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Repeat hydrography in the Mediterranean Sea, data from the *Meteor* cruise 84/3 in 2011

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Abstract

Here we report on data from an oceanographic cruise on the German research vessel *Meteor* covering large parts of the Mediterranean Sea during spring of 2011. 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 physical and biogeochemical properties, in order to compare those to historic data sets. During the cruise, 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/) was collected. The measurements include; salinity and temperature (CTD), an over-determined carbonate system, inorganic nutrients, oxygen, transient tracers (CFC-12, SF_6), Helium isotopes and tritium, and carbon isotopes. 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. Additionally, sampling in the Aegean, Adriatic and Tyrrhenian Seas were carried out. The sections roughly followed lines and positions that have been sampled previously during other programs, thus providing the opportunity for comparative investigations of the temporal development of various parameters.

Data coverage and parameter measured

Repository-Reference: doi:10.3334/CDIAC/OTG.CLIVAR_06MT20110405
Available at: Bottle data: http://cdiac.ornl.gov/oceans/Coastal/Meteor_Med_Sea.html;
CTD continuous profiles: http://cchdo.ucsd.edu/cruise/06MT20110405
Coverage: 33–42° N; 36° E–10° W
Location Name: The Mediterranean Sea

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Date/Time Start: 5 April 2011
Date/Time End: 28 April 2011

1 Introduction

The Mediterranean Sea is a relatively small, land-locked, ocean basin with an active deep and shallow overturning and complex upper layer circulation. The last few decades has seen dramatic changes in the circulation of the Mediterranean Sea. This is manifested amongst others as a shift of the deep water formation area from the Adriatic to the Aegean Sea in the Eastern Mediterranean Sea, and an intense deep water formation event in the mid 2000's in the Western Mediterranean Sea (e.g. Roether et al., 1996; Schroeder et al., 2008). The deep water formed from these two sources has different properties of salinity and temperature and different biogeochemical signature. The Mediterranean Sea is obviously not in steady-state and is potentially sensitive to climatic changes. The characteristic of the Mediterranean Sea is further such that it has the potential to sequester large amounts of anthropogenic CO_2, C_{ant}, i.e. the Mediterranean Sea has high alkalinity and temperature, which can rapidly be transported to depth by the overturning circulation (e.g. Schneider et al., 2010). The column inventories of C_{ant} in the Mediterranean is among the highest found anywhere in the world ocean; the Mediterranean Sea thus stores a significant portion of the global anthropogenic emissions of CO_2 despite its relatively small volume. However, few inorganic carbon data exist in the Mediterranean Sea, and knowledge about how recent changes in circulation are affecting the storage rate of C_{ant} is fundamental.

Here we report on a data-set obtained during spring 2011 on the German R/V *Meteor*, cruise M84/3 (EXPOCODE: 06MT20110405). The cruise was set-up to follow the demands and requirements of repeat hydrography as specified by the GO-SHIP group (http://www.go-ship.org/), i.e. with a comprehensive set of physical and chemical parameters measured to the highest standards. 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 the drivers of those changes. These data will support understanding and addressing 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. These objectives were achieved by measurements of physical parameters with CTD (including oxygen) and by on-board measurements of discrete water samples for oxygen, nutrients (nitrate, nitrite, phosphate and silicate), dissolved inorganic carbon (DIC), total alkalinity, pH, and the transient tracers SF_6 and CFC-12. In addition, samples were taken for the determination of ^{3}He and tritium, as well as for the carbon isotopes ^{14}C and ^{13}C, for later shore-based analyzes. Here we present a short description the M84/3 cruise that started in Istanbul (Turkey) on 4 April and ended in Vigo (Spain) on 28 April 2011. The cruise track is shown in Fig. 1. For a sub-set of the CTD stations, no chemistry was performed due to time limitations, and for another sub-set of stations a comprehensive tracer program with sampling for helium (including tritium) and carbon isotopes were performed; these sub-sets are marked with different colors in Fig. 1. A more comprehensive report from the observing program during cruise M84/3 can be found in the cruise report (Tanhua, 2013).

2 Instrumentation

2.1 CTD

Altogether, 61 standard hydrographic stations were occupied during the cruise, employing a SeaBird SBE911 plus CTD-O_2 probe, attached to a SeaBird carousel 24 bottle water-sampler. At most stations water samples were taken from 24 depth levels within the water column from the surface to the bottom. At least three of those were analyzed for salinity on-board using certified reference seawater 38H11 with a K15-factor of 1.07631 (24 °C). The CTD data were post-processed by applying Seabird software and MATLAB routines. At this stage, spikes were removed, 1 dbar average calculated,

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and temperature, salinity and oxygen 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 but somewhat less for oxygen.

Samples for chemical analysis of discrete water samples were drawn from 10 L Niskin bottles. The sampling order were always: helium, CFC12/SF_6, oxygen, DIC/Carbon isotopes, pH, alkalinity, nutrients, tritium, salinity and other samples. Below follows a short description of the various on-board measurements.

2.2 Dissolved oxygen

Dissolved oxygen was measured at all chemistry stations for all depths following the Winkler potentiometric method modified after Langdon (2010). Two independent reference materials for the iodate standard were used to calibrate the thiosulfate solution: Commercial potassium iodate solutions of 0.01° N (20 °C) provided by OSIL (UK) and a Wako (Japan). Three reproducibility exercises were performed along the cruise, resulting in an estimated precision of ±0.6 µmol kg^{-1} or better.

2.3 The carbonate system

All the stations and depths were sampled for total alkalinity (TA), dissolved inorganic carbon (DIC) and pH, in order to have an over-determined CO_2 system. The DIC content was determined using a SOMMA instrument. Samples were collected 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 h; the samples were kept at 20 (±0.2) °C during the analysis. An aliquot of approximately 26 ml was transferred to the instrument where it was acidified with phosphoric acid and the outgassed CO_2 was measured coulometricaly. The precision of the analysis was determined to ±0.6 µmol kg^{-1}

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by titration of several bottles filled from the same Niskin bottles. The accuracy was determined to be 2.5 µmol kg^{-1} by analyzing a total of 42 bottles of certified reference material (CRM, Andrew Dickson, Scripps, CA, USA, batch 108); the DIC of this batch is certified at 2022.70 ± 0.7 µmol kg^{-1}. Measurements of the CRMs were also used to daily correct the temporal drift in the coulometer cell; this correction was never larger than 3 µmol kg^{-1}.

Spectrophotometric pH in seawater was measured at every station and depth using a double-wavelength spectrophotometric procedure (Clayton and Byrne, 1993), and is reported at 25 °C and on the total scale; i.e. pH25T. Samples were collected in cylindrical optical glass 10-cm path-length cells, which were filled to overflowing and immediately closed. All the absorbance measurements were obtained in the thermo stated cell at 25 ± 0.2 °C. The absorbance was measured at three different fixed wave-lengths (434, 578 and 730 nm) and calculated using the formula in Clayton and Byrne (1993). A correction was applied to compensate for the injection of the indicator into the seawater. The magnitude of this correction over our range of pH is small, ranging from 0.003 to 0.0007 pH units. The accuracy of the pH measurements were determined by analyzing ten to fifteen samples per week of CO_2 reference material (CRM, batch 108). Since the pH in these CRMs are not given, the pH of this batch was calculated to 7.8782 using the dissociation constants from Mehrbach et al. (1973) refitted by Dickson and Millero (1987). At three occasions several samples collected from the same Niskin bottle were analyzed, giving the reproducibility of the pH measurements to be 0.0012 units.

Samples for Total Alkalinity (TA) determination were collected in 600 mL borosilicate bottles and were analyzed within a day after sampling. The TA samples were analyzed following a double end point potentiometric technique by Pérez and Fraga (1987) and Pérez et al. (2000). Measurements of CRM were performed in order to control the accuracy of the TA measurements; the pH as measured by the electrode was corrected to obtain the closest mean TA to the CRM; the pH correction was never larger than 0.05. The precision of the TA measurements was 0.1 µmol kg^{-1} determined from duplicate analysis of all samples. At some stations several samples were taken from the same

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Niskin bottle, and the uncertainty of the TA measurements (i.e. including sampling errors) is determined to be 0.6 µmol kg^{-1}. Additionally, the daily drift of the system was determined by regular measurements of a substandard (surface seawater); this drift was always very low.

2.4 SF_6 and CFC-12

During the cruise, two gas chromatograph/purge-and-trap (GC/PT) systems (PT2 and PT3) were used for the measurements of the transient tracers CFC-12 and SF_6, similar to the set-up described by Bullister and Wisegarver (2008). 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). Measurements were for the first half of the cruise conducted on instrument "PT2", and later, due to a defect Electron Capture Detector (ECD), conducted on instrument "PT3". During the transition between the instruments, samples were flame sealed in ~ 350 mL ampoules. The system "PT3" were not able to measure SF_6, so that only CFC-12 could be measured on board. However, samples from selected stations in the Western Mediterranean Sea were flame sealed for the measurement of SF_6; all flame sealed ampoules were measured onshore at the lab at IFM-GEOMAR in Kiel after the cruise. The CFC-12 data are reported on the SIO98 scale and SF_6 on the NOAA-2000 scale. Calibration curves were measured every few days to characterize the non-linearity of the system, and point calibrations were performed regularly to determine the short term drift in the detector. Replicate measurements were taken on a few stations and the reproducibility was determined to be 0.65 %/1.0 % for CFC-12/SF_6 measurements on PT2, and 0.34 % for CFC-12 measured on PT3, whereas the values are approximately twice as large for the off-line measurements of flame sealed ampoules. A detailed account for the CFC-12 and SF_6 measurements can be found in Stöven (2011).

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2.5 Nutrients

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; Phosphate – Method No Q-031-04 Rev. 2; Silicate – Method No Q-066-05 Rev. 3. The reproducibility of the nutrient measurements, as C_v %, were determined to: Nitrite + Nitrate: ≤ 1.5 %; Phosphate: ≤ 3.6 %; Silicate: ≤ 1.7 %, or if expressed as in µmol kg^{-1}: Nitrate 0.08; Phosphate 0.007; Silicate 0.10, based on measurements of replicate samples.

2.6 Helium and tritium

During the cruise, samples for helium isotope were taken for measurements by two different groups: at 10 stations samples were taken along the whole depth profile for measurement of ^{3}He and tritium at Institute of Environmental Physics at the University of Bremen, Germany. At 13 other stations, samples were taken for the analysis of ^{3}He at the Laboratoire de Sciences du Climat in LSCE-CEA, Saclay, France. The volume of the helium samples were either 40 or 6.4 mL for the two groups, respectively, and sampled in copper-tubes. Samples for tritium analysis were taken in 1 L plastic bottles and stored into zip-locked plastic bags. At station 301, a brine lake was sampled that contained very high concentrations of radiogenic helium, which lead to contamination of the Niskin bottles so that values for ^{3}He had to be flagged as questionable for stations 301, 303 and 305.

2.7 Carbon isotopes

During the cruise a total of about 280 samples were taken for the determination of the carbon isotopes ^{14}C and ^{13}C. The samples were taken in 500 mL. bottles and were poisoned with HgCl and sealed according to standard procedures. The samples were shipped to the National Ocean Sciences AMS Facility at Woods Hole Oceanographic

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Institution, USA, for analysis after the cruise. These results will become public available by the end of 2013.

2.8 Auxiliary data

Several additional and complementary measurement and sampling programs were carried out during the cruise, although the data are currently not available in the data repository at CDIAC due to long processing times. These measurements include: surface distribution of persistent organic pollutants (POPs), measurements of Polyfluorooctansulfonate (PFOS), dissolved barium, large volume samples collections for the determination of Ra isotopes, determination of microbiological community structure (Mapelli et al., 2013), determination of the isotopic composition, abundance and size of coccolithophores, aerosol sampling with daily resolution, incubation experiments for nitrogen fixation (Rahav et al., 2012), determination of methyl-mercury and trace metals, determination of neodymium isotopes.

3 Dataset

The data set from *Meteor* cruise M84/3 is composed of two main components; the continuous profiles from the CTD, and the discrete data from the water samples. The data set contains information from 61 hydrographic stations. Of these 47 were CTD-cast with chemistry samples, 6 stations were devoted to large volume sampling of Radium isotopes, and 8 stations were only for CTD measurements.

The CTD data are reported as 1 dbar for temperature, salinity and oxygen.

The bottle data are reported in standard World Hydrographic Program (WHP) Exchange format (Swift, 2008). This format is commonly used for reporting of bottle data, and is the format used by CDIAC and CCHDO, for instance.

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4 Data access

The hydrographic data set is published at two different repositories due to the different scope of the repositories. The bottle data is available at the Carbon Dioxide Information Analysis Center (CDIAC), Oak Ridge, TN, USA (Tanhua et al., 2012); http://cdiac.ornl.gov/oceans/Coastal/Meteor_Med_Sea.html.

The CTD profile data are available at the CLIVAR and Carbon Hydrographic Data Office (CCHDO), UCSD Scripps Institution of Oceanography, San Diego, CA, USA; http://cchdo.ucsd.edu/cruise/06MT20110405.

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Table 1. List of variables available from the *Meteor* cruise M84/3 in 2011.

Parameter	Short name	Unit	Flag name	Comment
Latitude	LATITUDE	$^\circ$N		
Longitude	LONGITUDE	$^\circ$E		
Pressure	CTDPRS	dbar		
Temperature	CTDTMP	$^\circ$C		in situ temperature ITS-90
Salinity	CTDSAL		CTDSAL_FLAG_W	PSS-78
Oxygen	CTDOXY	μmol kg^{-1}	CTDOXY_FLAG_W	From the CTD probe
Oxygen	OXYGEN	μmol kg^{-1}	OXYGEN_FLAG_W	From winkler titration
Silicate	SILCAT	μmol kg^{-1}	SILCAT_FLAG_W	
Nitrate	NITRAT	μmol kg^{-1}	NITRAT_FLAG_W	
Nitrite	NITRIT	μmol kg^{-1}	NITRIT_FLAG_W	
Phosphate	PHSPHT	μmol kg^{-1}	PHSPHT_FLAG_W	
CFC-12	CFC-12	nmol kg^{-1}	CFC-12_FLAG_W	
SF_6	SF6	fmol kg^{-1}	SF6_FLAG_W	
Dissoled Inorganic Carbon	TCARBN	μmol kg^{-1}	TCARBN_FLAG_W	
Total Alkalinity	ALKALI	μmol kg^{-1}	ALKALI_FLAG_W	
pH	PH_TOT		PH_TOT_FLAG_W	total scale at 25 $^\circ$C
Tritium (^{3}H)	TRITUM	Tritium Units (TU)	TRITUM_FLAG_W	
Uncertainty of tritium data	TRITER	Tritium Units (TU)		
Helium	HELIUM	nmol kg^{-1}	HELIUM_FLAG_W	
δ^3He	DELHE3	%	DELHE3_FLAG_W	
Uncertainty of δ^3He data	DELHER	%		
Neon	NEON	nmol kg^{-1}	NEON_FLAG_W	

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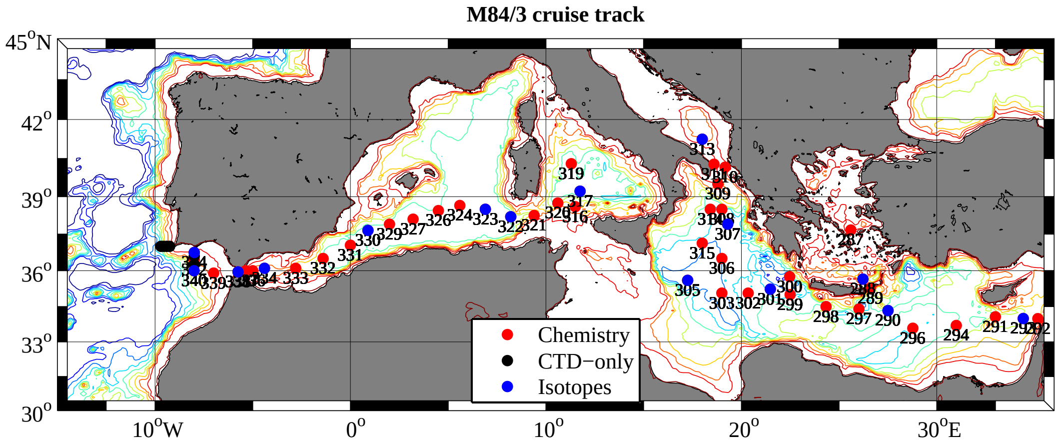

Fig. 1. Cruise Track of M84/3 with CTD stations marked in different colors based on the extent of measurements carried out.