Cruise report 64PE374 on RV Pelagia

MedBlack GEOTRACES leg 3

Istanbul (Turkey) 25-07-2013 to Lisbon (Portugal) 11-08-2013

Micha J.A. Rijkenberg

With contributions of participants

Royal Netherlands Institute for Sea Research

Acknowledgements

We would like to thank the Master of the RV *Pelagia* Pieter Kuijt and his crew for their excellent support during our cruise. The post-cruise data management by Hendrik van Aken and the data management group was excellent as usual. We thank NIOZ Marine Research facilities for their support. We also want to thank chief bottle washer Rachel Davidson who came especially from New Zealand (University of Otago) to help us cleaning the myriads of bottles in preparation of our cruises. We acknowledge NWO (project number: 822.01.015) and Royal NIOZ for financing of the ship time and part of the cruise support.

Front page: the titanium ultraclean CTD frame with 24 x 24L PVDF samplers in the Tyrrhenian Sea (Mediterranean) on the RV Pelagia with the Volcanic Island Stromboli in the background.

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Cruise summary

Research cruise
The MedBlack GEOTRACES leg 3 (64PE374) on RV *Pelagia* departed 25 July 2013 from Istanbul (Turkey) and arrived in Lisbon (Portugal) on 11 August 2013 with Micha Rijkenberg and Loes Gerringa (Royal NIOZ) as chief scientists.

Stations
During cruise 64PE374 we occupied a total of 19 full depth stations (Figure 1). Typically at each station we would have two casts to the bottom starting with the ultraclean CTD (UCC) followed by the high volume CTD (12L standard CTD). Details like the date, time and position of the actual deployments at each station can be found in Appendix 1.

During this cruise we encountered communication problems with the CTD's. However, under the professional guidance of Ruud Groenewegen we managed to complete almost all planned stations. Only one station (number 16) was not sampled by the UCC. In addition, at some casts of the 12L standard CTD some bottles did not close or closed at the same depth as another bottle. For reference, what follows here is an explanation where and when problems occurred. Bottle 12 of station 4 cast 2 with the 12L standard CTD came open on deck. Replacement of the top lid solved the problem. Station 8 had three casts. Due to a communication problem with the UCC CTD the first UCC cast was stopped. The second UCC cast called 1a was successful and sampled. At station 9, cast 2, 12L standard CTD, bottles 2-4 were closed at the same depth (500 m). Also at station 10 there was a problem with the communication with the UCC CTD. At station 10 the 12L standard CTD was used for the first cast and the UCC CTD for the second cast. Communication problems at station 11 resulted in the closure of two 12L standard CTD bottles at the same depth (bottle 1 and 2 at ~ 2540 m). At station 13 cast 1, UCC CTD, the bottles 15 – 19 did not close. Instead the bottles 20 - 24 sampled those depths (ucc_b20 = 250m, ucc_b21 = 205m, ucc_b22 = 150m, ucc_b23 = 125m, ucc_b24 = 100m). An extra cast 3 at station 13 sampled the 5 depths in the upper water column that were not sampled during cast 1. At station 14, bottle 13 of cast 1 with the UCC CTD was not sampled because the tap of this bottle was left open. Several UCC casts at station 16 failed due to communication problems resulting in not having any ultraclean samples taken at station 16. The 12L standard CTD came on deck with bottle 9 still open and also bottle 14 appeared to have deeper water in it. At the stations 17 and 19 bottle 9 of cast 2 with the 12L standard CTD was still open coming back on deck. Station 17 was a hyper station and the cross over station with the Spanish lead GEOTRACES cruise on the B/O Ángeles Alvariño (PI's: Patrizia Ziveri and Jordi Garcia-Orellana). Note that the actual station numbering is different from the original planned station numbering.

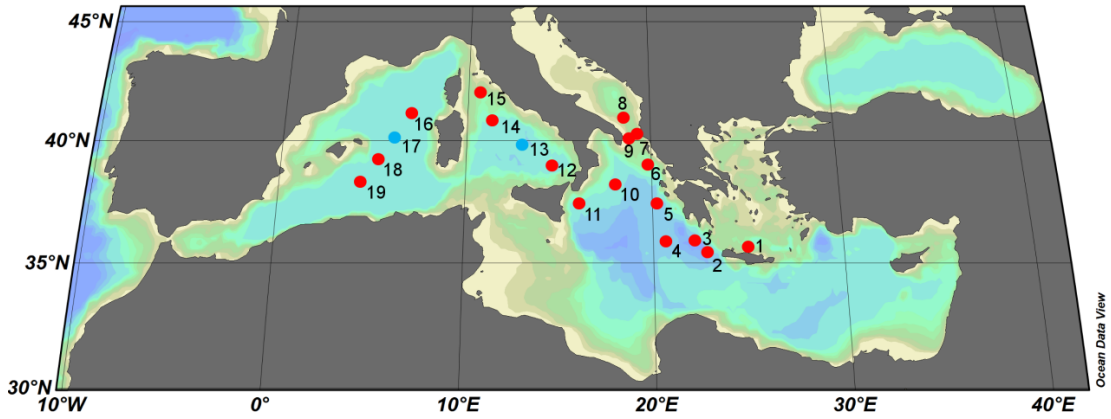

Figure 1. Cruise track of research cruise 64PE374 on the RV Pelagia in July/August 2013. Red dots represent normal stations with typically one full depth UCC cast and a full depth 12L standard CTD . Blue dots represent hyper stations with 2 to 3 full depth UCC casts and 1 full depth 12L standard CTD cast.

Cruise narrative

Originally 25 stations were planned for leg 3 of the MedBlack GEOTRACES cruises. However, because we did not get permission to sample in French waters we could only sample 19 stations. As a consequence we did not sample in the Ligurian Sea.

The participants boarded the RV Pelagia at 10:00 am on 25 July 2013. The Pelagia left Istanbul early in the afternoon for leg 3 of the MedBlack GEOTRACES cruises. The first station was on 27 July. All CTD's worked well at station 1. However, from station 8 onwards the CTD casts were plagued by communication problems between the CTD and the computer in the CTD control room. Due to this problems we missed 1 UCC CTD cast at station 16. All other stations and casts were nevertheless successfully sampled.

A cubic meter container was filled with ultraclean 0.2 µm filtered surface seawater for Hans Slagter and Loes Gerringa on 7 August 2013 between 05:55 am UTC (after station 18) and 18:40 UTC before station 19.

The weather conditions stayed good throughout the expedition. We arrived in Lisbon (Portugal) in the morning of 11 August.

Ship's clock

The ship left the harbour of Istanbul on 25 July 2013 with the ship's time set on Turkish local time (UTC+3). The clock was changed in the night from 6 on 7 August from UTC+3 to UTC+2. The clock stayed on UTC+2 until arrival in Lisbon (Portugal).

Weather

The weather conditions were excellent during most of the expedition (Figure 2). Some windforce 6-7 winds were encountered between station 6 and 9.

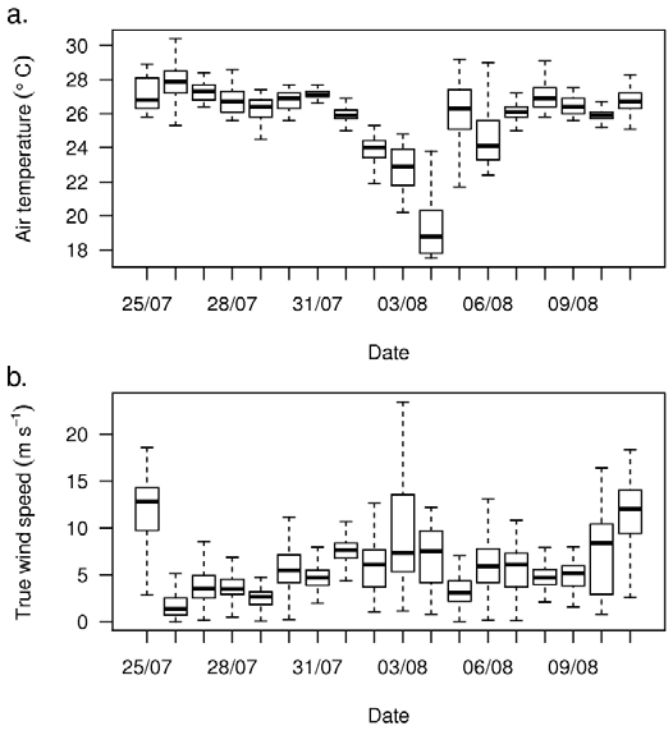

Figure 2. The air temperature (a.) and true wind speed (b.) during 64PE374.

General preliminary results

This paragraph shows the section plots (Figure 3) of some of the parameters which were measured on board. There are 4 sections A, B, C and D and each section is graphed against section distance in km where the section distance of 0 occurs at the tail end of the arrows in the below Figure 3.

Parameters measured on board were salinity and oxygen (from the CTD sensor, Figure 4 and 5), the nutrients (phosphate, silicate, nitrate and nitrite Figure 6-9) and fluorescence (Figure 10).

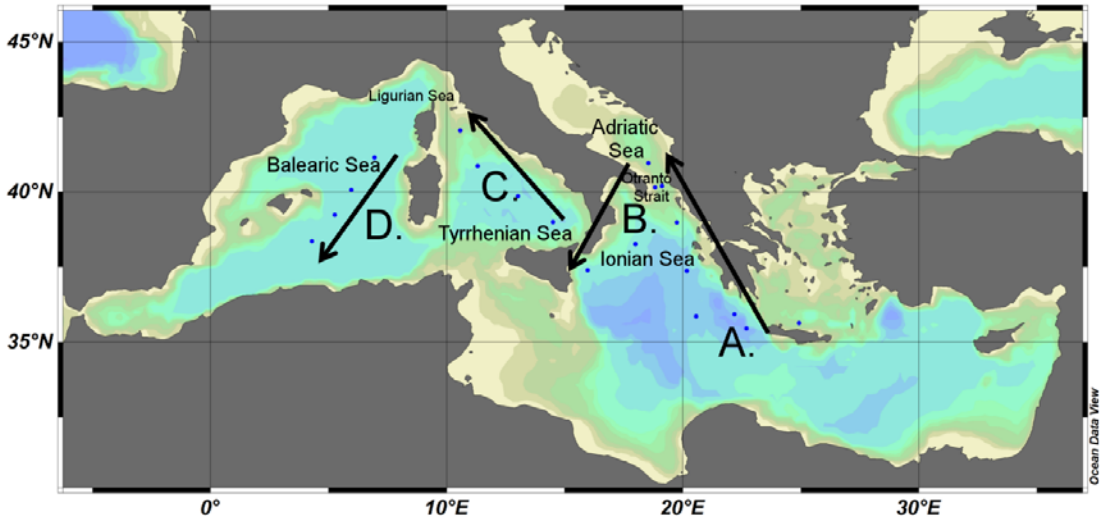

Figure 3. The cruise track of cruise 64PE374 is divided in 4 sections A, B, C and D. The section plots are based on section distance (km) where 0 km starts at the tail of each arrow in this section map.

During 64PE374 the salinity varied between 17 and 36.5 and was on average 20. The salinity section plots are used to give a strongly simplified indication of the water masses that we encountered during 64PE374. For the Ionian Sea (Figure 4A and B) information on water masses was used from Malanotte-Rizzoli et al. (1997). Figure 4A shows the eastern Ionian Sea transect with the highest salinities occurring in the surface waters (upper 200m) consisting of Modified Atlantic Waters (MAW) and Ionian Surface Waters (ISW). The surface waters on the western site of the Ionian Sea (Figure 4B) are less saline due to mixing of MAW/ISW with Adriatic Surface Waters (ASW). ASW originates in the northern Adriatic through mixing of coastal river outflows and denser interior waters. ASW flows out from the Otranto Strait as a current confined to the Italian coastline. The Levantine Intermediate Waters (LIW) lay below the surface waters between ~ 200-600m which mixes with the Adriatic Deep Water (ADW, 700-1600 m) above the ADW below 1600m which forms the bulk of the Eastern Mediterranean Deep Water (EMDW).

For the Tyrrhenian Sea information on water masses was used from Send et al. (1999) (Figure 4C). The Tyrrhenian Sea is located east of Sardinia (Figure 3). It is a basin that is nearly totally enclosed below about 400m depth. Its only deep connection is via the narrow Tyrrhenian Trough (1900 m depth) in the Sardinia Channel. Tyrrhenian Deep Water (TDW) is warmer and more saline than Western Mediterranean Deep Water (WMDW) and is formed by inflowing WMDW (along the bottom) mixing with overlying warmer and more saline LIW possibly mixed with some Atlantic Intermediate Water (AIW). The surface waters in the upper 200m of the Tyrrhenian Sea consists of MAW (Millot, 1999). Similar water masses are found in the Balearic Sea (Millot, 1999) (Figure 4D).

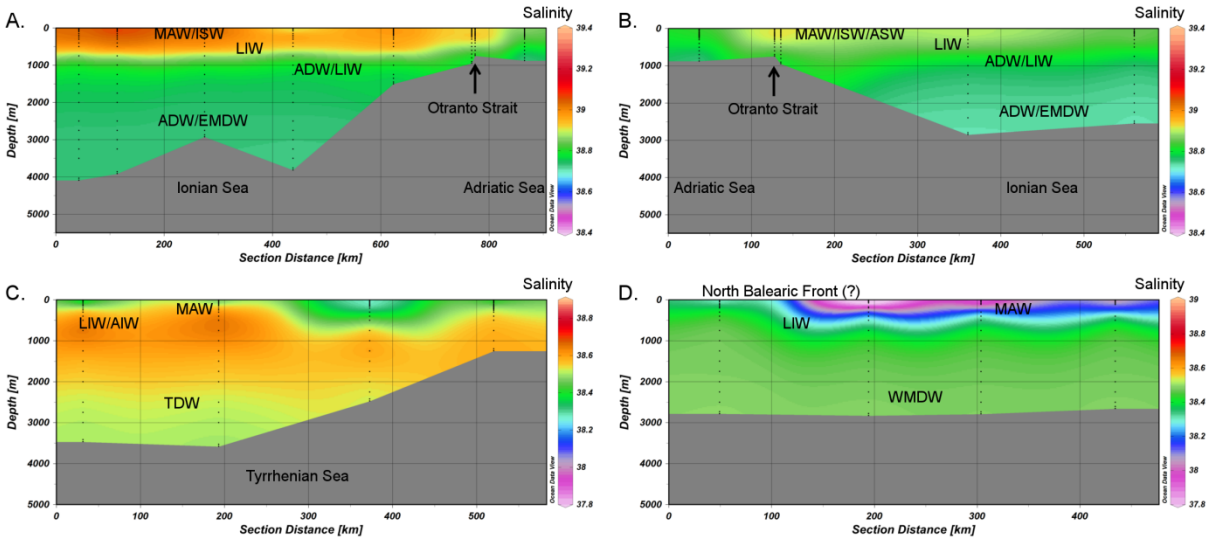

Figure 4. The section plots of preliminary salinity data (UCC sensor data) for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Ruud van Groenewegen and Mark Eveleens. Abbreviations surface waters: MAW: Modified Atlantic Water; ISW: Ionian Surface Water; ASW: Adriatic Surface Water. Abbreviations intermediate waters: LIW: Levantine IntermediateWater; AIW: Atlantic Intermediate Water. Abbreviations deep waters: ADW: Adriatic Deep Water; EMDW: Eastern Mediterranean Deep Water; TDW: Tyrrhenian Deep Water; WMDW: Western Mediterranean Deep Water .

In the eastern Mediterranean Sea, the surface waters and the waters of the Adriatic Sea contained relative high oxygen concentrations (Figure 5 A). An intrusion visible as relatively

high oxygen concentrations between 1000-2000 m depth in the Ionian Sea may indicate dense water formed in the Adriatic Sea (Manca et al. 2002). A similar signature of differences in the macro-nutrient concentrations compared to surrounding waters confirm this oxygen feature (Figures 6A-9A). High surface oxygen concentrations in the western Mediterranean coinciding with low salinities indicate the North Balearic Front (Figures 4C and D).

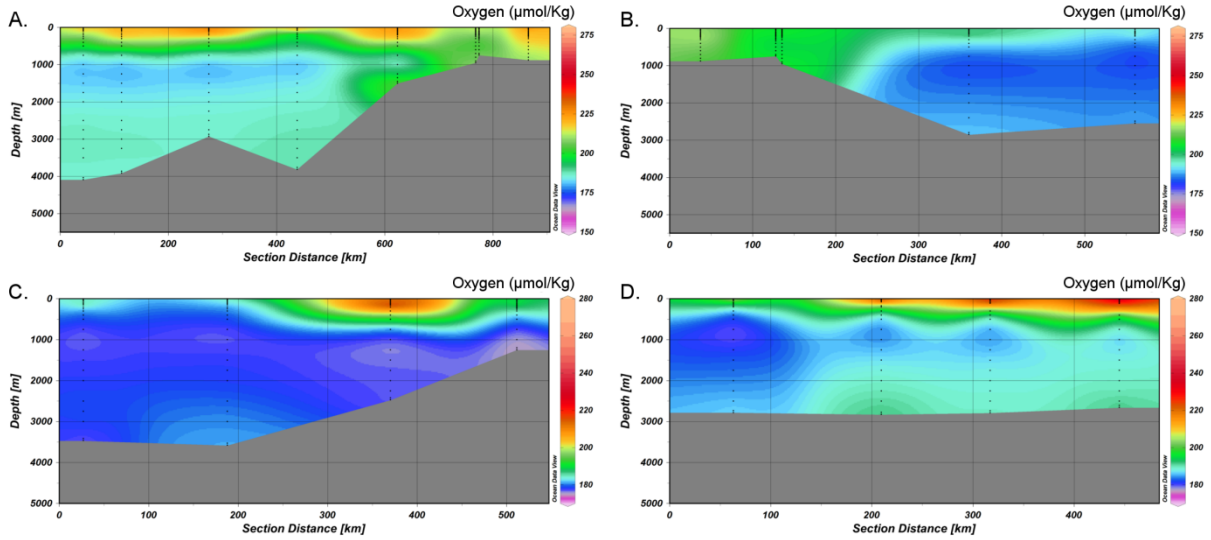

Figure 5. Section plots of preliminary oxygen data (UCC sensor data) for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Ruud van Groenewegen and Mark Eveleens

Phosphate concentrations varied from below the detection limit up to 8.5 µmol/L. Nitrate varied from from below the detection limit up to 6 µmol/L. Nitrite varied from below the detection limit up to 0.25 µmol/L and silicate varied from 0.1 to 330 µmol/L. In general, surface nutrient concentrations were lower in the eastern than in the western Ionian Sea (Figure 6A,B – 9A,B) but increased with depth. Nutrient uptake, as indicated by higher fluorescence in the eastern compared to the western Ionian Sea may explain this discrepancy in nutrient concentrations (Figures 10A and B). Except for nitrite, generally low nutrient concentrations were found in the surface waters compared to the deep waters of the western Mediterranean Sea (Figures 6C,D – 9C,D).

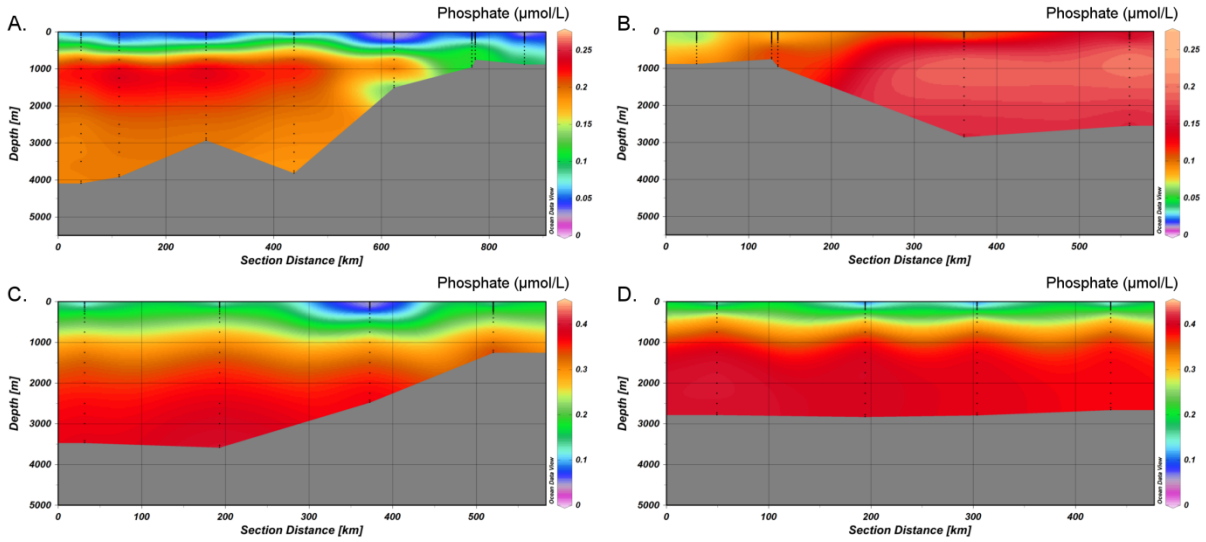

Figure 6. Preliminary phosphate data from the UCC for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Karel Bakker

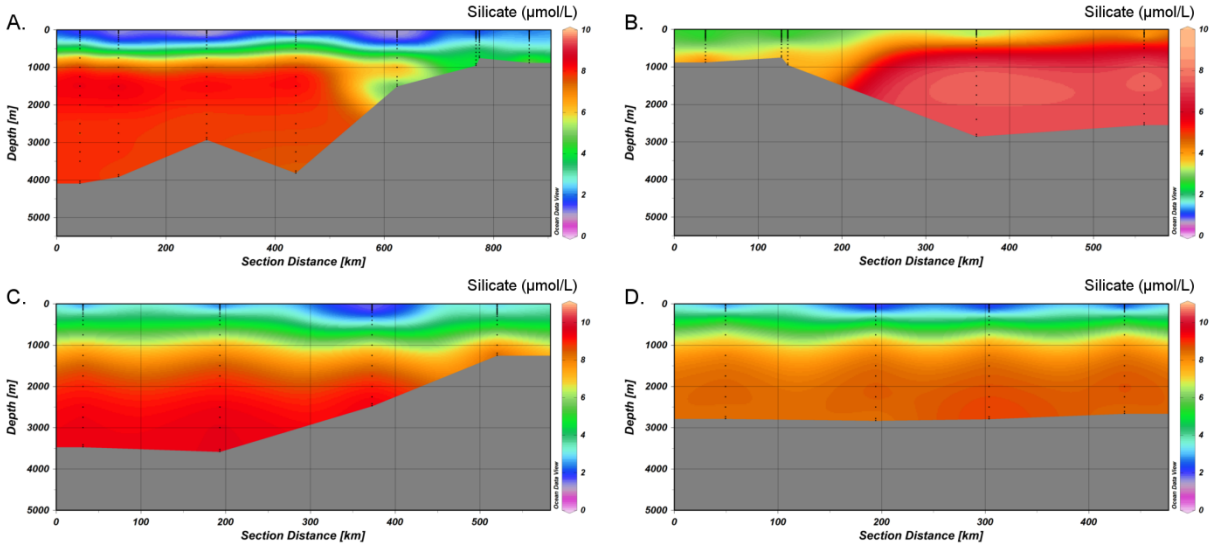

Figure 7. Preliminary silicate data from the UCC for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Karel Bakker

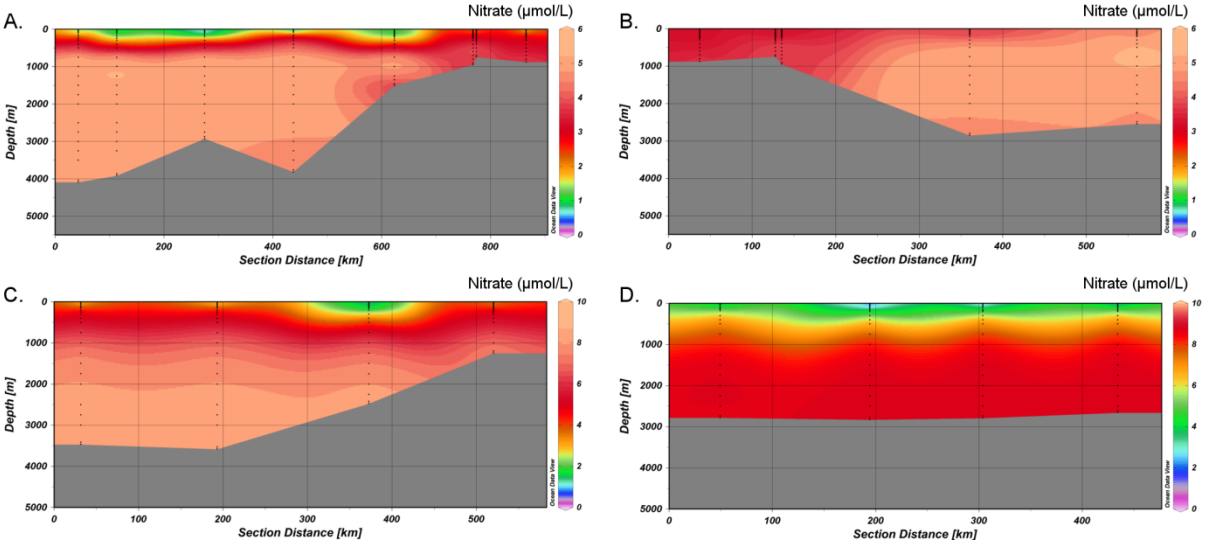

Figure 8. Preliminary nitrate data from the UCC for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Karel Bakker

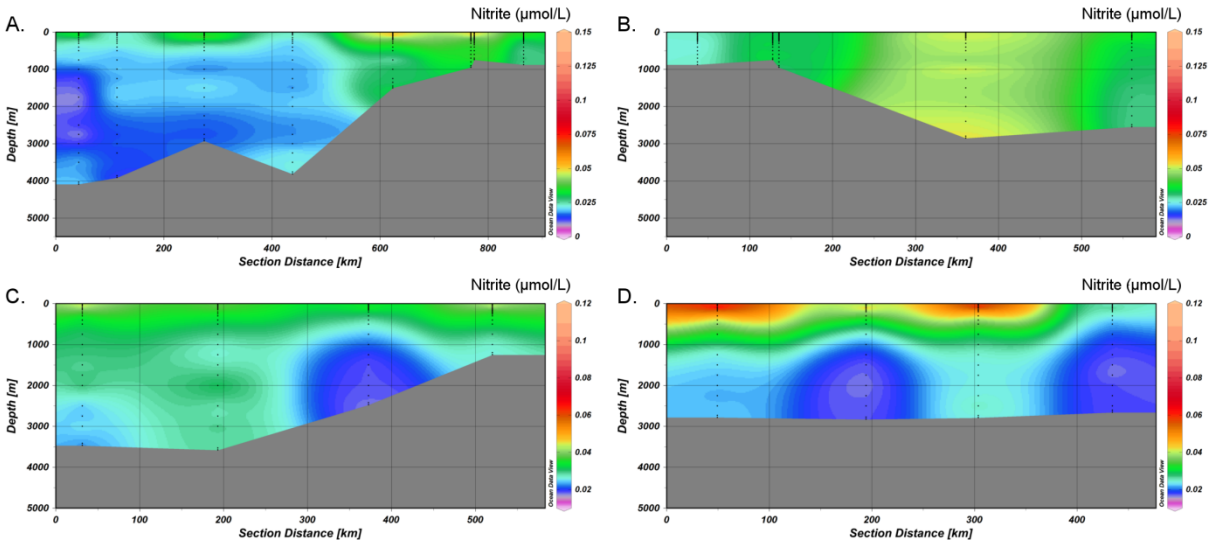

Figure 9. Preliminary nitrite data from the UCC for cruise 64PE374 in the northern Mediterranean Sea. Note that the color scale may change between graphs. Data: Karel Bakker

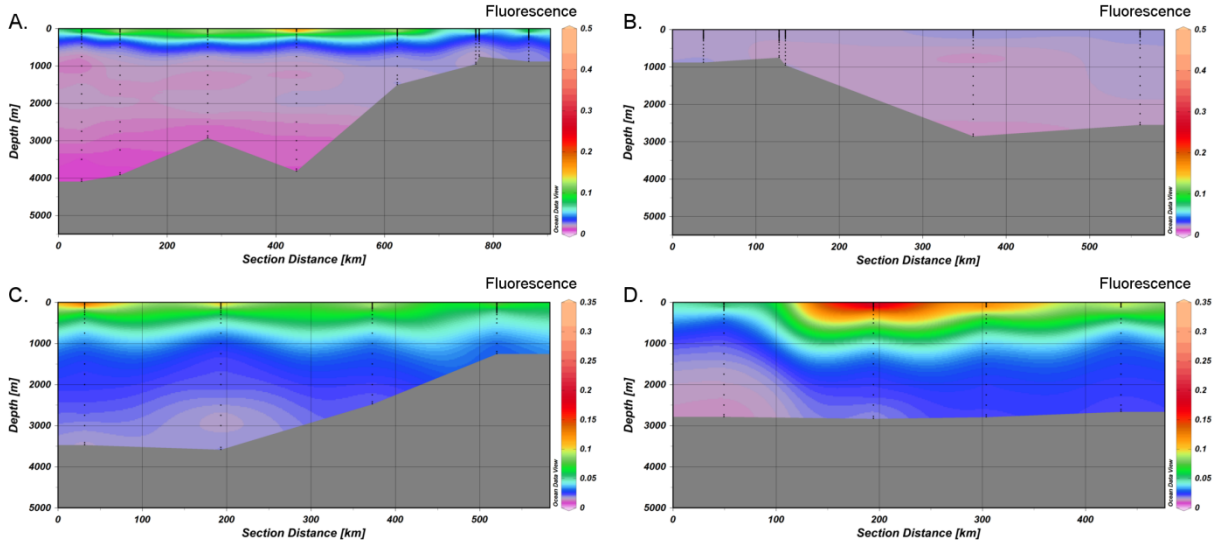

Figure 10. Preliminary fluorescence data for the upper 250 m of the water column from the UCC for cruise 64PE373 in the Black. Note that the color scale may change between graphs. Data: Sven Ober and Frank van Maarseveen

Underway surface data

Figure 11, 12 and 13 show the underway surface seawater data as measured by the ship's Aqua flow system (Chelsea Instruments). The sea surface temperature ranges between 18-30°C with the highest temperatures in the Tyrrhenian Sea (Figure 11). The sea surface salinity varied between 20 and 40 (Figure 12) and the fluorescence varied between 0 and 0.19 (Figure 13).

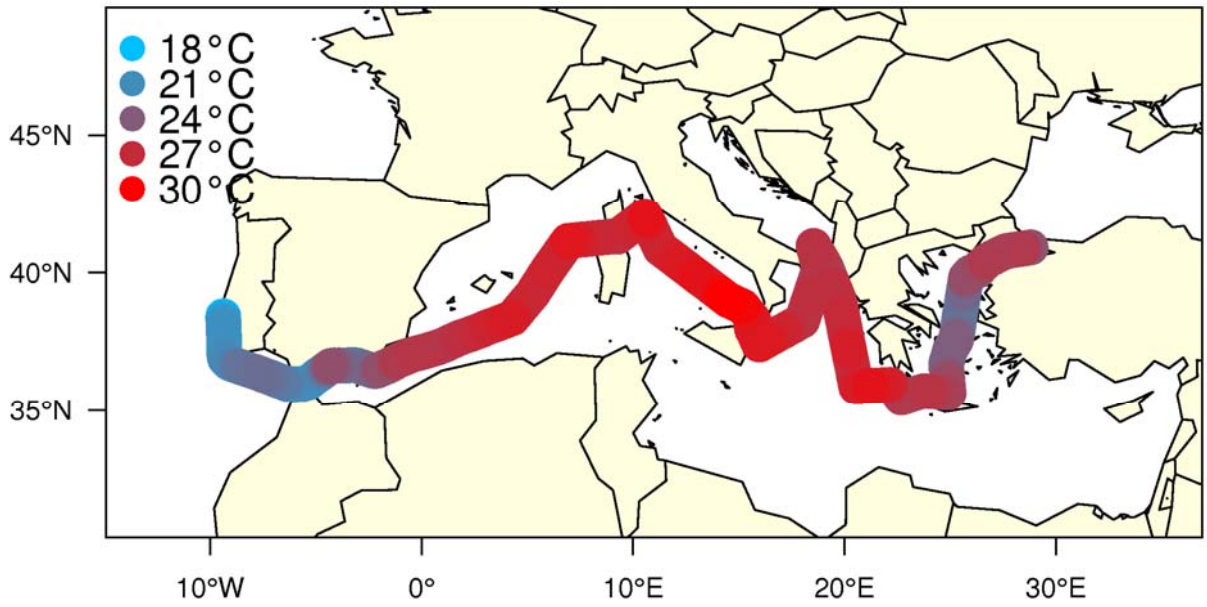

Figure 11. The preliminary sea surface temperature data as measured with the ship's underway system during 64PE374.

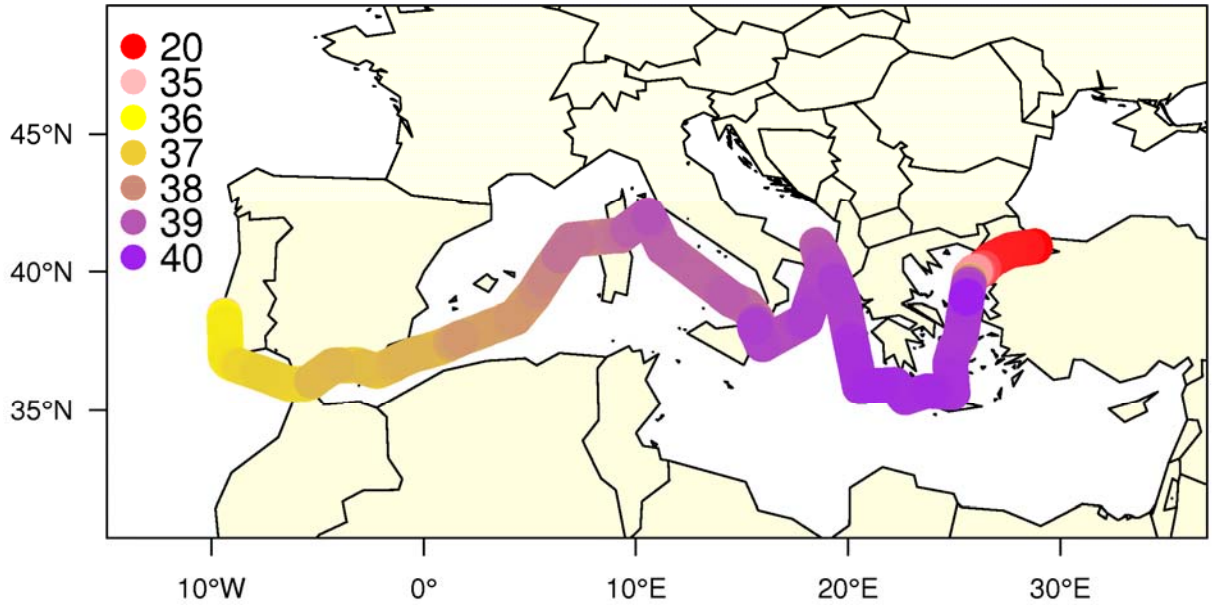

Figure 12. The preliminary sea surface salinity data as measured with the ship's underway system during 64PE374.

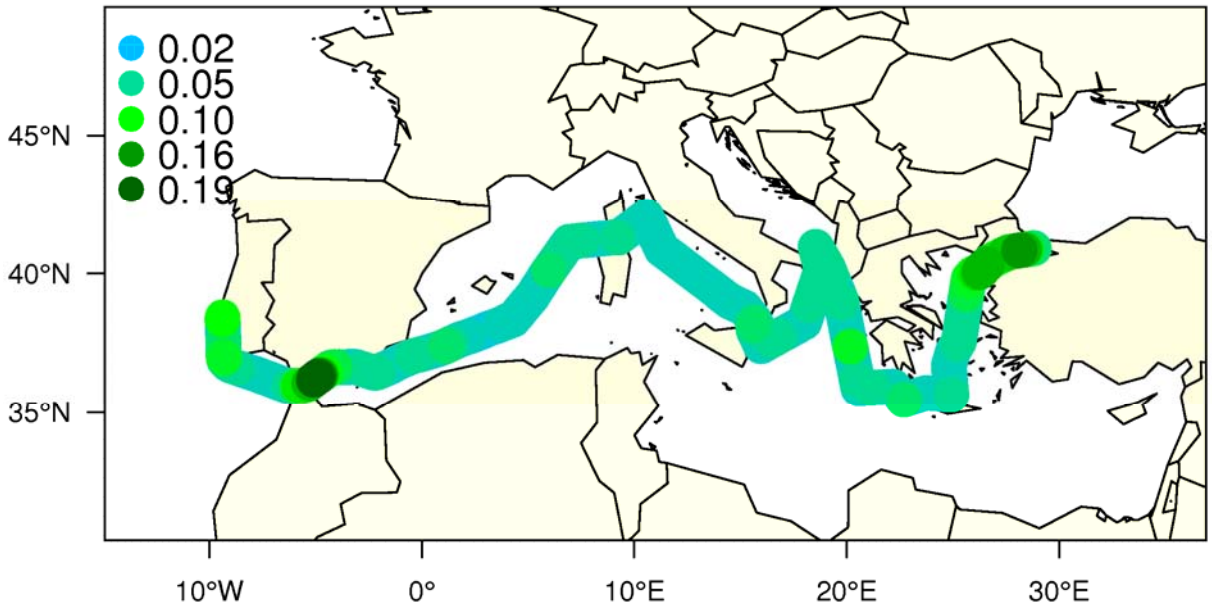

Figure 13. The preliminary sea surface fluorescence data as measured with the ship's underway system during 64PE374.

Description of sample equipment and deployment

We used a system for ultra clean trace metal sampling consisting of an all-titanium frame with 24 sample bottles of 27 L each made of PVDF plastic (abbreviated UCC), see Figure 14. A Kley France winch was used to deploy the UCC to deep Mediterranean waters by a 17.7 mm diameter Kevlar hydrowire with seven independent internal signal/conductor cables (Cousin Trestec S.A.). Sampling of the UCC occurred in a class 100 clean-room container (de Baar et

al., 2008). Filtered samples were directly filtered from the UCC sample bottles under nitrogen pressure using 0.2 µm Sartobran 300 cartridges (Sartorius).

To collect non trace metal clean samples a standard CTD frame of stainless steel was used equipped with 24 water samplers each with a volume of 12 liter manufactured by Ocean Test Equipment. More details about the CTD frames used can be found at page 23.

To collect low Fe surface seawater for use in the laboratory we pumped seawater into a trace metal clean laboratory container using a Teflon diaphragm pump (Almatec A-15, Germany) connected by a braided PVC tubing to a towed fish positioned at approximately 3 m depth alongside the ship. This surface seawater from the fish was filtered in-line using a Sartobran 300 filter capsule (Sartorius) with a 0.2 µm cut-off and subsequently stored in a cubic meter vessel.

Figure 14. The sample equipment used to take trace metal clean and non-trace metal clean water samples and particles during 64PE374.

Concluding

With 19 full depth stations we have completed the third and final leg of the Dutch part of the MedBlack GEOTRACES project aiming to determine the distribution of important trace elements and isotopes throughout the Mediterranean and Black Seas. The objective is to elucidate important biogeochemical processes, sources and sinks that determine the distribution of bio-essential and other trace elements in the Mediterranean Sea and Black Sea. We sampled an extensive set of parameters with direct on board measurement of the trace metals Fe and Al, the CO_2 system, nutrients and the organic speciation of Fe. We also sampled a large set of parameters for the international community including labile Fe, Co and Co speciation, Ag, Cu, Zn, Cd, Mn, Ba, U, Mo, the rare earth elements, the isotopes of Fe, Cu, Zn, Cd, Pb, Cr, Ni, Nd, Si, ^{15}N, ^{18}O, D, coccoliths, POC, particulates and other elements.

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2. General introduction of the Dutch GEOTRACES project in the Mediterranean and Black Sea

Many trace elements and especially iron (Fe), are critical for marine life and as a consequence influence the functioning of ocean ecosystems. Some trace elements are essential, others are toxic pollutants, while some, together with a diverse array of isotopes, are used to assess modern-ocean processes and the role of the ocean in past climate change. Until recently fragmentary data of trace elements and isotopes in the oceans restricted our knowledge of their biogeochemical cycles. GEOTRACES aims to improve our understanding of biogeochemical cycles and large-scale distribution of trace elements and isotopes in the marine environment and establish the sensitivity of these distributions to changing environmental conditions. The objective is to elucidate important biogeochemical processes, sources and sinks that determine the distribution of bio-essential and other trace elements in the Mediterranean Sea and Black Sea. As dust is a main transport pathway of bio-essential trace elements to the surface of the open ocean the heavy Saharan dust impact on the Mediterranean Sea is ideal to investigate the effect of dust on the biogeochemical cycles of trace elements and isotopes. The Black Sea is the largest anoxic basin of the world and forms an ideal natural laboratory to unravel the microbial driven reduction and oxidation reactions of trace elements and isotopes. For example, here results will have major implications for the isotope systematics of Fe and sulphur in ancient deposits such as the Banded Iron Formations that are studied to unravel the redox conditions of the ancient Earth.

GEOTRACES Mediterranean Sea and Black Sea

The Mediterranean Sea is the source of the warm and saline Mediterranean Outflow Water (MOW) which is a significant water mass to the North Atlantic Ocean (van Aken, 2000a; van Aken, 2000b) increasing the salinity of its deep waters (Reid, 1994). The MOW has enhanced concentrations of for example Fe, Al and Ni and may therefore act as a source of trace metals to surrounding North Atlantic water masses (Hydes, 1983; Boyle et al., 1985; Thuróczy et al., 2010; Middag et al., 2012). The Mediterranean Sea is also an ideal environment to study the strong link between the ocean, the atmosphere and the continent (http://www.cybaes.org/gtmed/) and is suspected to be very sensitive to climate change (de Madron et al., 2011). The Mediterranean Sea is one of the greatest receivers of continental dust input in the contemporary ocean and is in the last decade used as a natural laboratory to study the effects of dust deposition on the surface ocean (Quétel et al., 1993; Guerzoni et al., 1999; Bonnet and Guieu, 2006; Wagener et al., 2010; Ternon et al., 2011). This aspect is especially important as dust is the main external source of biological essential elements to the surface waters of the open ocean worldwide (Jickells et al. 2005). In the Mediterranean Sea, the eastern basin is a truly oligotrophic marine ecosystem limited by phosphorus deficiency, and Fe was suggested to stimulate primary production (Krom et al., 1991; Saydam, 1996). In the western basin, low residual concentrations of Fe after biological Fe removal from the water column may lead to changes in species succession or even growth limitation (Sarthou and Jaendel, 2001; Bonnet and Guieu, 2006). In the east and west basins, input of Saharan dust is the main source of Fe and phosphorus to the surface ocean, although in the eastern basin the Nile river may also contribute (Krom et al., 1999; Sarthou and Jaendel, 2001; Markaki et al., 2003). To really understand the coupling between the ocean and the

atmosphere it is necessary to also understand the distribution of TEIs with respect to other natural and anthropogenic sources, cycling and the Mediterranean hydrography.

The Black Sea is a meromictic sea with a strong vertical stratification (permanent halocline) determined by the strong vertical salinity gradient. The corresponding strong density stratification limits the supply of oxygen to the deep waters, making the Black Sea the world's largest anoxic basin and is therefore the reducing end-member of the spectrum of oceanic redox environments. The Black Sea is an ideal natural laboratory to unravel the microbial driven reduction and oxidation reactions of trace metals Fe, Zn, Cu, Cd, Mn and others, and the associated redox cycling of sulfur (S). The classical sequence of redox reactions for oxidation of organic matter exists worldwide in marine sediments and all anoxic basins including the brine basins in the deep East Mediterranean Sea. Yet here in the Black Sea, the complete redox sequence from oxic, to suboxic to anoxic=sulfidic waters can be found and sampled with a unique high vertical resolution over the first ~140 meters depth range (Murray, 1991). This allows sophisticated high resolution sampling of all redox gradients and their intrinsic major changes of concentrations and stable isotope ratio's. The cycling of Mn and Fe in the water column is related to the biogeochemical dynamics of oxygen, nitrogen, sulfur, metals, and organic particles (Lewis and Landing, 1991; Yemenicioglu et al., 2006). The scavenging behavior of manganese and iron in combination with their redox cycling determine the concentrations and distributions of these and possibly other metals like Co, Ni, Cd and Zn in the water column (Tankere et al., 2001). Oxidation of upward diffusing reduced Mn and Fe into the oxic zone leads to precipitation with potentially net incorporation and adsorption of other metals. The distribution of trace metals in the oxic surface layer of the Black Sea may therefore depend on the physical factors leading to upward mixing of reduced Fe and Mn, and further on other sources of TEIs like atmospheric input, rivers e.g. the Danube (Guieu et al., 1998), and the Black Sea hydrography. The Black Sea is also an ideal environment to investigate the expected strong isotope fractionations of notably 56Fe/54Fe due to microbial redox reactions but also Zn, Cu and Cd which precipitate as sulphides, likely resulting in isotope fractionation. We intend to do detailed vertical sampling for 56Fe/54Fe, 66Zn/64Zn, 65Cu/63Cu and 112Cd/110Cd and will invite an expert to also sample for sulfur isotopes. Results will have major implications for the isotope systematics of Fe and S in ancient deposits such as the Banded Iron Formations (BIF) that are studied to unravel the redox conditions of the ancient Earth (Johnson and Beard, 2006; Johnson et al., 2008). In addition, the understanding of all aspects involved in the fractionation of the stable isotopes of bio-essential metals Fe, Cu, Zn and Cd may be crucial in elucidating and quantifying the sources, cycling, fate and impact of those trace metals on marine ecosystems. The hypersaline (salinity up to tenfold regular compared to seawater) anoxic brines in depressions of the seafloor of the East Mediterranean are small features compared to the Black Sea. Yet these Bannock and Tyro Basins are very interesting to unravel the redox chemistry of trace metals (Saager et al., 1993; Schijf et al., 1993) and are awaiting the assessment of stable isotope fractionations at the anoxic brines interface of Fe, Cu, Cd, Zn and Mo (Reitz et al., 2007). At the moment we don't have a complete picture of the biogeochemical cycles that determine the distribution of TEIs in the Mediterranean Sea and Black Sea as for most TEIs data are extremely scarce and fragmentary in both seas, this making interpretation often difficult and speculative (Boyle et al., 1985; Saager et al., 1993; Saydam, 1996; de Baar et al., 2001; Zeri and Voutsinou-Taliadouri, 2003; Statham and Hart, 2005; Bonnet and Guieu, 2006). Increasing the very small available data sets with high resolution full depth transects throughout the Mediterranean Sea and Black Sea would provide

us with the overview to determine for the first time the important sources and processes explaining the distribution of TEIs.

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3. Participants and parameters

3.1. List of participants

1	**Micha Rijkenberg PI**	NIOZ; Biological Oceanography
2	**Loes Gerringa PI**	NIOZ; Biological Oceanography
3	**Karel Bakker**	NIOZ; MRF
4	**Barry Boersen**	NIOZ; MTEC
5	**Johann Bown**	NIOZ; Biological Oceanography
6	**Marie Boyé**	LEMAR IUEM
7	**Damien Cardinal**	UPMC
8	**Nikki Clargo**	NIOZ; Biological Oceanography
9	**Mark Eveleens**	NIOZ; MRF
10	**Raja Ganeshram**	University of Edinburgh
11	**Ejin George**	University of Otago
12	**Ruud Groenewegen**	NIOZ; MRF
13	**Paolo Montagna**	ISMAR, Bologna
14	**Matt Patey**	NOC, Southampton
15	**John Rolison**	University of Otago
16	**Simona Retelletti Brogi**	Istituto di Biofisica, Pisa
17	**Lesley Salt**	NIOZ; Biological Oceanography
18	**Leon Wuis**	NIOZ; MTEC
19	**Eyal Wurgaft**	Hebrew University of Jerusalem

For complete addresses and email see Appendix 2

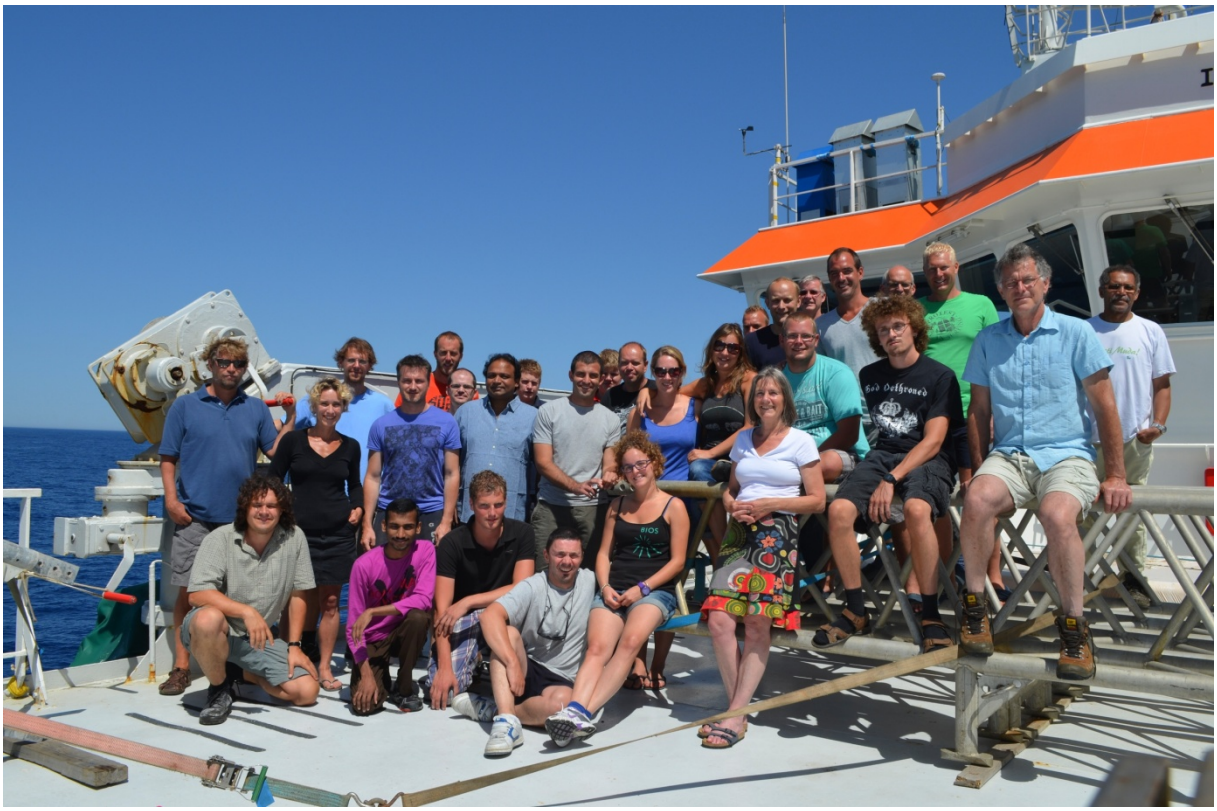

Figure 15. Scientists and crew during 64PE374 on the RV Pelagia in the Mediterranean Sea.

3.2. UCC Sample Team

The following people have been part of the general UCC sampling team in the ultraclean container:

1) Simona Brogi
2) Eyal Wurgaft
3) Damien Cardinal
4) Paolo Montagna
5) Raja Ganeshram
6) Marie Boyé
7) Micha Rijkenberg

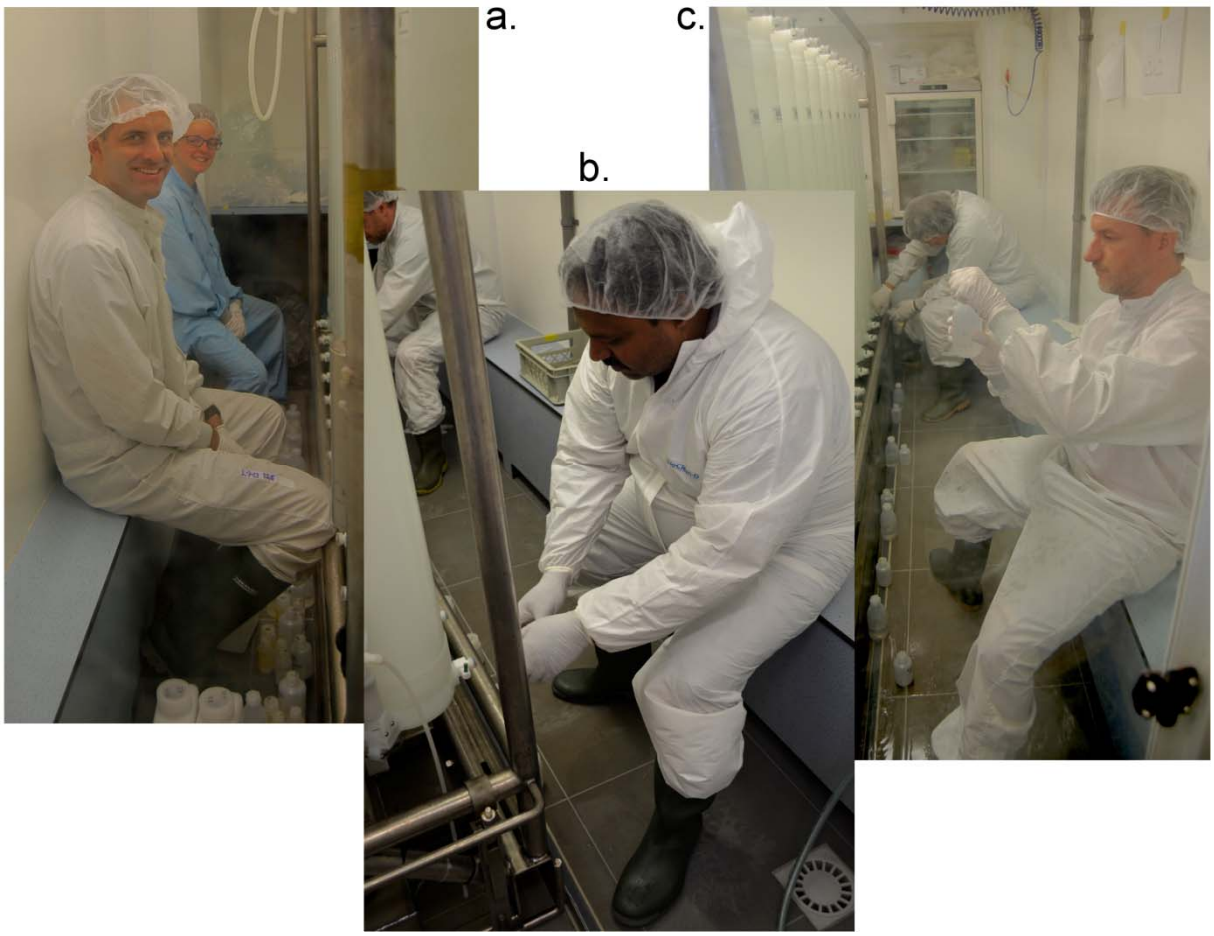

Figure 16. a) Eyal and Simona, b) Raja, c) Paolo and Micha in the ultra clean container (Pictures Damien Cardinal and Micha Rijkenberg).

3 .3. List of parameters

Samples	collected by	responsible for analysis and data
UC CTD (UCC)		
Library metals totals	M. Rijkenberg	P. Laan/M. Rijkenberg/H. de Baar
Library metals dissolved[1]	M. Rijkenberg	R. Middag/P. Laan/ M. Rijkenberg/H. de Baar
Nitrate/Nitrite (µM)	K. Bakker	K. Bakker
Phosphate/Silicate (µM)	K. Bakker	K. Bakker
Nitrate/Nitrite (nM)	M. Patey	M. Patey/E. Achterberg
Phosphate (nM)	M. Patey	M. Patey/E. Achterberg
Dissolved Fe	J. Bown	J. Bown/M. Rijkenberg
Fe ultra filtration	M. Rijkenberg/M. Boyé	J. Bown/M. Rijkenberg
Fe Speciation	L. Gerringa	L. Gerringa
Dissolved Al	E. George/J. Rolison	R. Middag/J. Rolison/E. George
Dissolved Cu	M. Boyé	Waeles/Pernet-Coudrier/Riso
Dissolved Ag	M. Rijkenberg	E. Achterberg
Dissolved Co	M. Boyé	G. Dulaquais/M. Boyé
Co-speciation	M. Boyé	G. Dulaquais/M. Boyé
Cu-speciation	M. Boyé	Waeles/Pernet-Coudrier/Riso
Co, Zn, Cd ultrafiltration	M. Boyé/M. Rijkenberg	G. Dulaquais/M. Boyé
Total dissolvable Co, Zn, Cd	M. Boyé	G. Dulaquais/M. Boyé
Total dissolvable Cu	M. Boyé	Waeles/Pernet-Coudrier/Riso
$^{15}NO_3/N^{18}O_3/^{15}NH_4$	R. Ganeshram	R. Ganeshram
Aerosols (mineral comp)	E. Wurgaft/S. Brogi	J.-B. Stuut
Aerosols (major ions, trace metals)	E. Wurgaft/S. Brogi	A. Baker
Dissolved Mo	L. Gerringa/UCC team	J.-M. Godoy
Dissolved Ba	L. Gerringa/UCC team	J.-M. Godoy
Dissolved U	L. Gerringa/UCC team	J.-M. Godoy
Dissolved ^{18}O	L. Gerringa/UCC team	J.-M. Godoy
Deuterium	L. Gerringa/UCC team	J.-M. Godoy
^{17}O	E. Wurgaft	E. Wurgaft/B. Luz
Dissolved Fe isotopes	J. Rolison	J. Rolison/C. Stirlinger
Dissolved Cd isotopes	J. Rolison	J. Rolison/C. Stirlinger
Dissolved $^{238}U/^{235}U$	J. Rolison	J. Rolison/C. Stirlinger
Pb isotopes	M. Rijkenberg/UCC team	S. Galer/W. Abouchami
Cr isotopes	M. Rijkenberg/UCC team	S. Galer/W. Abouchami
Dissolved Cu isotopes	M. Boyé	O. Rouxel
Dissolved Zn isotopes	J. Rolison	J. Rolison/C. Stirlinger
Ni isotopes	M. Rijkenberg/UCC team	S. Galer/W. Abouchami

Dissolved Si isotopes	D. Cardinal	D. Cardinal
Dissolved Nd isotopes	P. Montagna	P. Montagna/C. Jaendel/M. Frank
REE	P. Montagna	P. Montagna
Humic acids	M. Boyé	Waeles/Pernet-Coudrier/Riso
Coccoliths	M. Boyé	M. Boyé
Coccolith taxonomy	M. Boyé	M. Boyé
POC	M. Boyé	G. Dulaquais/M. Boyé
Particulate Co (other metals, CTD)	M. Boyé	G. Dulaquais/M. Boyé
DOC/CDOM	S. Brogi	C. Santinelli/C. Zeri/D. Hansell
$\Delta^{14}CO_2$ and DOCΔ^{14}C	S. Brogi	D. Repeta
Salinity	R. Groenewegen/M. Eveleens	S. Ober
12L standard CTD		
DIC & Alkalinity	N. Clargo/L. Salt	N. Clargo/L. Salt
Oxygen	N. Clargo/L. Salt	L. Salt/K. Bakker/S. Ober

[1] Rob Middag will use the chelating resin Nobias-chelate PA1 in an off-line pre-concentration manifold with magnetic sector inductively coupled plasma mass spectrometry (ICP-MS) detection for analysis of Y, Cd, La, Pb, Sc, Ti, V, Mn, Fe, Ni, Zn and Ga.

4. Sampling and analyses

4.1. General parameters

4.1.1. The CTD systems

Ruud Groenewegen and Marks Eveleens

Royal Netherlands Institute for Sea Research, Texel, the Netherlands

During the cruise 2 different CTD-systems were deployed.

- An Ultra Clean CTD-system for ultra clean trace metal sampling (23 casts).
- A standard Volume CTD for almost all the other sampling like CO_2, dissolved oxygen (DO) and phytoplankton (19 casts)

These systems are briefly described below.

The Ultra Clean CTD-system (UCC)
The system consists of 3 major modules:

- A box-shaped titanium CTD frame with 24 sampling bottles made of PVDF and titanium (Figure 17)
- A clean air container for contamination-free (sub)sampling
- A special deep sea winch with an iron-free Super Aramid CTD-cable

To avoid contamination, the frame of the UCC-system is made of titanium and all the electronic pressure housings and other parts are made of titanium or clean plastics like Teflon, PVDF or POM. The frame can be parked and 'seasave' secured inside the clean air container. Prior to a cast the frame is prepared inside that container and transported to the CTD-launching spot using a custom made aluminium pallet and a longbedded forklift. After the cast the frame can be returned to the clean air container within minutes avoiding contamination of the equipment with grease, rust or smoke particles from the ship. After closing of the container the air treatment system starts to clean the air using HEPA-filters, meeting class 100 clean-room specifications after 15 minutes, upon which sampling can start.

The electronic system consists of a SBE9plus underwaterunit, a SBE11plusV2 deckunit, a NIOZ developed multivalve bottle-controller, a SBE3plus thermometer, a SBE4 conductivity sensor, a SBE5T underwaterpump, a SBE43 dissolved oxygen sensor, a Chelsea Aquatracka MKIII fluorometer, a Wetlabs C-Star transmissiometer (25 cm, deep, red) and a Satlantic PAR-sensor for underwater-PAR.

For Ultra Clean watersampling 24 samplers (24 liter each) are applied. These samplers are produced by NIOZ and are made of PVDF and titanium. Due to the butterfly-type closure on both ends of the sampler the flow-through is excellent. The samplers are controlled with a hydraulic system. The heart of the sampling system is the NIOZ developed Multivalve.

For bottom-detection 2 devices are installed: A Benthos PSA-916 altimeter and a bottom switch with a weight on a 10 meter rope. The SBE11+ has a NMEA interface for navigational data and a voltage input for a surface-PAR sensor which is mounted on the foredeck. On the logging computer Seasoft for Windows is installed (Seasave V7.20 and SBE Data Processing V7.20).

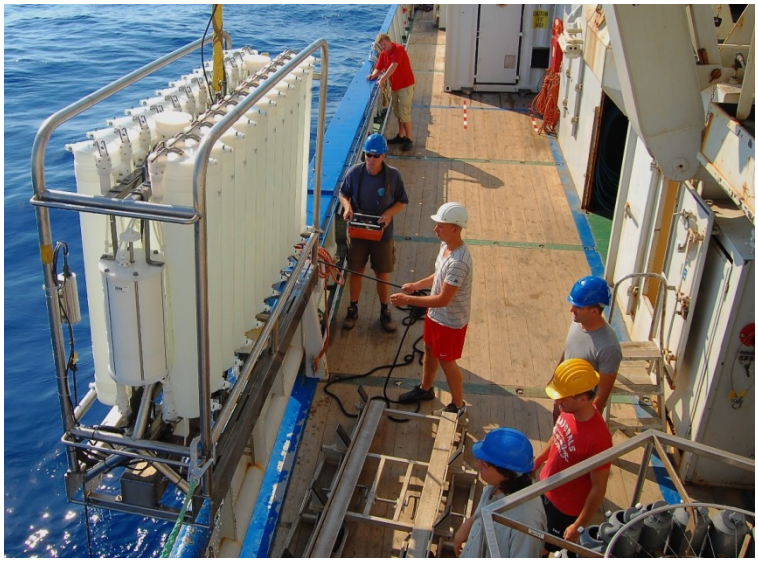

Figure 17. Recovery of the UCC CTD (Picture Damien Cardinal).

The standard CTD-system (ST-CTD)

The CTD-system consists of a SBE9plus underwaterunit, a SBE11plusV2 deckunit, a SBE32 caroussel, a SBE3plus thermometer, a SBE4 conductivity sensor, a SBE5T underwaterpump, a SBE43 dissolved oxygen sensor, a Chelsea Aquatracka MKIII fluorometer, a Wetlabs C-Star transmissiometer (25 cm, deep, red), a Satlantic logaritmic PAR-sensor for underwater PAR and a Satlantic lineair PAR-sensor for deck reference.

For watersampling 24 watersamplers each with a volume of 12 liters manufactured by Ocean Test Equipment are applied. These 12-liter samplers are equipped with an internal stainless steel spring (Figure 18).

For bottom detection 2 devices are installed: A Benthos PSA-916 altimeter and a bottom switch with a weight on a 10 meter rope. The SBE11+ has a NMEA interface for navigational data. On the logging computer Seasoft for Windows is installed (Seasave V7.20 and SBE Data Processing V7.20).

For in situ calibration of the profiling thermometer (SBE3) a high-accuracy reference-thermometer (SBE35) was installed for all of the casts.

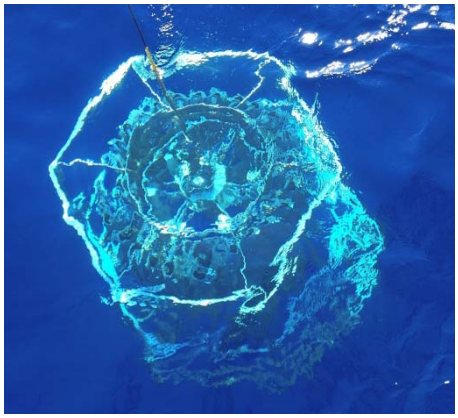

Figure 18. Deployment of the standard CTD (Picture Damien Cardinal).

Results

A total of 42 casts on were carried out and in spite of frequent communication problems with the watersampler on the UCC frame, all samplers got filled and verified at their appropiate depths time and again, with one exception only and that cast was rejected in total (UCC cast station 16). During the cruise, while trying to diagnose the communication problem, a few items were swapped. The problem appeared to have multiple causes and only got fully solved 2 stations before finishing the cruise. Meanwhile other problems had developed in both thermometer and conductivity read-out of the UCC-CTD, leading to pressure related drop-out. For all stations an uncorrupted CTD-profile from the standard CTD is always available.

For in situ calibrations of the profiling CTD-thermometers (type SBE-3) a Seabird reference-thermometer (type SBE35) was used. For the calibration of the C-sensor of the standard-CTD, salinity-samples were tapped on board for analysis back home. After that, the now preliminary postprocessing of the data will be corrected. Most of the casts of the standard-CTD, samples were tapped for Winkler titrations in order to calibrate the DO-sensors. With the titration results the DO-sensors of both CTD-systems will be calibrated as good as possible.

4.1.2. Dissolved oxygen

Lesley Salt and Nikki Clargo

Royal Netherlands Institute for Sea Research, Texel, the Netherlands

Dissolved oxygen was measured from three depths from all 19 of the regular 12L CTD casts to check the calibration of the oxygen sensor fixed to the CTD frame itself. A refined protocol of the spectrophotometric Winkler approach was conducted, where a continuous-flow analyzer is coupled with a custom-made autosampler holding up to 30 oxygen bottles (Reinthaler et al. 2006). The time required for analysis is 2 min per sample, and the precision is 0.05% at ~200 mmol O_2 m^{-3}. Dissolved oxygen was analysed in a thermostated lab container equipped with a Traacs 880 auto-analyser spectrophotometer measuring the intense yellow colour of the samples produced from the formation of iodine after the addition of acid. All measurements were calibrated with standards diluted in oxygen saturated surface sea water in the salinity range of the Atlantic Ocean stations.

Theory and Method

For the measurement of dissolved oxygen in the water column a refined protocol of the spectrophotometric Winkler approach (Winkler, 1888) was conducted in combination with a Traacs auto-analyser spectrophotometer. This method is based on the following redox-reactions:

$$2\ Mn^{2+} + 4\ OH^- \rightarrow 2\ Mn(OH)_2 \quad (1)$$

$$2\ Mn(OH)_2 + O_2 \rightarrow 2\ MnO(OH)_2 \quad (2)$$

$$2\ MnO(OH)_2 + 8\ H^+ + 6\ I^- \rightarrow 2\ Mn^{2+} + 2\ I_3^- + 6\ H_2O \quad (3)$$

$$2\ I_3^- + 2\ S_2O_3^{2-} \rightarrow 6\ I^- + S_4O_6^{2-} \quad (4)$$

In the Winkler method, manganese chloride is added to a known amount of seawater, followed by the addition of an alkaline sodium hydroxide-potassium iodide solution. The Mn^{2+} is oxidized by the dissolved oxygen to higher oxidation states resulting in a manganous hydroxide ($MnO(OH)_2$) precipitate in the water and forms a hydrated tetravalent oxide of manganese. Upon acidification, the manganese hydroxides dissolve to reduce the manganese back to the Mn^{2+} form and the tetravalent manganese acts as an oxidizing agent, which liberates iodine in the form of I_3^- ions from the iodide ions, which has an intense yellow colour. The iodine is equivalent to the dissolved oxygen in seawater and present as free iodine (I_2) and tri-iodide (I_3^-). The color of the sample is determined by the light transmission through the sample-bottle with a spectrophotometer and is based on measuring the absorbance of the colored I_2 and I_3^-. The concentration of oxygen is then calculated by comparing the absorbance in a sample against standards of known oxygen content made from potassium iodate (KIO_3) solutions.

Equipment

For the dissolved oxygen analysis, a custom-made autosampler was used in combination with a standard Technicon TRAACS 800 autoanalyzer (Bran + Luebbe, Germany). The

autosampler consists of an electric motor, a pneumatic sampling arm driven by compressed air at ~5 bar, and a magnetic stirrer. The parameters were adjusted to 30-s flushing with wash solution, followed by 3 picks of a sample and 90-s aspiration of the sample. The platform holds up to 30 bottles, and the autosampler is completely independent from the TRAACS analyzer and its software. The TRAACS analyzer was equipped with a standard tungsten filament lamp and a fixed band pass filter of 460 ± 10 nm. The flow cell had a volume of 7.85 mm^3, and the flow rate was set to ~1 cm^3 min^{-1} via the internal peristaltic pump. To maintain a stable temperature in the flow cell, a heat exchange element was installed in front of the cuvette. The analyzer was controlled via the commercial TRAACS analysis software (AACE version 5.40 for Windows).

Chemicals

The common Winkler reagents were used to determine oxygen concentrations:
Reagent (A): $MnCl_2$; Manganese Chloride ($MnCl_2 \cdot 4H_2O$; 600 g dm^{-3}; 3 mol L^{-1})
Reagent (B): KI/NaOH; Alkaline iodide reagent (NaOH; 250 g dm^{-3}; 6 mol L^{-1} + KI; 350 g dm^{-3}; 2 mol L^{-1})
Reagent (C): $5NH_2SO_4$; Sulfuric acid (H_2SO_4; 10 mol L^{-1})

After preparation, the reagent-grade chemicals were filtered through Whatman GF/F filters and subsequently stored in polycarbonate bottles at ~20°C in the dark. The standard stock solution was prepared with Potassium Iodate (KIO_3) (Malinckrodt Baker; primary standard). KIO_3 was dried at 180°C for 6 h, and 2.5g KIO_3 was dissolved in 250ml ultrapure Milli-Q water. Thus, 1ml KIO_3 stock solution is equivalent to 75.30 mmol O_2 L^{-1}. The prepared stock solution was divided into small 50 ml polycarbonate bottles and stored in a chamber with 100% humidity to prevent evaporation of water and therefore an increase in the concentration of the stock solution over long storage periods.

Glass bottles

Custom-made oxygen bottles made from borosilicate glass with a nominal volume in the range of 116 to 122ml were calibrated to the mm^3 level. Each borosilicate glass bottle and the corresponding ground-glass stopper were engraved with a unique number for later identification of the exact volume. A set of these bottles was used to prepare the calibration standards. In the analysis software of the instrument, we apply a single volume-correction factor calculated from the mean of the volume class, resulting in the automatic output of final oxygen concentrations.

Sampling

Samples of seawater were obtained in duplicate from the CTD sampler from only three depths as a calibration for the oxygen sensor fixed to the CTD frame itself (Figure 19). Seawater was siphoned into the 120 ml oxygen bottles with Tygon tubing overflowing each bottle by at least 3 times its volume and the first samples to be sampled from the CTD. The oxygen content in the bottle was fixed as quickly as possible with 1 ml reagent A ($MnCl_2$), followed by 2 ml reagent B (KI/NaOH), both added under the shoulder of the bottle with high-precision dispensers (Fortuna Optifix basic; precision ± 0.1%). After adding the reagents, the bottles were stoppered and shaken vigorously for approximately 20 sec. to mix the chemicals. The stoppering of the bottles were done as quickly as possible to prevent contamination of undersaturated samples by atmospheric oxygen and an elastic band ensured that the stopper remained well in place. The bottles were stored immersed in water baths (kept at in situ

container temperature) to avoid drying of the stopper seal. After approximately 20 mins, the fixed bottles were shaken again to ensure complete reaction of the chemicals. Samples need to be stored under water for at least 2 hours before measuring. Before starting the measurements on the TRAACS system, 1ml of reagent (C) (5NHCl) was added to the fixed samples. Subsequently, a small magnetic stirring flea was introduced carefully, and the bottle openings were covered with parafilm to avoid loss of volatile compounds. The bottles were immediately covered with dark plastic cylinders shielding ambient light as iodine is light sensitive. The samples were gently stirred for a few seconds with an external magnetic stirrer (Metrohm) until the precipitate in the bottles was dissolved. Finally, the bottles were placed on the autosampler. Before aspiration of the sample into the flow-through analyzer, the sample was agitated again with the built-in magnetic stirrer of the auto-sampler to ensure complete mixing of the solution, thereby preventing chemical stratification.

Calibration and Measuring Procedure

Instrument calibration involves the measurement of the baseline or wash solution, a primer, instrument calibration standards, and sensitivity drift standards. For the wash solution and standards used during work at sea, particle-poor oxygen saturated seawater was collected into an 20L polycarbonate carboy and acclimatized at 20°C. For the instrument calibration standards and the primer, seawater was poured into oxygen bottles with known volume. Subsequently, reagents A (1 ml), B (2 ml), and C (1 ml) were added in reverse order with the high-precision dispensers. After the addition of each reagent, the bottles were stoppered and vigorously shaken. Finally, the KIO_3 standard solution was added with highly accurate adjustable volume electronic pipettes. After a magnetic stirring flea was inserted into a bottle, the bottle was immediately covered with parafilm and a dark plastic cylinder. The correlation coefficient of the calibration line was never less than 1.000. The primer is equal to the highest standard and is used to adjust the baseline and gain setting of the photomultiplier to prevent the sample peaks from going off scale. Generally, calibration was done in the range of expected oxygen concentrations. For flow-through systems, it is necessary to provide a low concentration marker or baseline to separate consecutive peaks. To minimize carryover effects between the baseline and the samples, the wash solution was adjusted to an oxygen concentration slightly lower than the expected lowest value in the samples. The baseline is measured at the start and the end of an analytical run to correct for baseline drift if necessary. To correct for changes in the sensitivity of the photomultiplier (e.g., due to slight temperature variations), sensitivity drift standards were prepared with an O_2 concentration between the highest and lowest sample in the batch. The drift standards were placed after the instrument calibration standards, and at the end of the run. Both wash solution and sensitivity drift standards were prepared similarly to the calibration standards. A conventional blank is not required for calibration because standards and references include all the chemicals also used for regular samples. All preparations and measurements were done in the temperature controlled container set at 20°C. The calibration standards were diluted from the 71.320 mmol L^{-1} stock solution and were freshly prepared. Duplicate samples were measured from each station to control both the sampling procedure and the reproducibility of the spectrophotometer. The standard deviation of differences between duplicate samples was 0.33 μmol L^{-1}.

References

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Figure 19. Karel and Nikki taking oxygen samples from the standard 12L CTD (Pictures Damien Cardinal).

4.1.3. Nutrients

Karel Bakker[1] and Matthew Patey[2]

[1]Royal Netherlands Institute for Sea Research, Texel, The Netherlands
[2]National Oceanography Centre Southampton, United Kingdom

Introduction
Nutrient measurements were made on board by two separate systems and operators (Figure 20).
1) A Seal QuAAtro, gas-segmented continuous flow auto analyser was operated in an air-conditioned lab-container by Karel Bakker (NIOZ). Four channels were measured simultaneously: phosphate, silicate, nitrate and nitrite together, and nitrite separately. Samples were taken from all bottles from both the Ultra Clean CTD (UCC) and normal CTD rosette at each station. The sample rate was set at 60 samples per hour, measuring 950 samples during the cruise.
2) An in-house built gas-segmented continuous flow auto analyser, operated by Matt Patey (NOCS) in the chemistry laboratory. This system was used to measure surface samples (typically down to 500 m depth) from the UCC rosette. Two channels were measured simultaneously: nitrate and nitrite together, and phosphate. This system was adapted with a long path-length (2 metres) liquid waveguide capillary flow cell (LWCC) to enable very low detection limits (ca 0.5 nmol /L). Samples were measured at a rate of 15 per hour, with a total of approximately 270 samples measured during the cruise (Patey et al. 2008, 2010).

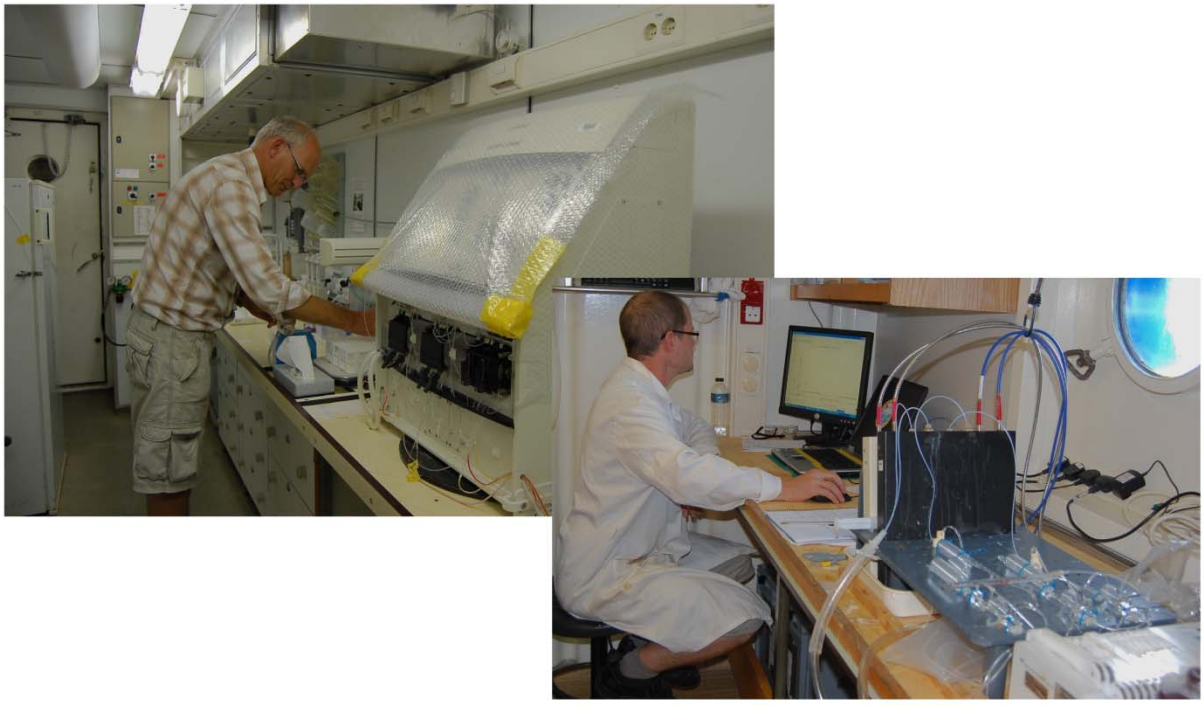

Figure 20. Karel measuring micromolar nutrients in the nutrient container and Matt measuring nanomolar nutrients in the chemistry lab on RV Pelagia (Pictures Damien Cardinal).

Equipment and Methods

From this point onwards, the QuAAtro four-channel analyser will be referred to as the micromolar system and the customised two-channel analyser with LWCC flow cells will be referred to as the nanomolar system.

The colorimetric methods used:

Phosphate:

Ortho-phosphate is measured by formation of a blue reduced Molybdophosphate-complex at pH 0.9-1.1. Potassium Antimonyltartrate used as the catalyst and ascorbic acid as a reducing agent. The absorbency is measured at 880nm (micromolar) and 700 nm (nanomolar system).
Described by J.Murphy and J.Riley, 1962. Analytica Chim.Acta

Silicate:

Measured as a blue reduced Silicomolybdenium-complex at 800nm.
Ascorbic acid is used as reducing agent and oxalic acid is used to prevent interference of phosphate.
Described by Strickland and Parsons, 1972. A practical handbook of sea water analysis.

Nitrite:

Diazotation of nitrite with sulfanylamide and N-(1-naphtyl)-ethylene diammonium dichloride to form a pink dye measured at 550nm.

Nitrate and Nitrite:

Nitrate is first reduced in a copperized cadmium-coil using imidazole as buffer and is then measured as nitrite at 550nm (micromolar) and 540 nm with reference correction at 700 nm (nanomolar).
Described by Grasshof, 1983. Seawater M methods practical handbook Weinheimverlag.

Sample handling

For the micromolar system, the samples were collected in 100ml high-density polyethylene sample bottles, taken directly from the CTD-rosette bottles. The samples were kept cool and dark stored in a refrigerator and analysed typically within 8 hours and 12 hours as a maximum. Analyses were carried out using high-density polyethylene "pony-vials" with a volume of 6 ml as sample cups. For duplicate analysis purposes in-between runs, the deepest sample at every CTD-station was capped in a pony-vial to be measured for a second time in the next run.

With the nanomolar system, samples were collected in 60 ml low-density polyethylene bottles, taken directly from the UCC rosette bottles. Prior to sampling, bottles were acidified with 1 mL concentrated HCl (analytical reagent grade) to prevent bacterial activity. Samples were stored in the dark in a refrigerator and analysed within 12 hours.

Calibration and Standards

Micromolar system:

Nutrient primary stock standards were prepared at the lab home by weighing nutrient salts p.a. in de-ionised water. All standards are kept in a so-called 100% humidity box at lab temperature to prevent any concentration change by evaporation.

The calibration standards were prepared daily by diluting the separate stock standards, using three electronic pipettes, into four volumetric 100ml PP flasks (pre-calibrated at the lab) filled with low nutrient sea water LNSW. The background values of the LNSW were measured on board and added to the calibration values.

Nanomolar system:
Stock standards (ca. 1 mmol/L) were prepared on the ship from pre-weighed dried (60C for 3 hours) NaNO2, KNO3 and KH2PO4. Calibration standards were prepared daily by diluting the separate stock standards into seven 100 ml volumetric flasks filled with low nutrient sea water. Background values of the LNSW were measured every day and added to the calibration values.

Cross-check of stock standards:
Both sets of stock standards were compared on both machines. Measured values were in agreement to within +/- 1%.

Cocktail standard:
This standard acts as a lab reference and its use is described under "quality control". It is made in the lab containing a mixture of phosphate, silicate and nitrate in demineralised water containing 40mg Hg2Cl2 per litre as a preservative. Every time it was used it was diluted 500 times (micromolar) or 10,000 times (nanomolar) with the same pipette, and the same volumetric flask. And measured as an internal control on the performance of the measurements and its number for the different components monitored over the runs.

Quality Control
Our standards have already be proven by inter calibration exercises like ICES and Quasimeme, and last years the RMNS exercise organised from Michio Aoyama MRI/Japan, to be within the best obtainable limits to the mean of the better laboratories. To gain some accuracy the Cocktail standard is monitored now since 1997, showing in-between runs reproducibility better than 1.0 % (Table 1).

Table 1) Measurements of the cocktails standard during cruise 64PE373. Reported are the values as measured after a 500 x dilution (micromolar measurements) and a 10,000 x dilution (nanomolar measurements).

	average uM/l	**S.D. uM/l**	**C.v.(%)**	**n**
micromolar (500x dilution):				
PO4	**0.457**	**0.004**	**0.93**	**57**
SiO2	**7.18**	**0.04**	**0.56**	**57**
NO3	**6.91**	**0.04**	**0.55**	**57**
nanomolar (10000x dilution):				
PO4	**0.0214**	**0.0010**	**4.9**	**17**
NO3+NO2	**0.3538**	**0.0073**	**2.1**	**17**

The advantage of a cocktail standard is like using a reference standard with three nutrients mixed in one bulk, giving each run a good overview of the machine's output. It also gives you a tool to normalise data from run to run for oceanographic purpose from station to station to produce transect plots.

Others have reported the use of a real reference sample supplied from deep water (2000m) but this might not be stable over a period longer than two weeks.

Statistics

The tables 2 and 3 give the mean detection limits for the micromolar and nanomolar systems and table 4 gives the precision of a single run for the micromolar system.

Table 2) **Mean Detection Limits** calculated (EPA norm) as 2.82 x S.D. of 2% (from the full range) spiked samples (**n=10**) for the micromolar system.

	M.D.L uM/l	Used ranges uM/l	Added to LNSW
PO4	**0.003**	**1.00**	**0.02 uM**
SiO2	**0.008**	**20.0**	**0.40 uM**
NO3+NO2	**0.017**	**15.0**	**0.31 uM**
NO2	**0.012**	**0.50**	**0.01 uM**

Table 3) **Mean detection limits** calculated as 2.82 x S.D of repeated sampling of LNSW (n=10) for the nanomolar system.

	M.D.L (nmol/l)	Measured LNSW concentration (nmol/l)
PO4	**0.7**	**3.1**
NO3+NO2	**1.9**	**24.0**

Table 4) **Precision of a single run:** 5 sample bottles at two depth levels with coefficient of variation for the micromolar system.

	level I uM/l	SD dev. uM/l	C.v. %	level II uM/l	SD dev. uM/l	C.v. %
PO4	**0.033**	**0.002**	**6.6**	**0.260**	**0.001**	**0.3**
SiO2	**0.98**	**0.003**	**0.3**	**3.21**	**0.01**	**0.3**
NO3+NO2	**0.05**	**0.001**	**2.4**	**6.31**	**0.02**	**0.3**
NO2	**0.020**	**0.001**	**7.1**	**0.037**	**0.001**	**3.5**

Cross-runs statistics

To obtain cross-run statistical values, analyses were carried out twice on the same sample from the bottle closed at the bottom layer in the first run, and in the consecutive run. This gave the possibility to estimate the precision from station to station in a horizontal way (Bottom bottle #1 from the two CTD casts at 18 Stations were analysed again in the next run). It's well known that the reproducibility in one calibrated run for an auto analyser is much better than measurements made across several runs, with each run having its own calibration settings. Analysis of these (cross runs) duplicate samples shows that the absolute differences for 35 cross run duplicates (Table 5).

Table 5) The absolute differences for 35 cross-run duplicates measured with the micromolar system.

	SD uM/l	at average level uM/l	C.V. %
PO4	**0.001**	**(0.237)**	**0.45**
SiO2	**0.013**	**(7.29)**	**0.18**
NO3+NO2	**0.002**	**(5.81)**	**0.04**
NO2	**0.003**	**(0.030)**	**8.54**

Accuracy

To gain accuracy this cruise, reference material for nutrients were measured parallel to the CTD samples all at **22°C** containing stable values for PO4, SiO2 and NO3 and NO2. Reference Material for Nutrients in Seawater (RMNS) produced by KANSO lot BY (low nutrient concentrations) (Table 6) and lot BU (comparable deep Med waters) (Table 7 and 8) were used.

Table 6) Results for the measurement of RMNS lot BY (low nutrient concentrations) with the micromolar system.

	RMNS BY uM/l	SD uM/l	
PO4	**0.041**	**0.008**	**(n=20)**
SiO2	**1.698**	**0.014**	**(n=20)**
NO3+NO2	**0.087**	**0.009**	**(n=20)**
NO2	**0.029**	**0.002**	**(n=20)**

Table 7) Results for the measurement of RMNS lot BU (high nutrient concentrations) with the micromolar system.

	RMNS BU uM/l	SD uM/l	
PO4	**0.359**	**0.006**	**(n=22)**
SiO2	**20.817**	**0.084**	**(n=22)**
NO3+NO2	**4.169**	**0.020**	**(n=22)**
NO2	**0.089**	**0.003**	**(n=22)**

Table 8) Results for the measurement of RMNS lot BY (low nutrient concentrations) with the nanomolar system.

	RMNS BY nmol/l	SD nmol/l	
PO4	**30.9**	**1.0**	**(n=18)**
NO3+NO2	**59.9**	**3.4**	**(n=20)**

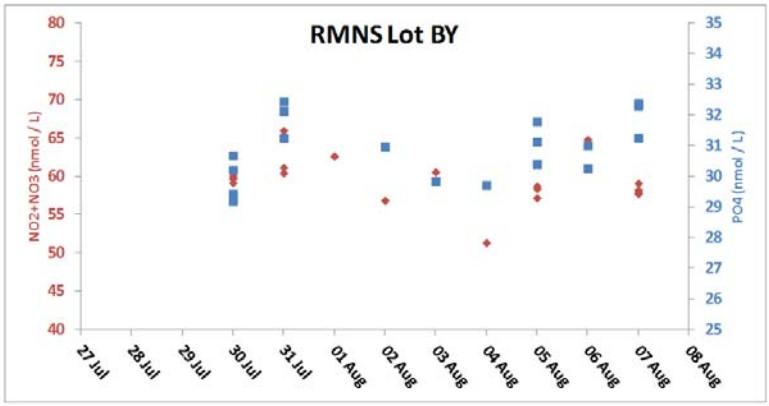

Figure 21. The concentrations PO4 and NO3+NO2 measured in RMNS lot BY (low nutrient concentrations) throughout the cruise with the nanomolar system.

Problems during the cruise

Looking at the (micromolar) cross run duplicates precision no corrections are necessary to be made except for one run with data for the CTD casts on station 10 where some drops in baseline on the NO2 channel could not be automatic corrected with the software. Correction for NO2 on this Station 10 will be done manually at NIOZ afterwards from a printed chart containing all peaks involved.

Post-cruise evaluation

For the nanomolar system further recalibration of the data is required to obtain the final dataset. Furthermore, using the repeated measurements of the reference material it may be possible to correct for shifts in the baseline, particularly for nitrate+nitrite.

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4.2. Sampling and analysis of key parameters

A. Metals and isotopes

4.2.A.1. Dissolved Fe

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Introduction
The Mediterranean Sea is an oligotrophic semi-enclosed sea which is characterized by a strong stratification during summer. Therefore, at this time of the year, nutrients and trace nutrients supply to surface waters might come from the atmosphere, riverine inputs, and lateral advection from the continental slope or islands shelves. Previous studies showed that atmospheric deposition is the predominant source for trace elements for surface Mediterranean waters (Guieu et al., 2010 and 2013) and that riverine inputs can be locally significant but are not thought to impact offshore sites such as the Levantine Sea. Iron can limit phytoplankton growth in HNLC (High Nutrient Low Chlorophyll) areas (Fitzwater and Martin, 1988) and can also acts as a nutrient co-factor for the nitrogenase enzyme in diazotrophic microorganisms and may influence nitrogen fixation in oligotrophic oceans (Falkowski, 1997; Gruber and Sarmiento, 1997). Investigation of the iron biogeochemical cycle in the Mediterranean Sea might bring new insights to our understanding of iron sources and sinks in different Mediterranean Sea basins and will also help to assess iron impacts on photosynthetics organisms in one of the most oligotrophic oceanic area in the world.

Work at sea
For 18 stations (24 depths from surface to bottom), dissolved iron (DFe) concentrations were measured directly on board by an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998 (Figure 22). Additionally, for some selected stations, Fe filtered through 0.02µm size fraction (Sartorius, Virosart CPV capsule) was also determined on board using FIA. Unfiltered samples (12 depths from surface to bottom) from all stations were acidified and stored to determine the total dissolvable Fe concentrations at the NIOZ laboratory after 12 months of dissolution.

Method
Filtered (0.2µm Sartobran 300 filter (Sartorius)) and acidified (pH 1.8, 2ml/L 12M Baseline grade Seastar HCl) seawater samples were concentrated on a column containing aminodiacetid acid (IDA). This material binds only transition metals and not the interfering salts. After washing the column with ultrapure water, the column is eluted with diluted hydrochloric acid and injected in a reaction loop where it is mixed with luminol, peroxide and ammonium. The oxidation of luminol with peroxide is catalyzed by iron and a blue light is produced and detected with a photon counter. The amount of iron is calculated using a standard calibration line, where a known amount of iron is added to low iron containing seawater. Using this calibration line a number of counts per nM iron is obtained. Samples were analyzed in duplicate and average DFe concentrations and standard deviations are given.

The standard deviation varied between 0% and 31% (the latter being exceptional), but was on average 1.3% and generally < 5% in samples with DFe concentrations higher than 0.1nM. Since samples containing less than 0.06nM DFe values are near the detection limit of the system; the standard deviation of these measurements were higher than the average value. The average blank was determined at 0.017nM and was defined as the intercept of a low iron sample loaded for 5, 10 and 20 seconds and measured daily. The average limit of detection was determined at 4.4 pM and was defined as the mean of the daily defined 3*standard deviation of the blank sample loaded for 10 seconds. To better understand the day to day variation a sample was measured at least 24h later. The differences between these measurements were in the order of 1-20%, while the largest differences were measured in samples with low DFe concentrations.

To apply a correction for day to day variation a so-called lab standard (sample acidified for more than 6 months) was measured daily. All data will be corrected for the mean average of this value after the cruise and all data presented so far is uncorrected for this day to day variation. The consistency of the FIA system over the course of the day was verified using a drift standard. Drift has been observed and seemed to be variable from day to day and in the order of 1-15%. All data will be corrected for this daily drift after the cruise and all results so far are not corrected.

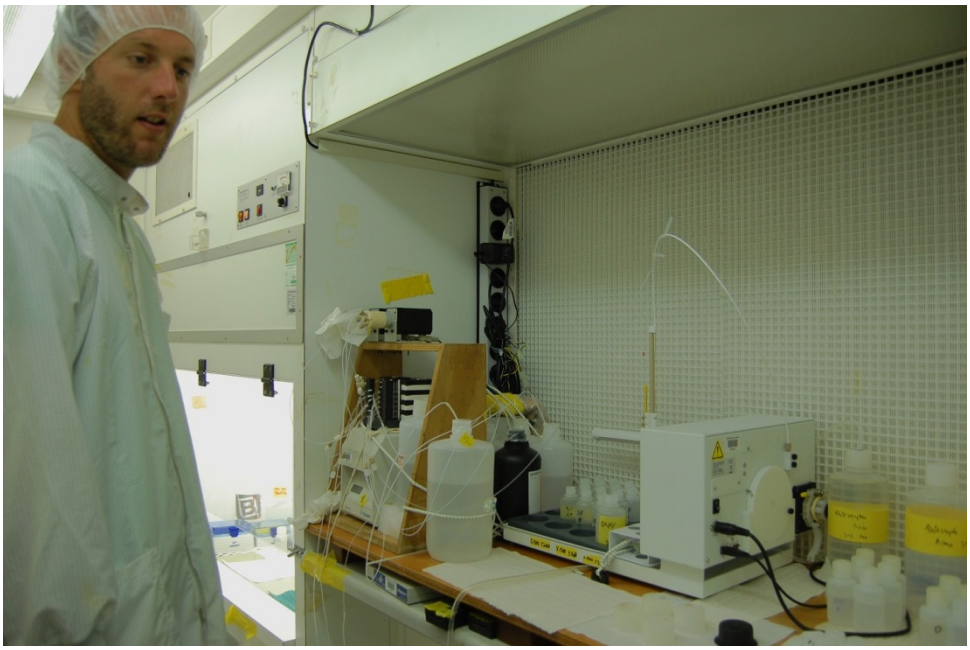

Figure 22) Johann in front of the flow injection analysis system for measuring DFe (Picture Damien Cardinal).

Results

Concentrations of DFe measured during the 64PE374 cruise ranged from 0.191 ± 0.003 nM close to the bottom of station 13 (Tyrrhenian Sea) up to 12.37 ± 0.086 nM the surface waters of station 5 in the Ionian Sea. Figure 23 shows an example of a depth profile of DFe.

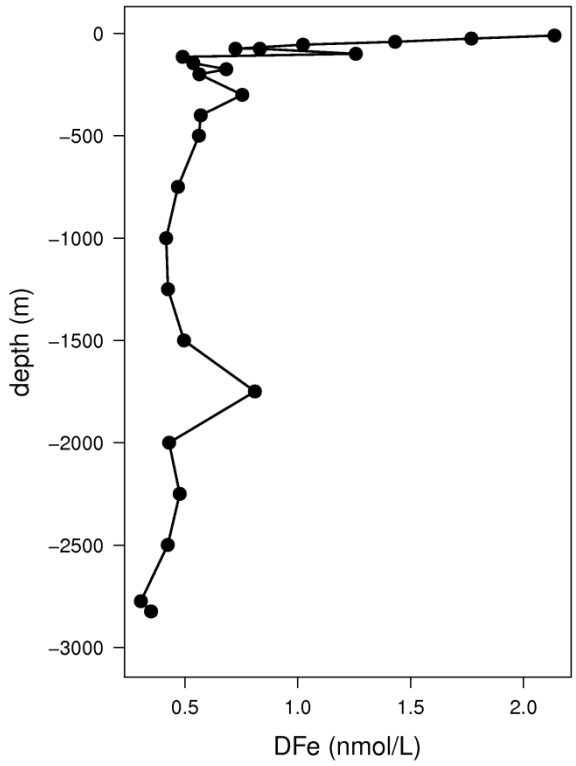

Figure 23. DFe depth profile at station 17 during 64PE374.

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4.2.A.2. Organic speciation of Fe

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Objectives

The low concentration of iron (Fe) in the oceans limits growth of phytoplankton (de Baar et al, 1990, 1995; 2005; Johnson et al, 1997). Dissolved organic molecules, called ligands, bind Fe. In this way the ligands increase the solubility of Fe, retard the precipitation of Fe (hydr)oxides and hence increase Fe availability for biological uptake in the upper parts of the ocean. Since 1994 it is known that around 99% of dissolved Fe in seawater is bound to organic molecules (ligands) that strongly bind Fe (Gledhill and van den Berg, 1994). The binding by dissolved organic ligands, prevents or at least retards precipitation of Fe as insoluble oxides and may play an important role in the dissolution of Fe from dust, and in keeping Fe from glacier melt water and hydrothermal sources in the dissolved phase. Organic complexation influences the photochemistry and bioavailability of Fe. To allow biological uptake of Fe, part of the organically complexed Fe pool must be biological available for phytoplankton and it is still not clear which part of the organically complexed Fe pool is available and how it is taken up.

Our objective is to measure organic speciation of Fe in the Mediterranean Sea to complete the research started during leg 1 (PPE64370, Geotraces Mediterranean leg1). The only data existing about organic Fe speciation in the Mediterranean are from Van den Berg (1995) in the western Mediterranean. We measure on-board using competing ligand exchange cathodic stripping voltammetry. During leg 1 DHN was used as the measuring ligand (van den Berg 2006, Laglera et al., 2013). Normally we use the measuring ligand TAC, however it was discovered that this chemical contained too much Fe. However, during leg 1 it was discovered that also the chemical DHN was not as clean as needed. Between legs 1 and 2 Gerringa and Slagter (scientist doing these measurements during leg 1) were able to obtain a clean batch of TAC. Therefore now again TAC was used as added ligand (Croot and Johanssen, 2000) as was used during leg 2 in the Black Sea.

During this cruise a cubic meter vessel was filled with filtered surface water for culture experiments at NIOZ for Hans Slagter. This filling took place during transit by means of a towed fish near station 19.

Table 9) Samples taken for Organic Fe complexation (FeL) during 64PE374.

Sample	Stations	Bottles per station
FeL	8,13,17	24,22,20,18,16,14,12,10,8,6,4,2; including Chl max and just below Chl max

Methods and equipment

~900 mL FeL samples were taken from the ultra clean CTD (UCC) (Table 9). The samples were filtered over a 0.2 µm Sartobran 300 filter (Sartorius) using N_2 overpressure and measured immediately.

The competing ligand 'TAC' (2-(2-Thiazolylazo)-p-cresol) with a final concentration of 10 µM is used and the complex $(TAC)_2$-Fe is measured after equilibration (> 6 h) by cathodic stripping voltammetry (CSV) (Croot and Johansson, 2000). The electrical signal recorded with this method (nA) is converted as a concentration (nM), then the ligand concentration and

the binding strength is estimated using the non-linear regression of the Langmuir isotherm (Gerringa and al., 1995).

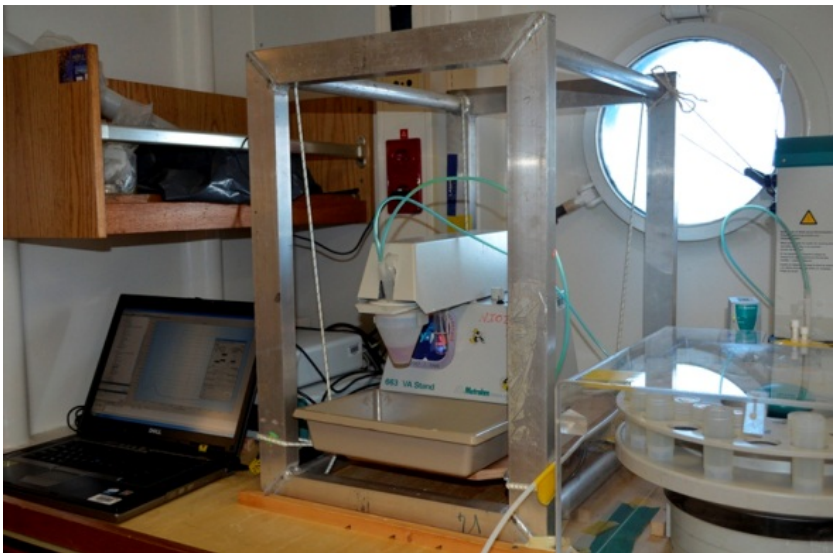

Figure 24. Equipment setup during 64PE374, showing the aluminium frame in which the 663VA stand is hanging via elastic bands to eliminate vibrations that interfere with the measurements.

Competing ligand exchange cathodic stripping voltammetry (CLE-CSV) was performed using two setups consisting of a µAutolab potentionstat (Metrohm Autolab B.V., formerly Ecochemie, The Netherlands), a 663 VA stand with a Hg drop electrode (Metrohm) and a 778 sample processor with ancillary pumps and dosimats (Metrohm), all controlled using a consumer laptop running Nova 1.9 (Metrohm Autolab B.V.) (Figure 24). The VA stands were mounted on elastic-suspended wooden platforms in aluminium frames developed at the NIOZ to minimize motion-induced noise while electrical noise and backup power was provided by Fortress 750 UPS systems for spike suppression and line noise filtering (Best Power). Sample manipulations were performed in laminar flow cabinets (Interflow B.V., The Netherlands).

Dissolved Fe necessary for the data interpretation was measured in separated samples taken from the bottles sampled for Fe complexation, with Flow Injection Analysis (FIA) on board by Johann Bown.

Results

Although the interpretation of the analyses was not finished at the end of the cruise, a pattern could be distinguished from the so far obtained results. In the surface layer (samples taken from bottle 24/22) the ligands were saturated with Fe. In this layer dissolved Fe concentrations were high, by external input, saturating the dissolved organic ligands. This was also the case in intermediate deep waters, where oxygen and nutrients were relatively low. These characteristics of relative high Fe, low oxygen and low nutrients, indicate relatively young water masses brought to larger depths by deep water formation during winter (Malanotte-Rozzoli,et al., 1997; Millot, 1999).

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4.2.A.3. Colloidal and truly soluble Fe

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Introduction

Iron (Fe) is a critical nutrient for oceanic primary productivity. It's an important element in many proteins, enzymes and pigments. Due to its low solubility, Fe limits phytoplankton growth in large parts of the ocean (Martin and Fitzwater, 1988; de Baar et al. 1990). The trace metal Fe is therefore one of the 6 key elements in the GEOTRACES Science plan. For GEOTRACES we took samples for DFe, total dissolvable Fe (unfiltered acidified seawater samples) and organic Fe complexation at 5 full depth stations. These stations were positioned to fill up gaps in our transect of cruise 64PE319.

Notwithstanding its low solubility concentrations of dissolved Fe (DFe, < 0.2 μm) are higher than predicted by its solubility product alone and vary widely over the water column and across the surface ocean. This variation in DFe concentrations can be explained by i) the chemistry of Fe in the dissolved phase, ii) the proximity of Fe sources, and iii) biological processes (e.g. high DFe at the oxygen minimum).

DFe consists of several distinguishable and measurable fractions such as a truly soluble Fe fraction (Fe(III) and Fe(II)), a truly soluble organically complexed Fe fraction and a colloidal Fe fraction. The distribution of these different chemical forms of Fe may depend on biological factors and the physical oceanography.

We used size fractionation (filters with 0.02 μm pore size) to investigate the distribution of the different size fractions of Fe over the upper water column (0-280 m depth). With this research we are especially interested in the interplay between these different Fe fractions and their relation to changes in environmental conditions.

Work at sea

Samples were taken with the NIOZ high volume ultraclean CTD: 24 novel PRISTINE® ultraclean water samplers of large 24L volume each placed on the titanium sampling frame. The novel samplers with butterfly valves at both ends, are constructed of ultraclean plastic (PVDF; manufactured ultraclean (www.georgfischer.at) for the semi-conductor industry) and some pivotal parts of titanium. The ultraclean CTD was deployed with kevlar hydrowire having internal signal cables.

After recovery, the ultraclean CTD was immediately placed in a clean room container (within the ISO Class 6 clean room requirements) (de Baar et al. 2008). In the clean room, CTD bottles were pressurized (~1 bar) using filtered N_2 and samples for dissolved metals were filtered over a < 0.2 μm Sartobran 300 cartridge (Sartorius).

For ultrafiltration (< 0.02 μm) samples were directly filtered from the UCC CTD bottles under N_2 pressure. The seawater was firstly filtered over a 0.2 μm Sartobran 300 cartridge and subsequently inline ultrafiltered using a Virosart CPV MidiCaps cartridge (Sartorius) with a double membrane of polyethersulfone, and the remainder parts made of polypropylene (Figure 25). For each UCC CTD bottle the 0.2 μm Sartobran 300 cartridge was firstly rinsed with 700 ml sample to replace the previous sample from the cartridge. The < 0.02 μm Virosart CPV MidiCaps cartridge was first emptied from its previous seawater sample and rinsed with 500 ml of the new sample before a final sample was taken.

Samples for DFe, total dissolvable Fe, and sizefractionated Fe concentrations were acidified within 24 hrs after sampling using ultrapure HCl (pH 1.8, 2ml/L 12M Baseline grade Seastar HC).

Figure 25. Ultrafiltration of seawater samples directly from the UCC CTD bottles.

The samples were measured on board using FIA with detection based on luminol chemiluminescence according to an improved chemiluminescence flow injection method (Klunder et al. 2011). At least 12h prior to analysis, 60 µL of 10 mM H_2O_2 (Suprapure, Merck 30%) was added to ensure the oxidation of any Fe(II) in the sample (Lohan and Bruland, 2006). The acidified sample was pre-concentrated for 120 s on a Toyopearl AF-Chelate-650M (TosoHaas, Germany) column. Hereafter the column was rinsed for 60 s with MQ water to remove interfering salts. The Fe was subsequently eluted from the column with 0.4 M HCl (Suprapure, Merck 30%) during 120 s. The eluted Fe/HCl mixture subsequently mixed with a 0.96 M ammonium hydroxide (Suprapur, 25% Merck), 0.3M hydrogen peroxide (Suprapure, Merck 30%) and luminol/TETA solution (3 ml luminol stock solution and 60 µL TETA 1 L ultrapure water). The luminol stock solution was prepared by dissolving 270 mg luminol (3-aminophtal-hydrazide, Aldrich) and 500 mg potassiumhydroxide in 15 ml ultra pure type 1 water (18.2 MΩ). Sample and reaction solution passed a 1.5 m length mixing coil placed in a 35°C water bath. The chemiluminescence was detected with a Hamamatsu HC135 Photon counter. Concentrations of dissolved Fe were calculated in nanomol/liter (nM) from the photon emission peak height.

The system was calibrated using standard additions from a 895 nM Fe stock solution (Fluka) to filtered acidified seawater of low Fe concentration that was collected in the sampling area. A five-point calibration and blank determination were made daily. The blank was determined as the intercept of the signals of increasing pre-concentration times (5, 10, 15 seconds) of the calibration water. A certified SAFe standard (Johnson et al. 2007) for the long term consistency and absolute accuracy was measured on a regular basis.

Preliminary results

At station 19 the colloidal fraction is highest in the surface waters and appears to become similar to the DFe fraction with depth (Figure 26).

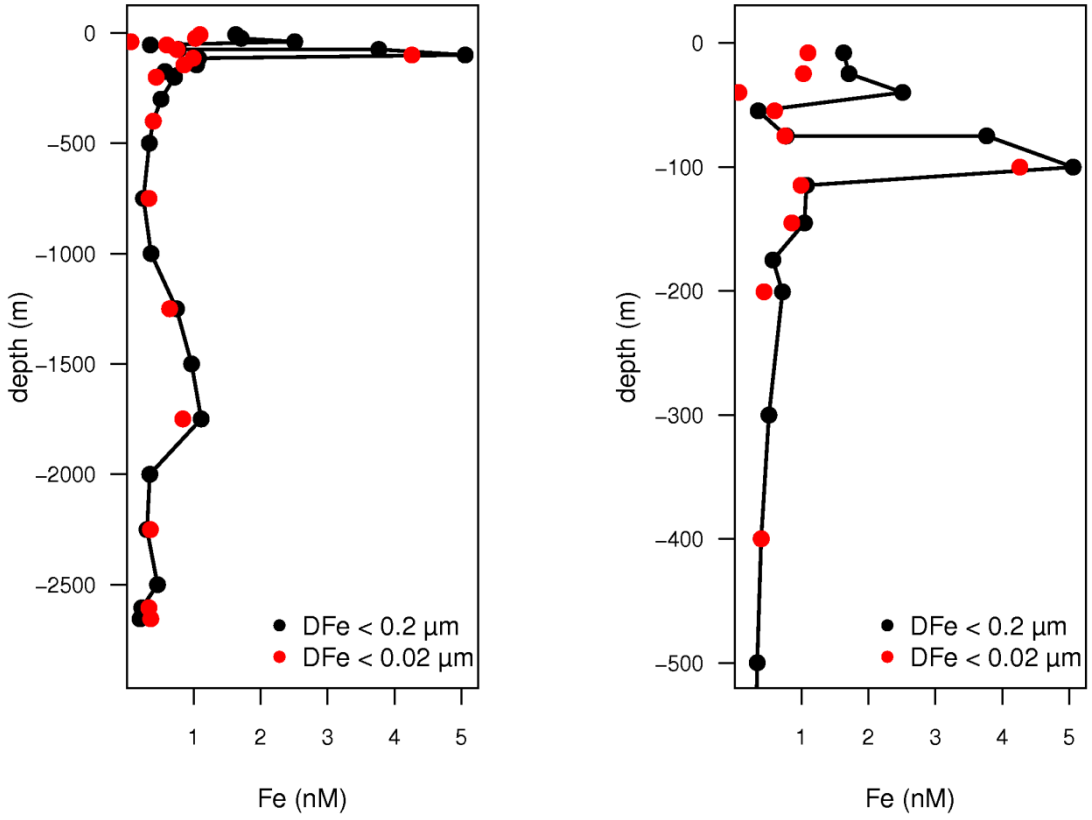

Figure 26. Depth profiles of size fractionated iron (0.2µm and 0.002µm) versus depth from station 19.

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4.2.A.4. The biogeochemical cycles of cobalt, and copper in the northern Mediterranean Sea (Leg 3)

Marie Boyé

On the behalf of the research group :
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Summary

Our research group at Brest proposes to constrain sources and biogeochemical cycling of key bioessential trace metals (copper and cobalt) in the Mediterranean Sea along the GEOTRACES-A04N section, using novel approaches, combining concentrations and speciation measurements with stable isotope ratios (for copper only, cobalt being mono-isotopic). In addition, we aim to calibrate for the first time proxies of Sea Surface Temperature (Sr/Ca and Li/Mg) and pH (B/Ca) as recorded in coccoliths. Samples have been collected during the LEG3 in the Northern Mediterranean Sea, in the water-column (in the dissolved, particulate and soluble fractions) and in the superficial sediment.

Objectives

Many trace elements are critical for marine life and as a consequence influence the functioning of ocean ecosystems. Some trace elements are essential like cobalt (Co) and copper (Cu), others are toxic pollutants like Cu at high concentrations, while some, together with a diverse array of isotope tracers, are used to assess modern-ocean processes and the role of the ocean in past climate change.

Until recently fragmentary data of trace elements and isotopes in the oceans restricted our knowledge of their biogeochemical cycles. The International GEOTRACES program aims to improve our understanding of biogeochemical cycles and large-scale distribution of trace elements and isotopes (TEIs) in the marine environment and establish the sensitivity of these distributions to changing environmental conditions. The third objective of GEOTRACES focus on the development of proxies for past change, yet it is still an uncovered theme. Our main objectives are thus *i) to elucidate important biogeochemical processes, sources and sinks that determine the distribution of the bio-essential trace elements Co and Cu along the section in the Mediterranean Sea; ii) to calibrate new proxies of environmental conditions sensitive to the climate change in the Mediterranean Sea (sea-surface temperature SST and pH); and iii) evaluate if copper flux in the ocean derived from atmospheric copper sources has characteristic isotope signatures that is distinct from benthic diagenesis and/or hydrothermal sources.*

The Mediterranean Sea is the source of the warm and saline Mediterranean Outflow Water (MOW) which may act as a source of trace metals to surrounding North Atlantic water masses (Boyle et al., 1985 ; Boye et al., 2006). The Mediterranean Sea is also an ideal environment to study the strong link between the ocean, the atmosphere and the continent. It is one of the greatest receivers of continental dust input in the contemporary ocean and is in the last decade used as a natural laboratory to study the effects of dust deposition on the surface ocean (Wagener et al., 2010 ; Quétel et al., 1993). Dust is the main external source of biological essential elements to the surface waters of the open ocean worldwide (Jickells et al., 2005). The Nile river may also contribute as a significant source of trace elements in the

eastern basin (Krom et al., 1999). Furthermore other sources have been characterized in the Mediterranean Sea, such as submarine volcano, hydrothermal vents, advective inputs from continental margins (Achterberg and van den Berg, 1997; Riso et al., 2004), and urban and industrial discharges (Michel and Averty, 1999). The eastern basin is a truly oligotrophic marine ecosystem limited by phosphorus deficiency, and probably by Fe (Krom et al., 1991 ; Saydam, 1996). In the western basin, low residual concentrations of Fe after biological removal may lead to changes in species succession or even growth limitation (Bonnet and Guieu, 2006). Associated with these biogeochemical features, contrasting internal cycles of TEIs are expected. Yet both the internal cycle and the impact on the primary production of other bio-essential trace elements such as Co and Cu are still unknow in the Mediterranean Sea.

At the moment there is no complete picture of the biogeochemical cycles that determine the distribution of TEIs in the Mediterranean Sea as for most TEIs data are extremely scarce and fragmentary in this Sea, this making interpretation often difficult and speculative. Hence by studying the cycle of the two understudied micro-nutrients Co and Cu, and the processes involved in the fractionation of the stable isotopes of Cu, it will undoubtely increase the very small available data sets with high resolution full depth transects throughout the Mediterranean Sea, and provide an overview to determine for the first time the important sources and processes explaining the distribution of these elements.

Studying the biogeochemical cycle of those elements includes their physical (dissolved, particulate, soluble, small colloids) and chemical (organic speciation) speciation, which is critical in understanding their bioavailability and geochemical dynamics. Although recognised for important properties like metal complexation or growth stimulation of planktonic species (Doblin et al., 1999), humic substances (HS), an important fraction of dissolved organic carbon, have been very poorly quantified in marine environments. Here we will examine HS with the aim to describe for the first time their distribution in seawater and to assess their relation with Cu and Co complexation.

In addition the Mediterranean Sea experiences the climate change with the highest sensitivity worldwide, notably in increasing SST and decreasing pH (IPCC, 2007). Proxies of such environmental changes, notably Sr/Ca and Li/Mg ratios in biominerals like corals and forams as tracer of SST, and B/Ca for pH, have been used to reconstruct the past climate variability and sometimes to improve the prediction of the futur climate (Smith et al., 1979 ; Hendy et al., 2002 ; Douville et al., 2010 ; Montagna et al., 2009). Yet the use of those proxies in the major producer of calcite the most widely distributed in the global ocean, the coccolithophorids (Archer et al., 2000), is paradoxally still in his infancy. The modalities of transfer of the SST- and pH-signals from the euphotic layer into the top sediment will be assessed in the coccoliths for the first time. These in-situ calibrations will help to further record and reconstruct the climate in the Mediterranean Sea.

Sampling

Samples have been collected in the seawater column with the Titanium-Frame (de Baar et al., 2008) (Table 10).

Different size-fractions have been collected for analyses of Co and to a later extend of Cu (total, particulate, dissolved, soluble) and those samples were acidified on board for later home-lab. measurements. The organic speciation of Co and Cu will be studied in the dissolved and frozen samples. The Cu-isotopes will be analyzed in the dissolved samples kept at room temperature until acidification at the home-laboratories. Proxies will be analyzed in

settling inorganic material and in the surficial sediment. Additional samples have been collected for taxonomy analyses and particulate carbon measurements.

Table 10) Inventory of the samples collected in the northern Mediterranean Sea

St.#	DCo DCu Humics	TCo TCu	Soluble Co	Organic Co	Organic Cu	Particulate trace metals	Cu-isotopes	POC/PIC	Proxies in coccoliths	Taxono-my
1	12	12				4		8	2	3
3	16									
5	24	16	16	12	8	6	7	12		3
6	16	16								
8	13	13								
9	15	13	12	10	9	6	7	12	2	4
11	12									
12	12	12					6			
13	24	16	16	12	10	6	8	12		3
15	12									
17	24	16		12	10	6	8	12		3
18	15		15							
19	13									

Analyses

The analyses will be performed in the home-labs at Brest. The analyses of Co will be performed by Flow-Injection-Analyses and Chemiluminescence detection according to the method we developped (Bown et al., 2011; Dulaquais et al., 2013), apart for the organic speciation of Co that will be analysed by Voltammetry (Bown et al., 2012). Particulate trace metals analyses will be performed by HR-ICPMS using Element II (Pôle Spectrométrie Océan, IUEM), following published method (Planquette and Sherrell, 2012). Total dissolved Cu will be analyzed by Anodic Stripping Voltammetry at a vibrating gold microwire electrode after UV-irradiation (Salaün et al., 2006). Humic substaces will be analysed by Adsorptive Square-Wave Cathodic Stripping Voltammetry at a static mercury drop electrode (Quentel et al., 1986). Total dissolved Cu-isotopes will be analyzed by multi-collector ICPMS (Pôle Spectrométrie Océan, IFREMER) after preconcentration onto a new Cu selective resin (Baconnais & Rouxel, in prep) and/or chelating resin with nitrilotriacetic acid functional groups (Rouxel and Auro, 2010). Analyses of Sr/Ca, Li/Mg, Mg/Ca and B/Ca will be performed by HR-ICPMS using Element II (Pôle Spectrométrie Océan, IUEM), following or adapting published methods (Stoll et al., 2002 ; Montagna et al., 2009 ; Douville et al., 2010). Analyses of the taxonomy will be achieved using inverted microscopy (B. Beker, LEMAR). Analyses of particulate stocks of carbon (POC, PIC) and nitrogen (PON, PIN) will be performed at LEMAR using a CHN-analyzer (Le Moigne et al., 2013).

Thanks-

After being for almost 1 month on board of the *RV Pelagia* I would like to adress special and warm thanks to the Captain, Officers, Crew Members and the Cook of the Research Vessel for their wonderfull work at sea, their professionnalism, and the excellent atmosphere on board. A big thanks to Micha, Loes and Hein who bring us-Brest people- to sample in the Mediterranean and earlier in the Black Sea. The LABEX-Mer is acknowledged for partly supporting our researches here.

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4.2.A.5. Aluminium

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Introduction

Dissolved Al is a trace metal with a scavenged-type distribution and an extreme difference between the extremely low concentrations in the North Pacific and the elevated concentrations in the North Atlantic; varying by greater than two orders-of-magnitude (Orians and Bruland, 1985). The distribution of dissolved Al in surface waters of the open ocean is influenced by atmospheric dust inputs (Measures et al., 2008) and variations in the intensity of removal by scavenging. The surface distribution of dissolved Al can potentially be a tracer of atmospheric Fe inputs. For Al there is no known biological function within the cell, but it has been shown Al is built into the siliceous frustules of diatoms (Gehlen et al., 2002). The incorporation of Al in the frustules decreases the solubility of the frustule (e.g. Van Bennekom et al., 1991, Gehlen et al., 2002), making the frustule more durable. Al is known to co-vary with Si, but this co-variance disappears with aging of the water masses and depends on the sources and sinks of both Al and Si (Middag et al., 2011).

Work at sea

Dissolved Al was measured directly from all samples collected with the ultra-clean CTD using shipboard FIA measurements. In a continuous FIA system, the acidified pH 1.8, filtered (0.2 μm) seawater is buffered to pH 5.5. The metal is concentrated on a column which contains the chelating material aminodiacetid acid (IDA). This material binds only transition metals and not the interfering salts. After washing of the column with ultra pure water (MQ) the column is eluted with diluted acid (0.1 M HCl). The Al is determined using lumogallion after Brown and Bruland (2008). Lumogallion is a fluorometric agent and reacts with aluminum. The change in the fluorescence detected by a fluorometer is used as a measure for the dissolved Al concentration. In order to verify the consistency of the analysis, every day a sample was measured from a check sample that was taken in the beginning of the cruise. Also a duplicate sample was taken every cast and this sample was analysed with the samples of the next cast to further check for inter daily variation. Furthermore, a GEOTRACES seawater reference sample was analysed regularly and the values are consistent with those found previously.

Preliminary results

The aluminium concentration in the surface waters of the northern Mediterranean Sea showed considerable variability with concentrations ranging from <30 nM in the western basin to >75 nM in more eastern portions of the sea. The deep water generally showed an increase in Al concentrations up to ~ 160 nM. These high values are thought to be due to high dust inputs. As a check of our day to day reproducibility of our Al measurements, an internal standard is analysed during every run. The values recorded for our internal standard measured during Leg 3 are presented in Figure 27.

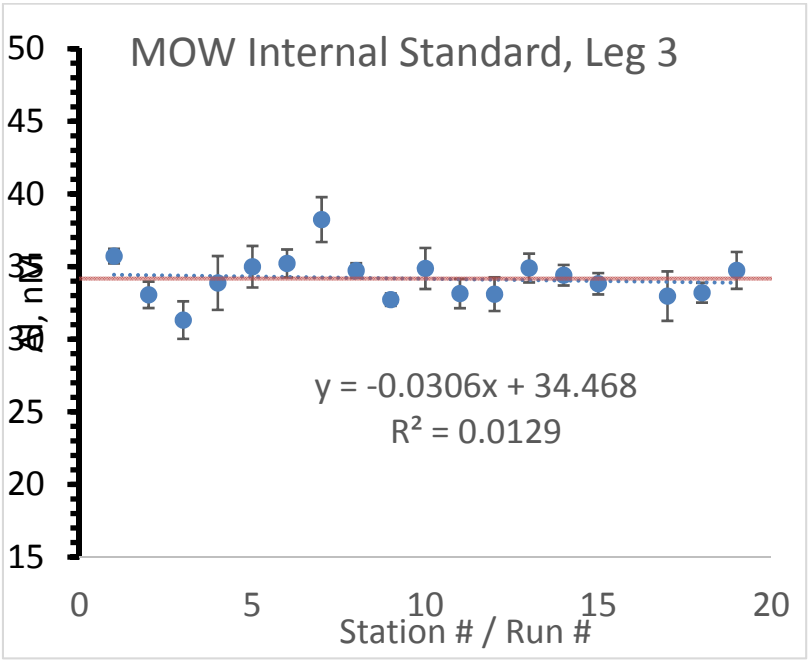

Figure 27. Repeated analysis of our internal standard during the MedBlack GEOTRACES Leg 3 cruise. Solid line represents the average of all 18 measurements ([Al] = 34.2 nM ± 1.5 nM) and the dashed line is the best fit line for the data which illustrates the lack of any trend in our day to day measurements. Error bars represent the standard deviation of the daily triplicate measurements.

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4.2.A.6. Multi-elements

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Introduction

Considerable progress has been made in the development of new multi-element methods (e.g. Sohrin et al., 2008; Lee et al., 2011; Milne et al., 2010; Biller and Bruland 2012) using chelating resins for off-line extraction, with subsequent detection with a high-resolution, magnetic sector, inductively coupled plasma mass spectrometer (ICP-MS). Samples will be processed using a modified version of the Biller and Bruland (2012) method. This current method includes the analysis of yttrium (Y), lanthanum (La), titanium (Ti) and gallium (Ga), in addition to manganese (Mn), iron (Fe), nickel (Ni), zinc (Zn), cadmium (Cd) and lead (Pb) that were determined in the original method. Moreover, a new 'element dilution' approach was used for extractions performed at sea that is less labor intensive then the gravimetrical method described by Biller and Bruland (2012) as the weighing of the samples (which cannot be done at sea) has been excluded. The extraction of the samples is the process where the trace metals of interest are separated from the original seawater matrix to remove interfering ions, as well as concentrating the samples via the use of a chelating column (Nobias-chelate PA1 resin in this method). The pre-concentration is necessary due to the low concentrations of trace metals in the open ocean in the high background salt matrix of seawater.

Work at sea

A multi-element stock standard with natural isotopic abundances of Mn, Fe, Co, Ni, Cu, Zn, Cd, Y, La, Ti, Ga and Pb, was made in 0.024 M HNO_3 from dilutions of 1000 ppm SPEX individual element standards. This mixed element standard was then used to make standard additions to natural seawater with low concentrations of metals for calibration. Five standards were used for calibration in this method. Besides this multi-element stock standard, also a stock of Lu and In was made in 0.024 M HNO_3 from dilutions of the respective 1000 ppm SPEX standards. This stock had a concentration of 2000 nM for both elements and every sample and standard was spiked with this solution to obtain a concentration of 5 nM. In addition to the seawater standard additions, also 5 standards were made up in the elution solution (elution acid standards). These standards (also spiked with Lu-In) as well as the extracted seawater standards will be analyzed on the ICP-MS. Comparison of the extracted seawater standards with the elution acid standards provides evidence for the extraction efficiency or recovery of each of the metals on the resin. The recovery of all elements with the exception of Ga and Ti are quantitative. All samples from the ultra-clean CTD are extracted at sea and the eluents will be run on the ICP-MS after the cruises (Figure 28).

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Figure 28) Ejin and John extracting multi-elements and measuring DAl.

4.2.A.7. Neodymium isotopes

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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 mass as isotopically distinct entities. The $^{143}Nd/^{144}Nd$ ratios vary in the Earth as a result of α decay of ^{147}Sm, and 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 $^{143}Nd/^{144}Nd$ value 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). Generally speaking, the water masses in the Western Mediterranean Sea have lower ε_{Nd} values, a fingerprint of the Atlantic water entering the Mediterranean Sea through the Strait of Gibraltar, whereas the Eastern basin displays more radiogenic values reflecting the contribution of partially dissolved Nile River particles (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 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; 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 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 objects during the cruise was to isotopically characterize the seawater masses that bath the modern corals (collected during previous cruises) in order to provide robust evidence 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 24 seawater samples from 9 profiles were collected along the major Mediterranean sub-basins (Aegean, Ionian Sea, Adriatic and Tyrrhenian Sea) (Table

11). 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) from the Ultraclean titanium CTD system. Seawater was filtered (Sartorius Sartobran®300 0.2 µm) before being collected into the cubitainers.

For station 17, seawater samples were also collected for the analysis of the Rare Earth Element (REE) concentration 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 trace metal grade HCl to pH = 2 and mixed with ~ 18mg of Fe in preparation for pre-concentration of the lanthanide and actinide elements (Figure 29). 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.

Figure 29. Paolo adds ammonium hydroxide to his Nd samples.

Geochemical analysis

The Rare Earth Elements co-precipitated with Fe will be processed and analysed at the *Laboratoire des Sciences du Climat et de l'Environnement* (LSCE) in Gif-sur-Yvette. Neodymium will be isolated from the other REEs through column chemistry and Nd isotopes will be analysed by multi-collector ICPMS (Neptune^{Plus}).

The REEs concentration will be analysed by a X-series^{II} CCT (Thermo Fisher Scientific) ICPQMS following a standard addition technique.

Acknoledgements
I would like to thank the chief scientists of Leg 3 (Micha Rijkenberg and Loes Gerringa), Hein de Baar, the captain Pieter Kuijt, and the crew as well as the scientific parties for the successful cruise. Sampling for Nd isotopes during Leg 3 was partly supported by the MISTRALS/PALEOMEX/COFIMED project, funded by the French CNRS and CEA.

Table 11) Locations and depths of the seawater samples collected for Neodymium isotopes during Leg 3 (Geotraces Mediterranean and Black Sea)

Station Number	Date	Lat	Long	Pressure (dbar)	Code
1	27-July-13	35 38.20 N	024 55.19 E	25.19 935.80	3.1.1.23 3.1.1.1
3	28-July-13	35 56.21 N	022 10.99 E	3911.11	3.3.1.1
8	31-July-13	40 09.23 N	018 32.14 E	24.50 234.74 873.81	3.8.1.23 3.8.1.9 3.8.1.1
9	31-July-13	40 09.25 N	018 49.01 E	739.28	3.9.1.1
11	01-Aug-13	37 24.04 N	015 58.23 E	24.81 2542.83	3.11.1.23 3.11.1.1
12	02-Aug-13	39 00.43 N	014 30.13 E	3464.05	3.12.1.1
13	03-Aug-13	39 52.68 N	013 00.60 E	19.71 400.04 499.47 999.99 1999.58 3576.27	3.13.3.4 3.13.1.13 3.13.1.12 3.13.1.10 3.13.1.6 3.13.1.1
15	04-Aug-13	42 03.05 N	010 34.05 E	24.80 299.41 1244.20	3.15.3.23 3.15.3.7 3.15.3.1
17	06-Aug-13	40 04.17 N	005 56.83 E	24.80 199.36 1499.77 2823.85 2499.07	3.17.1.23 3.17.1.14 3.17.1.7(*) 3.17.1.1 3.17.3.3

(*) Seawater sample for inter-comparison

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4.2.A.8. Silicon isotopic composition in the Mediterranean and Black Seas

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Objectives

Silicon (in the form of silicic acid in seawater, H_4SiO_4) is a macronutrient required for the growth of aquatic photosynthetic organisms siliceous organisms, dominated by diatoms in the ocean. This group of phytoplankton is actively involved in the marine biological carbon pump, which is participating to the oceanic anthropogenic carbon storage. Silicon has three stable isotopes (^{28}Si, ^{29}Si, ^{30}Si) and diatoms fractionate Si isotopes preferentially taking up light isotopes (De La Rocha et al., 1997). Consequently, in a similar way as for C and N isotopic systems, both the Si isotopic compositions of seawater in the euphotic zone and of diatoms reflect the extent of the Si nutrient reservoir use since the beginning of the growth season (Cardinal et al., 2005, 2007). The Si isotopic composition of seawater can also be used to quantify silicic acid supply to the mixed layer and to identify mixing processes (e.g. Fripiat et al., 2011). This proxy is increasingly used in paleoceanographic studies and is particularly powerful when compared with N and C isotopic compositions (Pichevin et al., 2009). There exists so far no published data on the Si isotopic signatures in the Mediterranean and Black Seas. In this project we aim more specifically at:

- Quantifying the degree of Si utilisation in surface by diatoms;
- Identifying the source of Si to the mixed layer (e.g. from which depth it has been supplied);
- Quantifying deep mixing and tracking recently formed deep waters;
- Better constraining the remineralisation of silica at depth;
- Comparing with other proxies from the same cruise (e.g. $\delta^{15}NO_3$ data by R. Ganeshram and ε_{Nd} by P. Montagna);
- Overall improving the understanding of silicon cycle in the Med. Sea and contributes to the calibration of Si isotopes as paleo-proxy in this region.

Materials & methods

Sampling

More than 240 dissolved silicon samples have been collected throughout the water column at 12 stations of Leg 3 using 0.2 µm filtered seawater (0.2 µm Sartobran 300 filter (Sartorius)) with variable volumes (Table 12). Samples are stored unacidified in the dark at 20°C in PP bottles pre-cleaned with dilute Suprapur grade HCl.

In addition, at each of these 12 stations, particles were collected at two depths (Figure 30):
- surface using the underway ship's seawater supply,
- deep chla-max using the normal Niskin CTD sampling rosette.

Between 1 and 6 litres of seawater were filtered in the wet lab on polycarbonate membranes (∅ 47mm, 0.4 µm porosity) within 12h of sampling (samples were stored in the fridge meanwhile) with a filtration time of max. 3h. Filtration was done under pressure using ship compressed air system at ~1.2 psi (Figure 31).

Filtration blanks were done twice by filtration of mQ water and twice by filtration of pre-filtered seawater. Station 16 was also sampled similarly for particles. Since UCC samples were not available at this station, 4 L of surface seawater (underway system) was filtered and stored as the other seawater samples.

Figure 30. Damien sampling seawater from the 12L CTD for particles.

Figure 31. Filtration system used for the collection of particles at surface and deep chl-a maximum to measure Si isotopic signatures of biogenic silica during Leg 3 of MedBlack GEOTRACES cruise.

Table 12) Volume of filtered UCC seawater collected for Si isotopic signature of silicic acid during Leg 3 of MedBlack GEOTRACES cruise.

	Station 1	Station 3	Station 5	Station 8	Station 9	Station 11	Station 12	Station 13	Station 15	Station 17	Station 18	Station 19
Bottle#	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)	Volume (L)
1	0.25	0.25	0.25	0.25	0.5	0.25	0.25	0.25	0.25	0.25	2.25	0.25
2	0.25	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.5	0.25	2.25	0.25
3	0.5	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.5	0.25	2.25	0.25
4	0.5	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.5	0.25	2.25	0.25
5	0.5	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.5	0.25	2.25	0.25
6	0.5	0.25	0.25	0.5	0.5	0.25	0.25	0.25	0.5	0.25	2.25	0.25
7	0.5	0.25	0.25	0.5	0.5	0.5	0.25	0.25	0.5	0.25	2.25	0.25
8	0.5	0.25	0.25	0.5	0.5	0.5	0.25	0.25	1	0.5	2.5	0.5
9	1	0.25	0.25	1	1	0.5	0.5	0.5		0.5	2.5	0.5
10		0.25	0.25			0.5	0.5	0.5	1	0.5	2.5	0.5
11	1	0.5	0.5			0.5	0.5	0.5		0.5	2.5	0.5
12		0.5	0.5	1	1	1	0.5	0.5	1	0.5	2.5	0.5
13		0.5	0.5			1	0.5	0.5		1	3	1
14		0.5	0.5				1	0.5		1	3	1
15	1	0.5	0.5	1	1	1		1	1		2	1
16		1	0.5				1	1		1	3	1
17		1	1				1	1			2	1
18	1	1	1	1	1	1			1	1	3	1
19		1	1				1	1			2	1
20	2	1	1	2	2	2	2	2	2	2	4	2
21		2	2								2	
22	4	4	4	4	4	4	4	4	4	4	6	4
23	4	4	4	4	4	4	4	4	4	4	6	4
24	4	4	4	4	4	4	4	4	4	4	6	4

Planned methods and analyses

On the shore-based lab, samples will be processed as follows:

- Seawater samples will be processed following Hendry et al. (2010) modification of Georg et al. (2006) purification method. Briefly, silicic acid will be pre-concentrated by brucite ($Mn(OH)_2$) scavenging at high pH (Cardinal et al., 2005). After dissolution in HCl, cationic exchange chromatography will be implemented to remove all cationic species. Anions will be monitored and, when necessary, normalisation of standard and samples will be done by addition of sulphate to prevent matrix effect during isotopic measurements (Hughes et al., 2011).
- Biogenic silica on particles' samples will be digested by hot NaOH 0.2M leaching; the lithogenic silica contamination will be monitored by Al analysis of the leachate (Ragueneau et al., 2005). If the amount of biogenic silica is sufficient (0.5 µmol Si needed) and if the lithogenic silica contribution is negligible (<5%), samples will be processed for chemical purification before isotopic analyses (Georg et al., 2006).
- Si isotopic analyses will be measured by sample – standard bracketing on a Multi Collector – Inductively Coupled Plasma – Mass Spectometer (MC-ICP-MS) with Mg doping to correct for the mass bias (Cardinal et al., 2003). Results will be presented in the form of $\delta^{30}Si$ and $\delta^{29}Si$ relative to NBS 28 reference material. Accuracy will be monitored by repeat analyses of the Diatomite secondary reference material (Reynolds et al., 2007). Depending on success in funding for a post-doc or a Ph. D., it is expected to process and analyse the samples within 2-4 years from now.

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4.2.A.9. Sample collection for stable N isotope analysis

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Introduction

The objective of the sampling programme Mediterranean-Black Sea GEOTRACES LEG 3 is to collect seawater and suspended particulate samples for stable nitrogen and oxygen analysis of dissolved nitrate and stable carbon and nitrogen analysis of suspended particulate organic matter at the Wolfson's Mass Spectrometer Laboratory at the University of Edinburgh. The specific objectives are as follows: (1) To delineate various water masses in terms of their stable N and O isotopic composition; (2) To estimate relative nitrate utilisation in surface waters by biota using stable N isotope systematics; (3) To identify nitrate contributions from atmospheric and terrestrial sources with respect to various water masses; (4) To investigate the magnitude of nitrogen fixation and its "new nitrate" contributions; and (5) To compare macronutrient and micronutrient sources and cycling in the Mediterranean Sea.

Filtered seawater was collected using online filtration (0.2 μm Sartobran 300 cartridge filter (Sartorius)) from the UCC roughly at alternate depths at stations 1, 3, 5, 8, 9, 11, 13, 15, 17, 18 and 19. The samples were stored frozen in HCl cleaned 250 ml Nalgene Polypropelene bottles.

Samples for suspended particles were collected from the standard 12L CTD from bottles corresponding to the depth of the Chlorophyll Maximum as deduced from the CTD's flourometer (Figure 32). Near surface samples were also collected from the ships underway pump system. Seawater is forced through 25 mm diameter ~0.7 μm pore size GF/F filters, previously muffle-furnaced at 400 ^{o}C for 4 hours using ships compressed air system from Nalgene HDPE carboys (Fig. 1). Filters with suspended matter were frozen and stored for analysis. Suspended particulate samples were collected from stations 1, 3, 5, 8, 9, 11, 13, 15, 16, 17, 18 and 19.

Analytical Protocols to be used for stable isotope analysis are as follows:

$\underline{\delta^{15}N_{NO3}}$ <u>analysis</u>

Isotopic signatures of nitrate nitrogen were determined using the denitrifier method and subsequent analysis by isotope ratio mass spectrometry (Sigman et al., 1999).

The denitrifier method utilises denitrifying bacteria that lack N_2O reductase activity, *Pseudomonas aureofaciens*, to convert dissolved inorganic nitrate in seawater samples into nitrous oxide gas of identical nitrogen isotopic composition. Samples are prepared for mass spectrometry using a custom-modified Analytical Precision gas-prep interface and purge-and-trap cryogenic focusing system. The cryogenically-focused sample is separated into distinct N_2O and CO_2 pulses by gas chromatography and then analysed on a VG Prism III isotope ratio mass spectrometer. Raw sample data are corrected to atmospheric N_2 using isotopic reference standards USGS-32, USGS-34 and USGS-35, with an analytical precision (1σ) of around 0.2 ‰. All $\delta^{15}N$ data are presented in the delta per mil notation compared to atmospheric N_2 ($\delta^{15}N$ ‰ $_{AIR}$).

POC, PN, $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ analysis

Bulk POC, PN and corresponding isotopic analyses were conducted using a method similar to Ganeshram et al. (2000). GF/F filters were kept for particulate organic carbon and nitrogen measurements, dried at 50°C overnight, and stored frozen at -20°C until analysis. Prior to analysis, the filters were decarbonated by wetting with Milli-Q water and fuming with HCl for 48 h and then drying at 50 °C. Filters were analysed for elemental POC, PN, $\delta^{13}C_{POC}$ and $\delta^{15}N_{PN}$ using a Carlo Erba NA 2500 elemental analyser in-line with a VG PRISM III isotope ratio mass spectrometer in helium carrier gas and corrected to PACS and acetanilide isotopic standards covering the full range of CN concentrations. All $\delta^{13}C$ data are presented in the delta per mil notation versus Vienna Pee Dee Belemnite ($\delta^{13}C$ ‰ $_{VPDB}$) and all $\delta^{15}N$ data are presented in the delta per mil notation versus N_2 gas in air ($\delta^{15}N$ ‰ $_{AIR}$).

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Figure 32. Raja sampling seawater from the standard 12L CTD to collect particles.

4.2.A.10. Oxygen isotopes

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Introduction

The triple isotopic composition of dissolved O_2 (^{16}O,^{17}O and ^{18}O) is unique tracer for aquatic processes. Since it was first introduced by Luz and Barkan (2000), it was extensively used by several research groups for estimating the rates of photosynthetic O_2 production in the mixed-layer of many regions of the ocean (e.g. Hendricks et al., 2004; Juranek and Quay 2005;Sarma et al.,2005). This application is made possible because the isotopic composition of atmospheric O_2 carries a small, yet measurable, signature of photochemical processes which take place in the stratosphere (Thiemens, 2001). Photosynthetic O_2 production tends to diminish this stratospheric signature, and therefore, provided that the rate of air-sea gas exchange is known, the rate of photosynthetic O_2 production can be estimated by measuring the triple isotopic composition of O_2. Respiration affects the isotopic composition of dissolved O_2, by preferentially consuming the lighter isotopolouges. This means that in a closed parcel of water in which O_2 is consumed by respiration, the relative abundance of the heavier isotopolouges (conventionally expressed in δ notation) will increase. However, the ratio of the increase in $\delta^{17}O$ to $\delta^{18}O$ has been experimentally determined for the major respiratory mechanisms (Angert et al., 2003; Luz and Barkan, 2005). This ratio (0.518) can be used in a simple equation, which describes the ^{17}O-excess ($^{17}\Delta$) over the expected value for a given $\delta^{18}O$, in a system in which O_2 is removed by respiration:

$$^{17}\Delta=\ln(\delta^{17}O/1000+1) - 0.518\ \ln(\delta^{18}O/1000+1) \qquad (5)$$

Since respiration increases the first term of the right-hand side of the equation on a slope of 0.518 relative to the second term, respiration alone would not result in a change in $^{17}\Delta$. Consequently, once a water parcel sinks below the phtoic zone, where neither air-sea gas exchange nor photosynthesis take place, $^{17}\Delta$ can only be changed by mixing with water of different $^{17}\Delta$. In this sense, it can be applied as a conservative tracer for mixing processes. Such application was recently demonstrated by Wurgaft et al., 2013.

Objectives

Recent measurements (unpublished data) have shown that in many parts of the deep (> 1000 m) ocean, the photosynthetic fraction of the dissolved O_2 is surprisingly high. In particular, such observations were made in the Atlantic Ocean. Since this photosynthetic O_2 had to come from the photic zone, tracing the origins of this signature may shed new light on the present global mixing regime of the ocean. If no feasible source will be found, the photosynthetic signature in the deep ocean will have to be explained by ecological and physical conditions which prevailed when the deep water was formed, and may therefore provide interesting insights on past climate, in the time-scale of the oceanic turnover.

In addition, we recently demonstrated how $^{17}\Delta$ can be used as a tracer for physical mixing process (Wurgaft et al., 2013). Our measurements, which were conducted in the Gulf of Aqaba, Israel, showed that rapid boundary mixing processes “inject” surface O_2 into the deep (>500 m) parts of the gulf, on a seasonal time scale.

Our objectives for sampling during the 3rd leg of the Geotracers Mediterranean and Black Sea cruise were twofold:
1) Obtain preliminary data of the isotopic composition of O_2 in the deep parts of the Mediterranean. In particular, we wanted to check whether the outflow through the Straits of Gibraltar can be a source to the photosynthetic O_2 we observed in the Atlantic Ocean.
2) Obtain preliminary data around the Adriatic Sea, in order to see if signatures of rapid O_2 injections exist in this area.

Sampling
In order to achieve the objectives mentioned above, seawater samples were taken from three stations along the route of the NIOZ RV-Pelagia (Figure 33). The first two stations were in the Adriatic Sea, and the third was the station nearest to the strait of Gibraltar. A table consisting the exact location and depths sampled is enclosed (Table 13).

Table 13) The locations and depths were samples for oxygen isotopes were taken.

Station	**8**	**10**	**19**
Latitude	40° 57.68' N	38° 16.04' N	38° 21.54' N
Longitude	18° 32.14' E	17° 59.81' E	4° 17.63' E
Bottom depth (m)	860	2562	2631
Depths sampled (m)	860 800 700 600 500 400 300 235 205 160 100 55 10	2562 2500 2250 2000 1750 1500 1250 1000 750 500 400 300 205 100 55	2631 2600 2500 2250 2000 1750 1500 1250 1000 750 500 400 300 200 145 100 55 10

Analysis
The water sampling procedure is thoroughly described in Luz et al. (2002). In brief, duplicate seawater samples (~150 mL) were transferred from Niskin bottles into pre-evacuated 300 mL gas extraction flasks with Louwers Hapert® O-ring stopcocks, using Tygon® tubing. Prior to their evacuation, 1 mL of $HgCl_2$ saturated solution was added to the flasks to arrest biological activity after sampling. Seawater was withdrawn from the Niskin bottles immediately after

the recovery of the rosette of water samples. No other samples were collected from the Niskin bottles prior to those of the isotopic composition of dissolved O_2.

No analysis or further processing of the samples was conducted on-board of the Pelagia. Sample preparation and mass-spectrometry measurements will be carried out in the home laboratory in Jerusalem, according to Luz et al. (2002) and Barkan and Luz (2003). Upon arrival to Jerusalem, the samples will be equilibrated for 24 h at room temperature. Each flask will be inverted, and the water will be drawn out into a suction bottle, with the valve slightly open, until only the headspace gases and a small volume (< 1 mL) of water remained in the flask. The flasks will then be stored at room temperature until analysis of the gases will take place. An automated preparation line will be used to extract the gases and purify O_2 and Ar out of the gas mixture, as described in Barkan and Luz (2003). This preparation will include drying, CO_2 removal and chromatographic separation of N_2. The ratios ^{18}O:^{16}O and ^{17}O:^{16}O in the purified O_2-Ar mixture were determined by dual inlet mass spectrometry on a multi-collector instrument (DELTA^{plus}XL mass spectrometer, Thermo Scientific).

Figure 33. Eyal taking samples form the standard 12L CTD for oxygen isotopes.

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4.2.B. CO_2 and DOC

4.2.B.1. Dissolved Inorganic Carbon, Total Alkalinity

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Royal Netherlands Institute for Sea Research, Texel, the Netherlands

Methodology
Sampling and analysis for carbonate system parameters broadly followed the standard operating procedures outlined by Dickson et al., 2007. Water samples of 0.6 L were collected from the Large Volume CTD at one cast of every station, at all 24 depths, into borosilicate sample bottles with plastic caps, using tygon tubing. In each profile, a minimum of two duplicate samples were collected at shallow and deep parts of the profile. Sample analysis commenced immediately after collection and analysis of profiles was in all cases completed within 12 hours after sampling (Figure 34). All analyses were performed on two VINDTA 3C (Versatile INstrument for the Determination of Total Alkalinity, designed and built by Dr. L. Mintrop, Marine Analytics and Data, Kiel, Germany). Samples were measured simultaneously on the two instruments (VINDTA #14 and #17, respectively). These instruments were slightly modified: the peristaltic sample pump was replaced with an overpressure system (~0.5 bar overpressure) and a 1 m long (though coiled) 1/8" stainless steel counter-flow heat exchanger that was placed between the sampling line and the circulation circuit. This setup allows for the rapid, convenient and bubble-free loading of the pipettes with sample of 25 ºC (± 0.1 ºC), irrespective of the samples' initial temperature.

Duplicate samples were analyzed first followed by the depth profile. The use of two machines increases our confidence in final results, and allows demonstration and quantification of measurement errors of the machines that would otherwise go unnoticed. No formal analysis and correction of the result have been performed yet.

Dissolved inorganic carbon (DIC)
Dissolved inorganic carbon (DIC) was determined by coulometric titration. An automated extraction line takes a 20 mL subsample which is subsequently purged of CO_2 in a stripping chamber containing ~1 mL of ~8.5% phosphoric acid (H_3PO_4). A stream of nitrogen carries the CO_2 gas into a coulometric titration cell via a condenser and acid trap, to strip the gas flow of any water. The CO_2 reacts with the cathode solution in the cell to form hydroxyethylcarbamic acid, which is then titrated with hydroxide ions (OH^-) generated by the coulometer. The current of the coulometer is then integrated over the duration of the titration to obtain the total amount of carbon titrated.

Total Alkalinity (TA)
Determinations of total alkalinity (TA) were performed by acid titration that combines aspects from both the commonly used ‘closed cell' method and the ‘open cell’ method, following the VINDTAs standard settings. A single 20 L batch of acid of ~0.1M and salinity 35 was prepared to be used by both VINDTAs. This acid was stirred for 2 minutes prior to the beginning of each run of analyses to ensure it was thoroughly homogenized. Potential drift in acid strength due to HCl-gas loss to acid vessel headspace is not accounted for.

Certified reference material (CRM, Batch #127) obtained from Dr. Andrew Dickson at Scripps Institute of Oceanography (San Diego, California) was used for calibration purposes

and quality control for both DIC and TA.

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Figure 34. Lesley measuring DIC and alkalinity in the dedicated CO_2 container.

4.2.B.2. Dissolved organic carbon (DOC)

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Introduction

Dissolved organic carbon (DOC) in the oceans plays a key role in the global carbon cycle. It contains an amount of carbon ($662 \cdot 10^{15}$ g C) (Hansell et al., 2009) comparable to that occurring in the atmosphere and is the main substrate for the growth of heterotrophic prokaryotes (Carlson, 2002). It can interact with metals modifying their bioavailability and toxicity and undergoes condensation reactions leading the formation of transparent exo-polimeric particles (TEP), that represent the starting point for the bio-film formation.

DOC concentration is the result of all the biological processes of production and consumption occurring in the sea and it is strongly affected by external inputs (river and atmosphere). Physical processes, such as deep water formation, thermohaline circulation, vertical stratification and mesoscale activities are the main drivers of its distribution (Hansell 2002; 2009; Carlson et al., 2010). Recently, a link between DOC distribution and circulation of the main water masses in the Mediterranean Sea has been detected and the role of DOC in C export and sequestration has been highlighted (Santinelli et al. 2010, 2012; 2013).

The DOC data collected during the GEOTRACES cruise represent a unique opportunity to (i) assess the DOC distribution in the different areas and water masses of the Mediterranean Sea and to investigate long-term variation in its distribution; (ii) confirm the role of DOC in C export and sequestration in the Mediterranean Sea; (iv) investigate the difference in DOC cycling between the Western and Eastern Mediterranean Sea.

Sample collection and analysis

Work at sea

Filtered seawater samples (0.2 µm, Sartobran 300 cartridges (Sartorius)) were collected from the ultraclean titanium CTD into 60 ml plastic (HDPE) bottles acid washed (Figure 35). Samples were stored at -20° and in the dark until the analysis. Samples were collected in all the stations at the following depths: 10, 25, 50, 75, 150, 200, 250, 300, 400, 500 m and every 250 m until the bottom.

In the Ionian Sea (St. 4), samples for $\Delta^{14}CO_2$ and DOCΔ^{14}C were collected at 10, 400, 2000 and 2920 m. Daniel Repeta (WHOI) is responsible for these analysis and data. Samples will be analyzed at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS).

DOC measurements

DOC measurements will be carried out with a Shimadzu Total Organic Carbon analyzer (TOC-Vcsn), by high temperature catalytic oxidation. Samples are acidified with HCl 2N and sparged for 3 minutes with CO_2-free pure air, in order to remove inorganic carbon. One hundred and fifty µl of sample is injected in the furnace (680°C) after rinsing with the sample three times. From 3 to 5 replicate injections are performed until the analytical precision is lower than 1% (± 1µM). A four-point calibration curve is done by injecting standard solutions of potassium hydrogen phthalate in the concentration range between 20 and 150 µM. At the beginning and end of each analytical day the system blank is measured using

low carbon water produced by a MilliQ system, the measurement reliability is assessed twice daily by comparison of data with DOC Consensus Reference Waters (CRM) (Hansell, 2005).

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Figure 35. Simona preparing sample bottles for DOC, sampling in the UCC container and changing aerosol filters together with Eyal.

4.2.B.3. Chromophoric dissolved organic matter (CDOM)

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Introduction

Chromophoric dissolved organic matter (CDOM) is the fraction of DOM that absorbs light over a broad range of ultraviolet (UV) and visible wavelengths; it determines the underwater light availability in open and coastal regions with important implication on primary production and biological activity. Though terrestrial inputs (rivers and atmosphere) represent an important source of CDOM, it is also produced in-situ by biological activity and it is mainly removed by photochemical degradation and microbial consumption. Deep ocean circulation drives its distribution (Siegel et al., 2002; Nelson et al., 2007). CDOM is the major factor controlling the attenuation of UV radiation in the ocean, it is highly photo-reactive and it easily undergoes photodegradation processes upon exposure to solar radiation. Through this process, CDOM is degraded into smaller compounds with lower molecular weight, lower internal energy, and different optical properties (Mopper and Kieber, 2000, 2002).

In the last years, the measurement of fluorescence excitation/emission matrixes (EEMs) combined with the parallel factorial analysis (PARAFAC) allowed the identification of different fluorescent compounds in the CDOM pool, that can be mainly identified as humic-like and protein-like substances (Stedmon and Bro 2008, Para et al., 2010, Kowalczuk et al., 2009, Yamashita et al., 2011).

The CDOM data collected during the GEOTRACES cruise represent the first data for the open-sea waters of the Mediterranean Sea on a basin scale and will be useful to:

1. Gain the first information about CDOM distribution in the surface, intermediate and deep waters for the whole basin
2. Investigate if CDOM shows different optical properties (absorption and fluorescence) in the surface waters of the Western and Eastern Mediterranean Sea and how they are related to the different trophic conditions
3. Study the relationship between DOC and CDOM in the different water masses of the Mediterranean Sea.

Sample collection and analysis

Work at sea

Filtered seawater samples (0.2 μm, Sartobran 300 cartridges) were collected from the ultraclean titanium CTD into 60 ml plastic (HDPE) bottles acid washed. Samples were stored at -20° and in the dark until the analysis. Samples were collected in all the stations at the following depths: 10, 25, 50, 75, 150, 200, 250, 300, 400, 500 m and every 250 m until the bottom.

CDOM

Absorption measurements

Absorbance spectra will be measured throughout the UV and visible spectral domains (230–700 nm) using a spectrophotometer UV-visible (Jasco Mod-7850), with a 10 cm quartz cell. Milli-Q water is used as reference and its spectrum is subtracted from each sample. The absorbance (A) is converted into absorption coefficients (a) as follows:

$$a_{(\lambda)} = 2.303\, A(\lambda)/l \qquad (6)$$

where $A(\lambda)$ is the absorbance at wavelength λ and l is the pathway expressed in meters. Absorption coefficient at 280 nm (a_{280}) and 355 nm (a_{355}) are calculated in order to gain information on protein-like (a_{280}) and humic-like (a_{355}) substances.

The spectral slope (S), is calculated in the range 275-295 nm (Fichot and Benner, 2012), using the following fitting equation:

$$y = a_{\lambda_0}\, e^{-S\,(\lambda-\lambda_0)} \qquad (7)$$

where a_{λ_0} is the absorption coefficient at λ_0.

Fluorescence measurements

Fluorescence excitation-emission matrixes (EEMs) will be measured by using the Aqualog fluorometer (Horiba), with a 10 × 10 mm^2 quartz cuvette. Excitation wavelength ranges between 250 and 450 nm at 5 nm increment, while emission spectra are measured between 212 and 619 nm at 3 nm increment. Each EEM is corrected for any inner-filter effect (Stedmon and Bro 2008) and for instrument bias in excitation and emission. EEMs are subtracted by the blank EEM measured by using Milli-Q water. Rayleigh and Raman scatters are removed by interpolating the data using a monotone cubic interpolation (shape-preserving) (Carlson and Fritsch 1989). Finally, the fluorescence intensity value is normalized by the integrated Raman band of Milli-Q water (λ_{ex} = 350 nm, λ_{em} = 371–428 nm), measured at the same day of the analysis (Lawaetz and Stedmon, 2009).

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Appendix 1. Station list & devices deployment

Station	Cast	Date	Time[1]	Latitude	Longitude	Device name	Action name
1	1	27/07/2013	05:11:10	35.636597	24.919905	Ultra Clean CTD	Begin
1	1	27/07/2013	05:27:11	35.636606	24.919682	Ultra Clean CTD	Bottom
1	1	27/07/2013	06:23:34	35.636624	24.919775	Ultra Clean CTD	End
1	2	27/07/2013	06:42:05	35.636629	24.91979	CTD 25L	Begin
1	2	27/07/2013	07:02:18	35.636466	24.919737	CTD 25L	Bottom
1	2	27/07/2013	07:54:54	35.636516	24.919817	CTD 25L	End
2	1	27/07/2013	20:17:28	35.457015	22.689144	Ultra Clean CTD	Begin
2	1	27/07/2013	21:24:40	35.457343	22.689245	Ultra Clean CTD	Bottom
2	1	27/07/2013	23:16:13	35.45696	22.689531	Ultra Clean CTD	End
2	2	27/07/2013	23:27:32	35.456902	22.689396	CTD 25L	Begin
2	2	28/07/2013	00:42:58	35.456894	22.688742	CTD 25L	Bottom
2	2	28/07/2013	02:31:06	35.457075	22.68928	CTD 25L	End
3	1	28/07/2013	06:47:14	35.936705	22.183233	Ultra Clean CTD	Begin
3	1	28/07/2013	07:51:48	35.93677	22.183126	Ultra Clean CTD	Bottom
3	1	28/07/2013	09:24:50	35.93677	22.183096	Ultra Clean CTD	End
3	2	28/07/2013	09:34:40	35.936831	22.182728	CTD 25L	Begin
3	2	28/07/2013	10:51:25	35.936808	22.183423	CTD 25L	Bottom
3	2	28/07/2013	12:50:23	35.937149	22.183669	CTD 25L	End
4	1	28/07/2013	22:09:33	35.865005	20.557523	Ultra Clean CTD	Begin
4	1	28/07/2013	23:00:47	35.864867	20.557592	Ultra Clean CTD	Bottom
4	1	29/07/2013	00:29:32	35.865026	20.557503	Ultra Clean CTD	End
4	2	29/07/2013	00:38:45	35.864946	20.557654	CTD 25L	Begin
4	2	29/07/2013	01:32:03	35.864838	20.557674	CTD 25L	Bottom
4	2	29/07/2013	02:58:58	35.864944	20.557607	CTD 25L	End
5	1	29/07/2013	13:04:06	37.378125	20.163713	Ultra Clean CTD	Begin
5	1	29/07/2013	14:03:14	37.378112	20.163758	Ultra Clean CTD	Bottom
5	1	29/07/2013	15:40:17	37.378063	20.163695	Ultra Clean CTD	End
5	2	29/07/2013	15:51:11	37.37814	20.163701	CTD 25L	Begin
5	2	29/07/2013	16:58:52	37.37815	20.163789	CTD 25L	Bottom
5	2	29/07/2013	18:46:25	37.377986	20.163657	CTD 25L	End
6	1	30/07/2013	05:22:38	38.992878	19.741828	Ultra Clean CTD	Begin
6	1	30/07/2013	05:47:35	38.992926	19.741783	Ultra Clean CTD	Bottom
6	1	30/07/2013	06:48:08	38.99279	19.741746	Ultra Clean CTD	End
6	2	30/07/2013	07:01:38	38.992887	19.741926	CTD	Begin
6	2	30/07/2013	07:28:06	38.99273	19.741645	CTD	Bottom
6	2	30/07/2013	08:26:03	38.992985	19.74178	CTD	End
7	1	30/07/2013	18:02:46	40.204949	19.109507	Ultra Clean CTD	Begin
7	1	30/07/2013	18:19:10	40.205189	19.109795	Ultra Clean CTD	Bottom
7	1	30/07/2013	19:07:57	40.205237	19.10943	Ultra Clean CTD	End
7	2	30/07/2013	19:22:18	40.205212	19.109481	CTD	Begin
7	2	30/07/2013	19:38:53	40.205178	19.109385	CTD	Bottom

7	2	30/07/2013	20:25:38	40.205283	19.109487	CTD	End
8	1	31/07/2013	02:50:43	40.961261	18.536037	Ultra Clean CTD	Begin
8	1	31/07/2013	02:56:34	40.961224	18.536064	Ultra Clean CTD	Bottom
8	1	31/07/2013	02:56:37	40.961222	18.536059	Ultra Clean CTD	End
8	1a	31/07/2013	03:03:19	40.961335	18.53576	Ultra Clean CTD	Begin
8	1a	31/07/2013	03:17:45	40.961259	18.535828	Ultra Clean CTD	Bottom
8	1a	31/07/2013	04:06:19	40.961244	18.535699	Ultra Clean CTD	End
8	2	31/07/2013	04:16:51	40.96124	18.535742	CTD 25L	Begin
8	2	31/07/2013	04:33:59	40.961194	18.535633	CTD 25L	Bottom
8	2	31/07/2013	05:17:41	40.961188	18.535618	CTD 25L	End
9	1	31/07/2013	10:34:54	40.153839	18.816331	Ultra Clean CTD	Begin
9	1	31/07/2013	10:55:21	40.153151	18.816705	Ultra Clean CTD	Bottom
9	1	31/07/2013	11:43:30	40.153708	18.817067	Ultra Clean CTD	End
9	2	31/07/2013	11:53:18	40.154041	18.817111	CTD 25L	Begin
9	2	31/07/2013	12:07:42	40.153799	18.816524	CTD 25L	Bottom
9	2	31/07/2013	13:03:10	40.153794	18.816731	CTD 25L	End
10	1	01/08/2013	04:09:49	38.267434	17.996877	CTD 25L	Begin
10	1	01/08/2013	04:59:34	38.267282	17.997026	CTD 25L	Bottom
10	1	01/08/2013	06:22:28	38.267529	17.996493	CTD 25L	End
10	2	01/08/2013	06:35:49	38.267458	17.996816	Ultra Clean CTD	Begin
10	2	01/08/2013	07:21:38	38.267162	17.996698	Ultra Clean CTD	Bottom
10	2	01/08/2013	08:30:18	38.267322	17.996537	Ultra Clean CTD	End
11	1	01/08/2013	20:02:43	37.400596	15.970509	Ultra Clean CTD	Begin
11	1	01/08/2013	20:44:45	37.400627	15.97041	Ultra Clean CTD	Bottom
11	1	01/08/2013	22:17:23	37.400531	15.970449	Ultra Clean CTD	End
11	2	01/08/2013	22:27:19	37.400418	15.970473	CTD 25L	Begin
11	2	01/08/2013	23:14:13	37.400711	15.970403	CTD 25L	Bottom
11	2	02/08/2013	00:31:45	37.400492	15.970781	CTD 25L	End
12	1	02/08/2013	15:42:41	39.007414	14.502213	Ultra Clean CTD	Begin
12	1	02/08/2013	16:37:08	39.007331	14.502181	Ultra Clean CTD	Bottom
12	1	02/08/2013	18:21:37	39.007453	14.502132	Ultra Clean CTD	End
12	2	02/08/2013	18:32:21	39.007409	14.502211	CTD	Begin
12	2	02/08/2013	19:33:05	39.007298	14.502132	CTD	Bottom
12	2	02/08/2013	21:15:36	39.007674	14.502203	CTD	End
13	1	03/08/2013	06:48:58	39.878063	13.010024	Ultra Clean CTD	Begin
13	1	03/08/2013	08:12:51	39.877781	13.010132	Ultra Clean CTD	Bottom
13	1	03/08/2013	09:47:03	39.877701	13.010246	Ultra Clean CTD	End
13	2	03/08/2013	09:59:17	39.877764	13.010174	CTD 25L	Begin
13	2	03/08/2013	11:02:50	39.877854	13.0101	CTD 25L	Bottom
13	2	03/08/2013	12:46:36	39.87775	13.009948	CTD 25L	End
13	3	03/08/2013	12:54:12	39.877825	13.01001	Ultra Clean CTD	Begin
13	3	03/08/2013	13:13:29	39.877844	13.010105	Ultra Clean CTD	Bottom
13	3	03/08/2013	13:13:38	39.877845	13.010107	Ultra Clean CTD	End
13	4	03/08/2013	14:21:57	39.877949	13.010129	Ultra Clean CTD	Begin

13	4	03/08/2013	15:18:11	39.878015	13.010319	Ultra Clean CTD	Bottom
13	4	03/08/2013	17:01:16	39.877952	13.010223	Ultra Clean CTD	End
14	1	04/08/2013	03:48:58	40.87003	11.299366	Ultra Clean CTD	Begin
14	1	04/08/2013	04:29:20	40.869996	11.299287	Ultra Clean CTD	Bottom
14	1	04/08/2013	05:51:52	40.869882	11.29927	Ultra Clean CTD	End
14	2	04/08/2013	06:05:01	40.869876	11.299303	CTD	Begin
14	2	04/08/2013	06:47:15	40.86983	11.299247	CTD	Bottom
14	2	04/08/2013	08:13:33	40.869999	11.299266	CTD	End
15	1	04/08/2013	16:49:26	42.05074	10.567496	Ultra Clean CTD	Begin
15	1	04/08/2013	17:10:02	42.050721	10.567509	Ultra Clean CTD	Bottom
15	1	04/08/2013	18:14:17	42.050794	10.567333	Ultra Clean CTD	End
15	2	04/08/2013	18:24:56	42.051012	10.567358	CTD	Begin
15	2	04/08/2013	18:46:40	42.050787	10.567303	CTD	Bottom
15	2	04/08/2013	19:37:18	42.050824	10.567377	CTD	End
15	3	04/08/2013	19:47:20	42.050793	10.567405	Ultra Clean CTD	Begin
15	3	04/08/2013	20:07:47	42.050826	10.567285	Ultra Clean CTD	Bottom
15	3	04/08/2013	21:00:04	42.050836	10.567306	Ultra Clean CTD	End
16	1	05/08/2013	15:59:22	41.143868	6.943174	Ultra Clean CTD	Begin
16	1	05/08/2013	16:20:50	41.143801	6.942755	Ultra Clean CTD	Bottom
16	1	05/08/2013	16:24:56	41.143805	6.942731	Ultra Clean CTD	End
16	2	05/08/2013	16:33:59	41.143932	6.94274	CTD	Begin
16	2	05/08/2013	17:20:19	41.143917	6.942574	CTD	Bottom
16	2	05/08/2013	18:47:51	41.143866	6.942607	CTD	End
16	3	05/08/2013	19:17:40	41.143918	6.942559	Ultra Clean CTD	Begin
16	3	05/08/2013	20:01:31	41.143813	6.942568	Ultra Clean CTD	Bottom
16	3	05/08/2013	21:40:41	41.143954	6.94291	Ultra Clean CTD	End
16	4	05/08/2013	21:42:07	41.143923	6.942848	Ultra Clean CTD	Begin
16	4	05/08/2013	22:28:34	41.143883	6.942825	Ultra Clean CTD	Bottom
16	4	05/08/2013	23:39:13	41.143794	6.942895	Ultra Clean CTD	End
17	1	06/08/2013	08:59:20	40.06954	5.947094	Ultra Clean CTD	Begin
17	1	06/08/2013	09:43:45	40.06961	5.947111	Ultra Clean CTD	Bottom
17	1	06/08/2013	11:14:55	40.069429	5.947079	Ultra Clean CTD	End
17	2	06/08/2013	11:26:20	40.069452	5.947095	CTD 25L	Begin
17	2	06/08/2013	12:05:45	40.069636	5.947149	CTD 25L	Bottom
17	2	06/08/2013	13:46:13	40.069605	5.947018	CTD 25L	End
17	3	06/08/2013	13:59:52	40.06983	5.947076	Ultra Clean CTD	Begin
17	3	06/08/2013	14:45:02	40.069582	5.947089	Ultra Clean CTD	Bottom
17	3	06/08/2013	16:10:40	40.069513	5.947009	Ultra Clean CTD	End
18	1	06/08/2013	23:09:36	39.245416	5.262891	Ultra Clean CTD	Begin
18	1	06/08/2013	23:57:38	39.245172	5.262769	Ultra Clean CTD	Bottom
18	1	07/08/2013	01:17:07	39.245274	5.26263	Ultra Clean CTD	End
18	2	07/08/2013	01:26:10	39.245257	5.262779	CTD	Begin
18	2	07/08/2013	02:17:04	39.245257	5.26271	CTD	Bottom
18	2	07/08/2013	03:39:47	39.245134	5.263225	CTD	End

19	1	07/08/2013	11:46:39	38.359114	4.293955	Ultra Clean CTD	Begin
19	1	07/08/2013	12:29:07	38.359069	4.293792	Ultra Clean CTD	Bottom
19	1	07/08/2013	13:46:21	38.359071	4.29369	Ultra Clean CTD	End
19	2	07/08/2013	13:53:20	38.35898	4.293748	CTD	Begin
19	2	07/08/2013	14:37:51	38.358959	4.29395	CTD	Bottom
19	2	07/08/2013	15:58:09	38.358971	4.293923	CTD	End

[1] Time in UTC

Appendix 2.

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