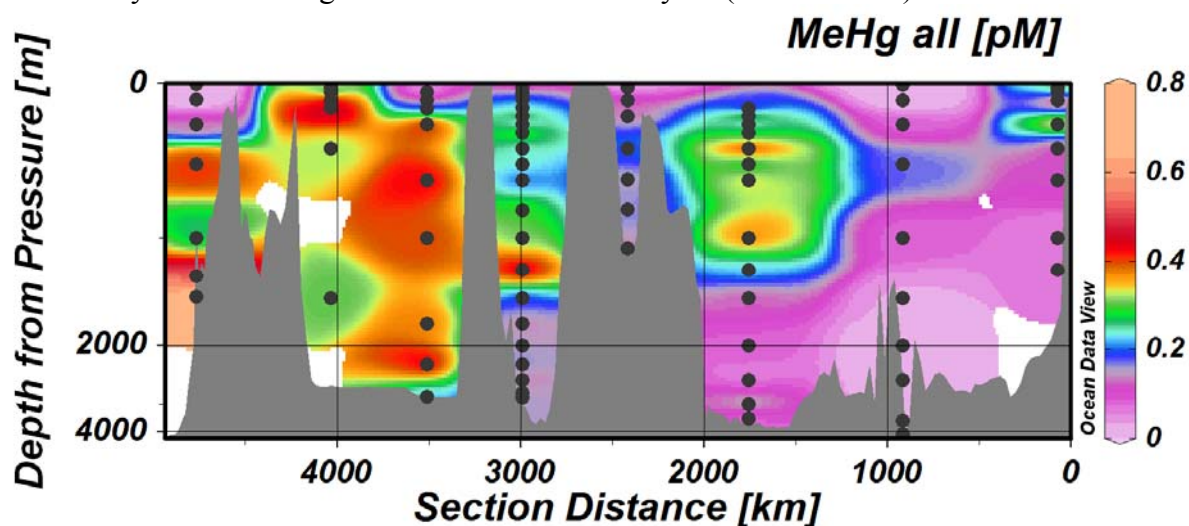


Figure 5.18: MeHg distribution along the M84/3 West-East transect, east is to the right in the figure. All shown data were measured at the GET laboratory via propylation, followed by GC-SF-ICP-MS.

Samples for trace metals were taken at the same stations as for MeHg. A total of 176 samples at 11 stations were sampled for (Mn, Ni, Cu, Zn, Cd, and Pb). The sampling was done similar to the MeHg samples and will be measured by graphite furnace atomic absorption spectrometry (GFAAS) after pre-concentration on chelex 100 resin. The sampling was done similar to MeHg sampling. The samples were prepared on the ship and will be analyzed later on-shore.

5.17 Radium Isotopes

(V. Rodellas, M. Feldman, J. Garcia-Orellana, Y. Weinstein)

The main objective of our participation in the cruise M84/3 was to determine the concentration of ^{228}Ra (and also ^{226}Ra) in the Mediterranean Sea in order to estimate the Submarine Groundwater Discharge along the Mediterranean Basin.

Submarine Groundwater Discharge (SGD) is defined as any flow of water at continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force. The flux of submarine groundwater discharge is considered to be a pathway for enriching coastal waters in essential nutrients, trace metals and carbon. Much of the chemical composition of SGD is the result of reactions occurring in the subterranean estuary, where meteoric groundwater mixes with intruding seawater. The composition of SGD differs from that predicted by simple mixing because biogeochemical reactions in the subterranean estuary modify its chemistry. In this context, Ra isotopes have been proven to be a very powerful tool to estimate submarine groundwater discharge fluxes. Because Ra isotopes are highly enriched in salty coastal groundwater relative to the ocean, small inputs of SGD can be recognize as a strong signal. Reviews on this topic in Burnett et al. (2006) and Moore (2010).

Our strategy for determining the submarine groundwater discharge to the Mediterranean Sea derives from the fact that radioactive decay is the primary sink for ^{228}Ra in the Mediterranean. To maintain a steady state, these losses must be balanced by fresh inputs of ^{228}Ra to the Mediterranean Sea. If other sources can be evaluated, the ^{228}Ra flux that must be sustained by SGD can be determined. By using the ^{228}Ra content of groundwater in coastal aquifers, the ^{228}Ra flux can be converted to an SGD flux to the Mediterranean Sea.

Sampling:

During the M84/3 cruise track, 47 stations of surface waters (circa 350L each) were collected from the MEMBRANE PUMP of the vessel (at 6-8 m depth). At 18 stations, additional samples were taken for replicates. At 6 stations (295, 304, 312, 318, 325, 335), large volume samples of 120L (i.e. by combining the content of 12 Niskin bottles) were collected at 200-400m and at 1500m depth in order to characterize the ^{228}Ra content in LIW and in deep waters.

These large volumes of water were passed through columns loaded with MnO_2 -impregnated acrylic fiber (hereafter Mn-fiber) at a flow rate lower than $1\text{L}\cdot\text{min}^{-1}$, which quantitatively extracts Ra isotopes. In order to check for complete Ra uptake, 29 samples were filtered through two Mn-fiber columns connected in series.

Measurements:

All the samples (Mn-fiber) will be analyzed to determine the concentration of ^{228}Ra in water samples, following three different approaches. The comparison of three different approaches will allow us to test the different methods but also achieve more accurate results.

- Measurement of ^{228}Ra via RaDeCC: The RaDeCC system allows the quantification of short-lived Ra isotopes (^{224}Ra and ^{223}Ra). However, measurements of ^{224}Ra after it has equilibrated with ^{228}Th on the Mn-fiber (about 1 month after the sample collection) are actually measurements of ^{228}Th . Additional measurements of ^{228}Th after 6-12 months from the first measurement will be used to assess the ingrowth from ^{228}Ra on the Mn-fiber, and thus, the initial activity of ^{228}Ra . This method is not destructive and provides a simple way to measure additional elements, such as ^{228}Th and ^{227}Ac (Moore and Arnold, 1996)
- Measurement of ^{228}Ra via gamma spectrometry: After the RaDeCC measurements, the Mn fiber will be ashed and transferred to hermetically sealed counting vials to determine ^{228}Ra (and also ^{226}Ra) using a well type Ge-detector (Charette et al., 2001).

- Measurement of ^{228}Ra via MC- ICPMS: The multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) is used to determine ^{226}Ra and ^{228}Ra concentrations and the $^{228}\text{Ra}/^{226}\text{Ra}$ isotopic ratio. After the gamma measurements, the Mn fibers are prepared for purification of Ra using two ion exchange columns (Hsieh and Henderson, 2011).

5.18 Neodymium Isotopes (P. Montagna)

Neodymium isotopes as water mass circulation tracers in the past. The neodymium (Nd) isotopes, often reported as ϵ_{Nd} , represent an important tracer capable to “fingerprint” water masses as isotopically distinct entities. The $^{143}\text{Nd}/^{144}\text{Nd}$ ratios vary in the Earth as a result of α decay of ^{147}Sm ; in the ocean the values reflect the age of the continental sources of dissolved Nd. In the modern ocean the different water masses ultimately derive their $^{143}\text{Nd}/^{144}\text{Nd}$ values through continental weathering, erosion and particle-seawater interactions. Neodymium isotopes behave like a quasi-conservative tracer and the isotopic variations are generally consistent with water mass mixing.

The landmasses bordering the Mediterranean Sea have a distinct Nd-isotopic composition and this makes it possible to distinguish between different regional inputs (Tackikawa et al., 2004; Scrivner et al., 2004; Jeandel et al., 2007; Montagna et al., 2010). In particular, the Western Mediterranean Sea is characterized by Atlantic values entering the Mediterranean through Gibraltar whereas the Eastern basin displays more radiogenic values reflecting the input of major rivers such as the Nile (Scrivner et al., 2004). However, the quasi-conservative behaviour of ϵ_{Nd} has yet to be fully investigated and there are several processes, such as the interaction of sediments deposited on the continental margin (Boundary Exchange) that can negatively affect the simple quasi-conservative scenario.

Differently to most of the other geochemical tracers used in paleoceanography the neodymium isotopes are not fractionated by biological processes in the water column and during the uptake process into marine carbonates. This proxy has been successfully applied on marine sediment-cores, in the dispersed authigenic ferromanganese oxide precipitates in sediments (Rutberg et al. 2000; Piotrowski et al., 2005), on foraminiferal shells (Vance et al., 2004) and on fossil fish teeth (Martin and Scher, 2004). Very recently, cold-water corals have been shown to record the neodymium isotopic composition of ambient seawater, (Colin et al., 2010; Copard et al., 2010; van de Flierdt et al., 2010; Montagna et al., 2010), opening new possibilities to obtain water mass signals and quantify mixing of water masses via paired neodymium isotopes and radiocarbon analyses of absolutely dated (U/Th) fossil corals.

Specific Objectives during the cruise M84/3 and Sampling strategy:

The possibility to reliably track the water masses in the past through the Nd isotopic composition of the carbonate skeleton of cold-water corals rely, as first step, on the careful comparison between the isotopes of living corals and the ambient seawater radiogenic signature. Therefore, one of the main objects during the M84/3 cruise was to isotopically characterize the seawater masses that surround the modern corals in order to provide robust evidences that the corals preserve the seawater Nd isotope composition. In addition, due to the peculiar physico-chemical features of the Mediterranean Sea, the study of the Nd isotopes of the different water masses flowing within this semi-enclosed basin will shed new light on the processes affecting the Nd budget of the Mediterranean.

To achieve these goals 23 seawater samples from 13 profiles were collected along the major Mediterranean sub-basins (Aegean, Eastern Mediterranean, Ionian Sea, and Tyrrhenian Sea) (Table 1). These sampling locations and depths were chosen based either on the sites

where modern corals have been previously collected or the presence of the principal water masses flowing in the Eastern and Western Mediterranean Sea.

For the analysis of Nd isotopes the seawater samples were collected in 4L acid-cleaned (0.5M HCl) cubitainers (Fisher Scientific) through a Tygon tubing connected to the spigot of the niskin bottle. A filter cartridge (AcroPak 500 capsule filter, 0.8µm/0.45µm) was connected to the other end of the tubing and the seawater was filtered before being collected into the cubitainers.

For the analysis of the Rare Earth Element (REE) concentration the seawater samples were collected in 125ml acid-cleaned (1M HCl) bottles, acidified to pH ~ 2, sealed with parafilm and stored with double-bags.

Sample processing on board: The samples for Nd isotopes were immediately acidified with double distilled HCl to pH = 2 and mixed with ~ 25mg of Fe in preparation for pre-concentration of the lanthanide and actinide elements. After one day of equilibration the samples were treated with Optima grade ammonium hydroxide to force the precipitation of ferric hydroxide by adjusting the pH to ~ 8. After the precipitation of Fe/REEs the cubitainers were sealed with parafilm and stored in double-bags.

Geochemical analysis: The Rare Earth Elements co-precipitated with Fe will be processed at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE) in Gif-sur-Yvette. The neodymium will be isolated from the other REEs through column chemistry and analysed as an oxide for its isotopes on a 6 Faraday Collector FINNIGAN MAT 262 THERMAL IONIZATION MASS SPECTROMETER. The REEs concentration will be analyzed by a X-seriesII CCT (Thermo Fisher Scientific) inductively coupled plasma mass spectrometer at the Laboratoire des Sciences du Climat et de l'Environnement following a standard addition technique.

6. Ship's Meteorological Station (H. Rentsch)

When RV METEOR left the port of Istanbul on 5th of April at 10:00 local time the skies were overcast and looked grey. The reason for that was an upper trough which included the Black Sea, Aegean and the eastern Mediterranean Sea. At this time the winds calmed down and wave heights did not exceed 1 m. Even the next day on the sea was characterized by a ridge of high pressure which extended from Northwest to Southeast to bring fine weather and scattered clouds. At the same time we had an increase of winds from north up to 6 Beaufort (bft) and a sea between 2.5 and 3 m. During the passage of „Samos“, a Greek Island, the wind increased due to topographic effects up to 32 Knots. Already in the night to the 7th of April the pressure gradient decreased slowly and we got north-westerly winds of force 5 bft and the wave heights reached 1.5 m. During the day winds of Beaufort 3 to 4 and a fine, mostly sunny weather had established.

At the end of first week on our cruise we got cyclonal dominated weather with showers. Even some thunderstorms were observed in sight of the ship near of the coast of Lebanon. After that winds turned back to west and increased up to 5-6 bft, followed by higher sea and swell up to 3 m. On the back side of a cold front on 10th of April, dryer air came into the area of our ship-track near the Cretan Sea and so the sunshine came back. At the same time we had northerly winds of 5 Beaufort, thus the sea reached 1.5 to 2 m. After that easterlies with 15 to 20 Knots against the ships track dominated during the cruise of METEOR until the entrance to Adriatic Sea.

On the 14th of April a cold front and cold air came from Adriatic Sea together with isolated showers and north-westerly winds of wind force 5 to 6 bft. Besides this unstable air we got only wave heights up to 2.5 m. On the second half of the week a ridge of high pressure over France extended towards the Northern Ionian Sea causing a calmed sea and much sunshine.

On the weekend (16.4 - 18.4), during our station work in the Southern Adriatic and northern Ionian Sea, a complex upper trough extends from Corsica across Sicily to Eastern Mediterranean. Rain and showers were observed, the sea state became moderate (around 3 m) at north-easterly winds up to 28 Knots. Already at our way to the Street of Messina the influence of high pressure reached us and a northerly winds up to 20 Knots blew directly against the ships course. At the passage of the narrowest place in the Street of Messina we measured for a short time a wind speed of nearly 7 Beaufort, although the sea remained calm.

The sunny and calmed weather continued until the half of the week. Then, on the 21st of April a warm front entered the ship from Southwest, bringing rain together with increasing easterly winds up to 6 bft, and the sea state increased to 3 (slight) too. On Good Friday the last rain clouds of a frontal system moved towards the north and on its back side we had south-westerly winds of force 4 to 5 bft. The wave heights did not exceed 2 m, and on the sky there were only cumulus clouds. Until the beginning of last week of our cruise the influence of low pressure dominated, it extended from Spain across Gibraltar to the north coast of Algeria. Nearby an upper trough warm air came from Africa into our operation area. This caused some isolated showers on Easter Sunday 100 Miles east of the Strait of Gibraltar, even thunderstorms were observed. On Monday, the 25th of April, during the passage of the Strait of Gibraltar the sea remained calmed and wind was weak and variable, but with arrival of the Atlantic Ocean we measured a swell of 1 to 1.5 m.

During the last days of METEOR's cruise the High of Azores dominated the wind field and sea-state in the eastern Atlantic Ocean. Light north-easterly trade winds (3 to 4 Beaufort) and a swell up to 2 m were the extreme weather features which were observed from Monday 25th to Thursday 28th of April. - The ship arrived "Vigo", our destination port, together with light and variable winds and a decreasing swell below 1 m, on 28th in the morning at a temperature of 13°C.

7			Station List								Samples																
STAT.	CAST	DATE	TIME	POSITION		POSITION		BOTTOM																			
NO	TYPE	ddmmyy	UTC	LATITUDE	LONGITUDE	DEPTH	He3	He	CFC	O2	C14	DIC	pH	Alk	Nut	H3	Ba	Sal	Ra	PFOS	Hg	TM	Nd	DNA	Coc	Bio	
M287	CTD	060411	1127	37	40.00 N	25	35.99	E	799		1	1	1		1	1	1	1	1				1	1	1	1	
M288	CTD	070411	0222	35	38.99 N	26	13.00	E	2248	1	1	1	1	1	1	1	1	1		1	1			1	1	1	
M289	CTD	070411	0655	35	16.45 N	26	36.21	E	815			1	1		1	1	1	1	1	1				1		1	
M290	CTD	070411	1449	34	19.99 N	27	29.99	E	2567	1		1	1	1	1	1	1	1							1	1	
M291	CTD	080411	2128	34	03.99 N	32	59.99	E	2454			1	1	1	1	1	1	1		1	1	1			1	1	
M292	CTD	090411	1014	33	59.39 N	35	10.35	E	1631			1	1		1	1	1	1			1	1			1	1	
M293	CTD	090411	1544	33	59.99 N	34	25.21	E	1984	1		1	1	1	1	1	1	1							1	1	
M294	CTD	100411	1059	33	42.00 N	31	00.00	E	2411			1	1		1	1	1	1					1		1	1	
M295	CTD	100411	0001	33	34.80 N	28	46.21	E	2858										1								
M296	CTD	110411	0217	33	34.80 N	28	46.20	E	2860		1	1	1		1	1	1	1			1	1			1	1	
M297	CTD	110411	1828	34	23.94 N	26	01.11	E	4092			1	1		1	1	1	1			1	1			1	1	
M298	CTD	120411	0517	34	29.99 N	24	19.97	E	3198		1	1	1		1	1	1	1					1	1	1	1	
M299	CTD	120411	1601	34	59.99 N	22	30.00	E	3047			1	1		1	1	1	1			1	1			1	1	
M300	CTD	120411	2309	35	45.00 N	22	28.00	E	4498		1	1	1		1	1	1	1								1	
M301	CTD	130411	0744	35	13.99 N	21	29.01	E	3421	1		1	1	1	1	1	1	1								1	
M302	CTD	130411	1542	35	03.99 N	20	21.01	E	2886			1	1		1	1	1	1							1	1	
M303	CTD	140411	0041	35	03.99 N	19	00.02	E	3482		1	1	1		1	1	1	1								1	
M304	CTD	140411	1123	35	36.02 N	17	14.99	E	3931										1								
M305	CTD	140411	1358	35	36.02 N	17	14.99	E	3931	1		1	1	1	1	1	1	1								1	
M306	CTD	150411	0209	36	30.01 N	19	00.00	E	3414			1	1		1	1	1	1			1	1	1		1	1	
M307	CTD	150411	1210	37	53.99 N	19	17.98	E	3212	1		1	1	1	1	1	1	1							1	1	
M308	CTD	150411	1847	38	30.01 N	18	59.96	E	3366			1			1			1	1		1	1		1	1	1	
M309	CTD	160411	0145	39	29.99 N	18	48.01	E	781			1	1		1	1	1	1				1			1	1	
M310	CTD	160411	07.08	40	10.01 N	19	09.98	E	940		1	1	1		1	1	1	1							1	1	
M311	CTD	160411	10.23	40	16.99 N	18	35.99	E	138			1	1			1									1	1	
M312	CTD	160411	1711	41	14.99 N	17	59.98	E	1074										1								
M313	CTD	160411	1842	41	14.99 N	17	59.98	E	1074	1		1	1	1	1	1	1	1			1	1			1	1	
M314	CTD	170411	1207	38	30.01 N	18	24.99	E	2794			1	1		1	1	1	1							1	1	
M315	CTD	170411	2235	37	07.78 N	17	59.99	E	3238			1	1		1	1	1	1							1	1	
M316	CTD	190411	1008	38	36.01 N	11	29.99	E	1648		1	1	1		1	1	1	1					1		1	1	
M317	CTD	190411	1538	39	13.20 N	11	45.02	E	3189		1	1	1	1	1	1	1	1				1			1	1	

STAT.	CAST	DATE	TIME	POSITION		POSITION		BOTTOM	Samples																				
									NO	TYPE	ddmmyy	UTC	LATITUDE	LONGITUDE	DEPTH	He3	He	CFC	O2	C14	DIC	pH	Alk	Nut	H3	Ba	Sal	Ra	PFOS
M318	CTD	190411	2336	40	18.00	N	11	17.99	E	2872											1								
M319	CTD	200411	0155	40	18.00	N	11	17.99	E	2872			1	1		1	1	1	1		1	1		1	1	1		1	1
M320	CTD	200411	1449	38	45.00	N	10	36.61	E	2471			1	1		1	1	1	1		1	1					1	1	
M321	CTD	200411	2207	38	14.98	N	9	23.98	E	1550			1	1		1	1	1	1		1	1				1	1	1	
M322	CTD	210411	0526	38	12.01	N	8	11.98	E	2660	1		1	1	1	1	1	1	1		1	1	1				1	1	
M323	CTD	210411	1328	38	29.99	N	6	54.01	E	2835	1		1	1	1	1	1	1	1		1	1	1				1	1	
M324	CTD	210411	2200	38	39.02	N	5	35.99	E	2829			1	1		1	1	1	1		1	1		1	1	1		1	1
M325	CTD	220411	0529	38	26.99	N	4	30.02	E	2714											1								
M326	CTD	220411	0751	38	27.00	N	4	30.03	E	2715			1	1		1	1	1	1		1	1					1	1	
M327	CTD	220411	1605	38	05.99	N	3	11.99	E	2763			1	1		1	1	1	1		1	1				1			
M328	CTD	220411	2351	37	54.00	N	2	00.03	E	2714																			
M329	CTD	230411	0247	37	54.00	N	2	00.00	E	2680			1	1		1	1	1	1		1	1					1	1	
M330	CTD	230411	1023	37	38.99	N	0	53.97	E	2745	1		1	1	1	1	1	1	1		1	1	1			1		1	1
M331	CTD	230411	1805	37	03.02	N	0	00.02	W	2691			1	1		1	1	1	1		1	1			1	1		1	1
M332	CTD	240411	0250	36	29.99	N	1	24.02	W	2321			1	1		1	1	1	1		1	1	1				1	1	
M333	CTD	240411	1046	36	05.98	N	2	48.01	W	1700		1	1	1		1	1	1	1		1	1			1	1		1	1
M334	CTD	240411	1942	36	06.04	N	4	23.97	W	1213	1	1	1	1		1	1	1	1		1	1					1	1	
M335	CTD	240411	2341	36	00.01	N	4	59.98	W	803											1								
M336	CTD	250411	0050	36	00.00	N	4	59.99	W	802			1	1		1	1	1	1		1	1					1	1	
M337	CTD	250411	0412	36	00.04	N	5	21.76	W	910			1	1		1	1	1	1		1	1					1	1	
M338	CTD	250411	0721	35	56.98	N	5	45.08	W	322	1		1	1	1	1	1	1	1		1	1	1			1	1	1	
M339	CTD	250411	1341	35	54.00	N	7	00.00	W	910			1	1		1	1	1	1		1						1	1	
M340	CTD	250411	1919	35	59.94	N	8	00.07	W	1511			1	1	1	1	1	1	1		1				1		1		
M341	CTD	250411	2215	36	14.99	N	8	00.01	W	1256																			
M342	CTD	260411	0034	36	26.99	N	8	00.02	W	848			1	1		1	1	1	1		1						1		
M343	CTD	260411	0248	36	35.99	N	8	00.01	W	761																			
M344	CTD	260411	0450	36	44.99	N	8	00.00	W	703			1	1		1	1	1	1		1				1		1		
M335	CTD	240411	2341	36	00.01	N	4	59.98	W	803											1								
M336	CTD	250411	0050	36	00.00	N	4	59.99	W	802			1	1		1	1	1	1		1	1					1	1	
M337	CTD	250411	0412	36	00.04	N	5	21.76	W	910			1	1		1	1	1	1		1	1					1	1	
M338	CTD	250411	0721	35	56.98	N	5	45.08	W	322	1		1	1	1	1	1	1	1		1	1	1		1		1	1	
M339	CTD	250411	1341	35	54.00	N	7	00.00	W	910			1	1		1	1	1	1		1						1	1	

[illegible]

8 Data and Sample Storage and Availability

In Kiel a joint Datamanagement-Team is active, which stores the data from various projects and cruises in a web-based multi-user-system. Data gathered during M84/3 are stored at the Kiel data portal, and is proprietary for the PIs of the cruise. The bottle data are publicly available at CDIAC (the Carbon Dioxide Information Analysis Center), http://cdiac.ornl.gov/oceans/Coastal/Meteor_Med_Sea.html that specialize in carbon data sets. The CTD data are publicly available at CCHDO (the CLIVAR and Carbon Hydrographic Data Office, <http://cchdo.ucsd.edu/cruise/06MT20110405>) that specialize in repeat hydrographic data. There is no recognized data repository for Prokaryotic Community Composition (ARISA) marine samples, but these data are available <http://www.ocean-sci-discuss.net/10/291/2013/osd-10-291-2013-discussion.html> as supplement to an article by Mapelli et al. (2013). The data from the nitrogen fixation experiments are published by Rahav et al. (2013).

For a few of these data streams that require long post-cruise treatment, the data will be submitted to the appropriate data center at a later time, see Table 8.1

Variable	PI	Data submission (when and where)
Persistent Organic Pollutants (POP)	Detlef Schulz-Bull detlef.schulz-bull@io-warnemuende.de	The data will be publicly available at CDIAC one year after measurements, i.e. by the end of 2014.
Methyl Mercury	Lars-Eric Heimbürger heimburger@get.obs-mip.fr	The data will be publicly available at CDIAC one year after measurements, i.e. by the end of 2014.
Radium Isotopes	Jordi Garcia-Orellana jordi.garcia@uab.cat Yishai Weinstein weinsty@012.net.il	The data will be made publicly available at CDIAC 2 years after the samples are analyzed, i.e. Dec. 2015.
Neodymium Isotopes	Paolo Montagna paolo.montagna@bo.ismar.cnr.it	The data will be publicly available at CDIAC one year after measurements, i.e. by the end of 2013.
PFOS	Dr. Nobuyoshi Yamashita nob.yamashita@aist.go.jp	The data will be publicly available at CDIAC one year after measurements, i.e. by the end of 2014.
Barium	Stéphanie Jacquet Stephanie.JACQUET@univmed.fr	The data will be made publicly available at CDIAC 2 years after the samples are analyzed, i.e. Dec. 2015.
Coccolithophores Assemblages	Patrizia Ziveri Patrizia.Ziveri@uab.cat	Data will be submitted to CDIAC by the end of 2013.

Table 8.1: Off-line measurements carried out during M84/3 still not reported (or measured) to public data repositories.

9 Acknowledgements

We like to thank captain Thomas Wunderlich, his officers and crew of RV METEOR for their support of our measurement program and for creating a very friendly and professional work atmosphere on board. The ship time of METEOR was provided by the German Science Foundation (DFG) within the core program METEOR/MERIAN. Significant support for the cruise was provided by the Senatskommission für Ozeanographie der DFG through the “Koordinatorantrag M84”.

10 References

- Bloom, N., 1989. Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. *Canadian Journal of Fisheries and Aquatic Sciences*, 46(7): 1131-1140.
- Bonnet, S., O. Grosso, and T. Moutin (2011). Planktonic dinitrogen fixation in the Mediterranean Sea: a major biogeochemical process during the stratified period?, *Biogeosciences*, 8, 1197-1225
- Byrne R. H. (1987). Standardization of standard buffers by visible spectrometry. *Analytical Chemistry*, 59, 1479-1481.
- Bullister, J. L., and Weiss, R. F.: Determination of CCl₃F and CCl₂F₂ in seawater and air, *Deep-Sea Res.*, 35, 839-853, 1988.
- Burnett, W.C., Aggarwal, P.K., Aureli, A., Bokuniewicz, H., Cable, J.E., Charette, M.A., Kontar, E., Krupa, S., Kulkarni, K.M., Loveless, A., Moore, W.S., Oberdorfer, J.A., Oliveira, J., Ozyurt, N., Povinec, P., Privitera, A.M.G., Rajar, R., Ramessur, R.T., Scholten, J., Stieglitz, T., Taniguchi, M., Turner, J.V. (2006). Quantifying submarine groundwater discharge in the coastal zone via multiple methods. *Sci. Total. Environ.* 367, 498-543.
- Charette, M.A., Buesseler, K.O., Andrews, J.E. (2001). Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnol. Oceanogr.* 46, 465–470.
- Clayton and Byrne (1993). Spectrophotometric seawater pH measurements: total hydrogen ion concentration scale concentration scale calibration of m-cresol purple and at-sea results. *Deep-sea Research I*, Vol. 40, 10, 2115-2129.
- Colin C., Frank N., Copard K., Douville E. (2010). Neodymium isotopic composition of deep-sea corals from the NE Atlantic: implications for past hydrological changes during the Holocene. *Quaternary Science Reviews* 29, 2509-2517.
- Cossa, D., Averty, B., Bretaudeau, J., Sénard, A.S., 2003. Spéciation du mercure dissous dans les eaux marines : Dosages du mercure total, gazeux, réactif, mono et diméthylmercure. In: (IFREMER), I.F.d.R.p.I.E.d.d.I.M. (Editor). Quae, Nantes cedex 0.
- Copard K., Colin C., Douville E., Freiwald A., Gudmundsson G., De Mol B., Frank N. (2010). Nd isotopes in deep-sea corals in the North-eastern Atlantic. *Quaternary Science Reviews* 29, 2499-2508.
- Dickson, A.G., Millero, F.J. (1987). A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media. *Deep-Sea Research* 34, 1733–1743.

- Heimbürger, L.E., Cossa, D., Marty, J.-C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010. Methyl mercury distributions in relation to the presence of nano- and picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). *Geochimica Et Cosmochimica Acta*, 74(19): 5549-5559.
- Hsieh, Y-T. and Henderson, G.M. (2011) Precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and Ra concentrations in seawater samples by multi-collector ICP mass spectrometry, *Journal of Analytical Atomic Spectrometry*. 26, 1338-1346.
- Ibello, V., C. Cantoni, S. Cozzi, and G. Civitarese (2010). First basin-wide experimental results on N₂ fixation in the open Mediterranean Sea *Geophysical Research Letters*, 37, doi: 10.1029/2009gl041635.
- Jeandel C., Arsouze T., Lacan F., Dutay J.-C., Ayoub N., Techine P. (2007). Nd isotopic compositions and concentrations of the lithogenic inputs into the ocean: a compilation, with an emphasis on the margins. *Chemical Geology* 239, 156.
- Langdon, C (2010). Determination of dissolved oxygen in seawater by winkler titration using the amperometric technique. *IOCCP Report N°14*, ICPO publication series N 134.
- Law, C. S., Watson, A. J., and Liddicoat, M. I.: Automated vacuum analysis of sulphur hexafluoride in seawater: Derivation of the atmospheric trend (1970-1993) and potential as a transient tracer, *Mar. Chem.*, 48, 57-69, 1994.
- Mapelli, F., Varela, M. M., Barbato, M., Alvariño, R., Fusi, M., Álvarez, M., Merlino, G., Daffonchio, D., and Borin, S.: Biogeography of planktonic bacterial communities across the whole Mediterranean Sea, *Ocean Sci.*, 9, 585-595, 10.5194/os-9-585-2013, 2013.
- Martin, E.E., and Scher, H.D. (2004). Preservation of seawater Sr and Nd isotopes in fossil fish teeth: bad news and good news. *Earth and Planetary Science Letters* 220, 25-39.
- Montagna P., Goldstein S., Taviani M., Frank N., McCulloch M. Neodymium isotopes in biogenic carbonates: reliable archive of ϵ_{Nd} . AGU Fall Meeting, 13-17 December 2010, San Francisco, USA.
- Merzbach, C., Culberson, C.H., Hawley, J.E., Pytkowicz, R.M. (1973). Measurement of the apparent dissociation constants of carbonic acid in seawater at atmospheric pressure. *Limnology and Oceanography*, 18, 897-907.
- Mintrop, L., F. Fernández-Pérez, M. González Dávila, A. Körtzinger and J.M. Santana Casiano (2000). Alkalinity determination by potentiometry- intercalibration using three different methods. *Ciencias Marinas*, 26, 23-37.
- Moeseneder MM, Winter C, Arrieta JM, Herndl GJ (2001). Terminal-restriction fragment length polymorphism (T-RFLP) screening of a marine archaeal clone library to determine the different phylotypes. *J Microbiol Methods* 44:159-172
- Mohr, W., Grosskopf, T., Wallace, D. W. R. & LaRoche, J. (2010). Methodological Underestimation of Oceanic Nitrogen Fixation Rates. *Plos One* 5, doi:10.1371/journal.pone.0012583 (2010).
- Monperrus, M., Tessier, E., Veschambre, S., Amouroux, D., Donard, O., 2005. Simultaneous speciation of mercury and butyltin compounds in natural waters and snow by propylation and species-specific isotope dilution mass spectrometry analysis. *Anal. Bioanal. Chem.*, 381(4).

- Moore, W.S. The effect of Submarine Groundwater Discharge on the Ocean (2010). *Annu. Rev. Mar. Sci.*, 2, 59-88.
- Moore, W.S., Arnold, R. (1996). Measurement of ^{223}Ra and ^{224}Ra in coastal waters using a delayed coincidence counter. *J. Geophys. Res.* 101, 1321–1329.
- Pérez, F.F. and F. Fraga (1987). A precise and rapid analytical procedure for alkalinity determination. *Marine Chemistry*, 21, 169-182
- Pérez, F.F., A.F. Ríos, T. Rellán and M. Álvarez (2000). Improvements in a fast potentiometric seawater alkalinity determination. *Ciencias Marinas*, 26, 463-478.
- Piotrowski A.M., Goldstein S.L., Hemming S.R., Fairbanks R.G (2005). Temporal relationships of carbon cycling and ocean circulation at glacial boundaries. *Science* 307, 1933– 1938.
- Rahav, E., Herut, B., Levi, A., Mulholland, M. R., and Berman-Frank, I.: Springtime contribution of dinitrogen fixation to primary production across the Mediterranean Sea, *Ocean Sci.*, 9, 489-498, 10.5194/os-9-489-2013, 2013.
- Ribera d'Alcala', M., G. Civitarese, F. Conversano, and R. Lavezza, Nutrient ratios and fluxes hint at overlooked processes in the Mediterranean Sea, *J. Geophys. Res.*, 108(C9), 8106, doi:10.1029/2002JC001650, 2003.
- Rutberg R.L., Hemming S.R., Goldstein S.L. (2000). Reduced north Atlantic deep water flux to the glacial southern ocean inferred from neodymium isotope ratios. *Nature*, 405, 935–938.
- Scrivner A.E., Vance D., Rohling E.J. (2004). New neodymium isotope data quantify Nile involvement in Mediterranean anoxic episodes. *Geology*, 32, 565–568.
- Stoichev, T., Martin-Doimeadios, R.C.R., Amouroux, D., Molenat, N., Donard, O.F.X., 2002. Application of cryofocusing hydride generation and atomic fluorescence detection for dissolved mercury species determination in natural water samples. *Journal of Environmental Monitoring*, 4(4): 517-521.
- Stöven, T.: Ventilation processes of the Mediterranean Sea based on CFC-12 and SF6 measurements, Diploma, Leibniz-Institut für Meereswissenschaften der Mathematisch-naturwissenschaftlichen Fakultät, Christian-Albrecht-Universität zu Kiel, Kiel, 2011.
- Tachikawa K., Roy-Barman M., Michard A., Thouron D., Yeghicheyan D., Jeandel C. (2004). Neodymium isotopes in the mediterranean sea: Comparison between seawater and sediment signals. *Geochimica et Cosmochimica Acta* 68, 3095.
- Taniyasu S, Kannan K, So MK, Gulkowska A, Sinclair E, Okazawa T, Yamashita N. (2005) *J Chromatogr A*. 1093(1-2): 89–97
- Taniyasu S, Kannan K, Yeung LWY, Kwok KY, Lam PKS, Yamashita N. (2008) *Anal. Chim. Acta*, 619(2): 221–230.
- Thurnherr, A.M., Visbeck, M., Firing, E., King, B.A., Hummon, J.M., Krahmann, G., Huber, B., 2010: A Manual for acquiring lowered Doppler Current Current profiler Data. *IOCCP Report N°14*, ICPO publication series N 134.
- Vance, D.A.E., Scrivner, P., Beney, M., Staubwasser, G.M., Henderson, and Slowey, N.C. (2004). The use of foraminifera as a record of the past neodymium isotope composition of seawater. *Paleoceanography*, 19, doi:10.1029/2003PA000957.

- van de Flierdt, T., Robinson, L.F, Adkins, J.F. (2010). Deep-sea coral aragonite as a recorder for the neodymium isotopic composition of seawater. *Geochimica et Cosmochimica Acta*, 74, 6014-6032.
- Varela MM, van Aken HM, Sintes E, Herndl GJ (2008). Latitudinal trends of Crenarchaeota and Bacteria in the meso- and bathypelagic water masses of the Eastern North Atlantic. *Environ Microbiol.* 10: 110-124.
- Yogev, T., E. Rahav, E. Bar-Zeev, D. Man-Aharonovich, N. Stambler, N. Kress, O. Beja, M. R. Mulholland, B. Herut, and I. Berman-Frank (2011). Is dinitrogen fixation significant in the Levantine Basin, East Mediterranean Sea? *Environmental Microbiology*, 13, 854-871