Cruise report 64PE370 on RV Pelagia

MedBlack GEOTRACES leg 1

Lisbon (Portugal) 14-05-2013 to Istanbul (Turkey) 05-06-2013

Micha J.A. Rijkenberg

With contributions of participants

Royal Netherlands Institute for Sea Research

Acknowledgements

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Front page: deployment of the titanium ultraclean CTD frame with 24 x 27L PVDF samplers in the Sea of Marmara on the RV Pelagia

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The MedBlack GEOTRACES leg 1 (64PE370) on RV *Pelagia* started 14 May 2013 departing from Lisbon (Portugal) and ended in Istanbul (Turkey) on 05 June 2013 with Micha Rijkenberg (Royal NIOZ) as chief scientist.

The GA04 GEOTRACES transect was sampled in a combined effort involving two research vessels. Both research vessels followed a similar cruise track. The Spanish research vessel B/O Ángeles Alvariño concentrated on i) large volume sampling for the sampling of (radio) isotopic elements, ii) include biological systems, and iii) the carbon system. The NIOZ research vessel *Pelagia* concentrated on the distribution of the GEOTRACES trace elements and isotopes (TEIs) and many other trace elements and isotopes that necessitates trace metal clean sampling. A large volume non trace metal clean CTD system allowed for sampling of many additional parameters as the carbon system and algae pigments.

Stations

During cruise 64PE370 we occupied a total of 37 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 (25L CTD). When there was a high demand for ultraclean seawater samples from the upper 500m of the water column we performed a third shallow cast with the UCC. Generally, the demand for ultraclean seawater samples was high at the hyper stations 5, 11, 18 and 21 resulting in an extra cast of the UCC to the bottom. Due to complications regarding permissions to sample in territorial waters of the many North African, Asian and European countries it proved impossible to occupy a cross over station with the GA04S cruise track of the Spanish research vessel B/O Ángeles Alvariño. Details like the date, time and position of the actual deployments at each station can be found in Appendix 1. Note that station positions of the original station schedule may have changed slightly at certain locations.

Before arriving at station 1 we did two test stations with the ultraclean CTD (UCC). These test stations did not get a station number. At both test stations there were some problems with the pump for the oxygen sensor of the UCC. On our first cast at station 1 the UCC was deployed to the bottom to rinse the PVDF CTD bottles. On its way up most communications with the UCC CTD failed. However, all bottles could be closed at 1500m depth to sample the deep sample for the isotope intercomparison exercise. Also during the second cast with the high volume CTD (25L CTD) were communication problems with the CTD frame. Only the deepest 7 of the 24 bottles of the 25L CTD were closed and sampled for DIC, alkalinity, nutrients and microbiology. During cast 3 the remainder of the 24 depths were sampled with the 25L CTD. Cast 4 was the regular UCC cast to the bottom and cast 5 was a shallow dip to collect a large volume of seawater at 25m for a shallow sample for the isotope intercomparison exercise. The communication problems were caused by contact problems in the bulkhead-connector of the CTD-underwater unit. It was solved by taking away the bulkhead-connector of the CTD-underwater unit.

Due to heavy swell station 10 was sampled by the UCC CTD till a depth of 1500m. The bottles were closed while the UCC CTD was brought up.

Station 17 started with the deployment of a mooring for Jan-Berend Stuut (deployed on 26 May 2013 at 10:15 UTC, position: 34°57.919N, 18°02.397E) with 1 sediment trap to collect Saharan dust during one year. After the deployment of the mooring RV Pelagia relocated to 1 nautical mile from the deployed mooring to execute its regular station casts.

The bottles of the 25L CTD at station 21 did not close. Instead deep samples for DIC and alkalinity were sampled from the UCC CTD. A second dip of the 25L CTD to 200m provided the remainder of the samples for DIC and alkalinity in the upper water column. At station 25 the multivalve bottle-controller of the UCC got broken due to a mistake during deck-transport of the UCC-frame. Because repairs would take a reasonable long time only the cast with the 25L CTD was executed here.

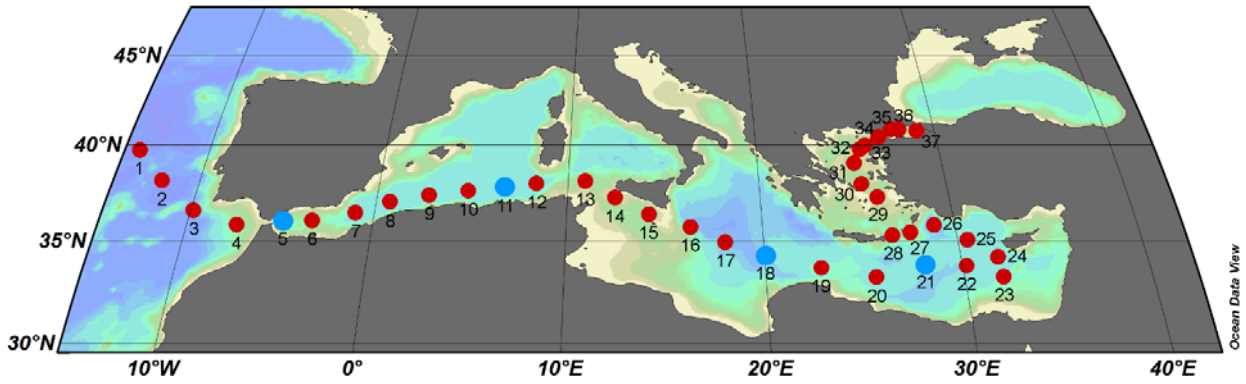

Figure 1. Cruise track of research cruise 64PE370 on the RV Pelagia in May-June 2013. Red dots represent normal stations with typically one full depth UCC cast or a full depth UCC and 25L CTD cast to the bottom. Blue dots represent hyper stations with 2 full depth UCC casts and 1 full depth 25L CTD cast.

Cruise narrative

About half of the participants boarded the RV *Pelagia* on Texel on 8 May joining the trip to Lisbon (cruise 64PE369). During 64PE369 a cubic meter container was filled with trace metal clean seawater (see cruise report Hans Slagter). The time on board between 8-14 May was further used to set up and test equipment and preparing the ship for the arrival of the participants boarding in Lisbon. The RV Pelagia arrived in the evening of 13 May in Lisbon. After embarkation of the remainder of the participants the RV *Pelagia* set out for the first leg (64PE370) of the MedBlack GEOTRACES cruises in the morning of 14 May at 11:00 UTC (13:00 time on board). We immediately entered relatively rough weather leaving Lisbon.

We arrived at station 1 on 15 May at 17:00 a bit more over 24 hours after leaving Lisbon. The first station was immediately the hardest of the whole cruise and took till 19:30 the next day to complete. In rough weather we sampled station 1 as if it was a hyper station. In addition, we sampled large volumes of trace metal clean seawater for the stable isotope intercomparison exercise. The weather became calmer when we crossed the Strait of Gibraltar. We sampled station 5 on 19 May with the Spanish mainland within sight, see Figure 2.

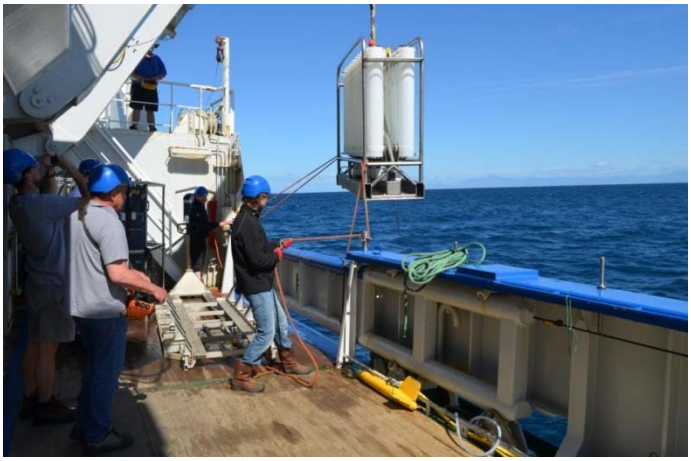

Figure 2. Deployment of the UCC at station 5 after crossing the Strait of Gibraltar into the Mediterranean Sea. Spain can be seen on the horizon.

On 20 May we entered Algerian waters. An Algerian observer boarded RV Pelagia close to station 7 and was picked up again by the Algerian coastguard on 22 May at 06:00 UTC. During the stay of the Algerian observer we had some rough weather delaying the cruise. The weather cleared up and the sea went calm after station 11. At station 17 on 26 May we deployed the mooring with the sediment trap of Jan-Berend Stuut to collect Saharan dust, see Figure 3 a. The Saharan dust event that we encountered 3 days later on 29 May was too early to be recorded in the sediment trap (Figure 3 b, c) but was sampled by the aerosol collectors above the bridge.

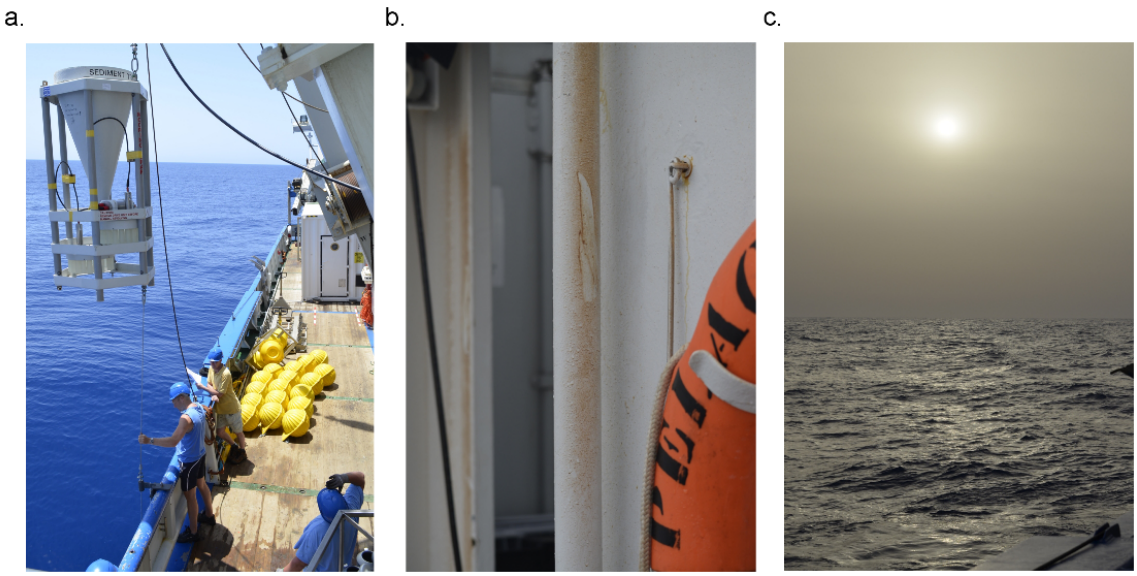

Figure 3. a.) Deployment of the mooring with a sediment trap at station 17 on 26 May 2013. b.) A dusty ship after a Saharan dust event on 29 May 2013. c.) Saharan dust in the sky fading the sun on 29 May 2013.

Jan van Ooijen also collected 4 cubic meter vessels with nutrient poor seawater on 26 May around 08:00 UTC. Hans Slagter collected 1 cubic vessel with ultraclean sampled seawater on

29 May between station 20 and 21 (Fish in 06:35 UTC at 33°22.0N, 26°14.0E and FISH out 12:35 UTC at 33°40.1N, 27°25.3E).

In the morning of 31 May we reached station 24 where the Turkish observer boarded RV Pelagia. The Turkish observer stayed on board until disembarkation in the port of Istanbul. We arrived in Istanbul at 11:30 local time on 5 June 2013. The RV Pelagia was brought into the harbor at 21:00 local time. The participants disembarked in the afternoon of 6 June 2013.

Ship's clock

The ship left the harbour on 14 May 2013 with the ship's time set on UTC+2. The ship's time was advanced in the early morning of 28 May 2013 to UTC+3.

Weather

The weather conditions were excellent during most of the expedition. Combinations of wind and swell made work difficult on 14-16 May and at station 10 on 22 May (Figure 4).

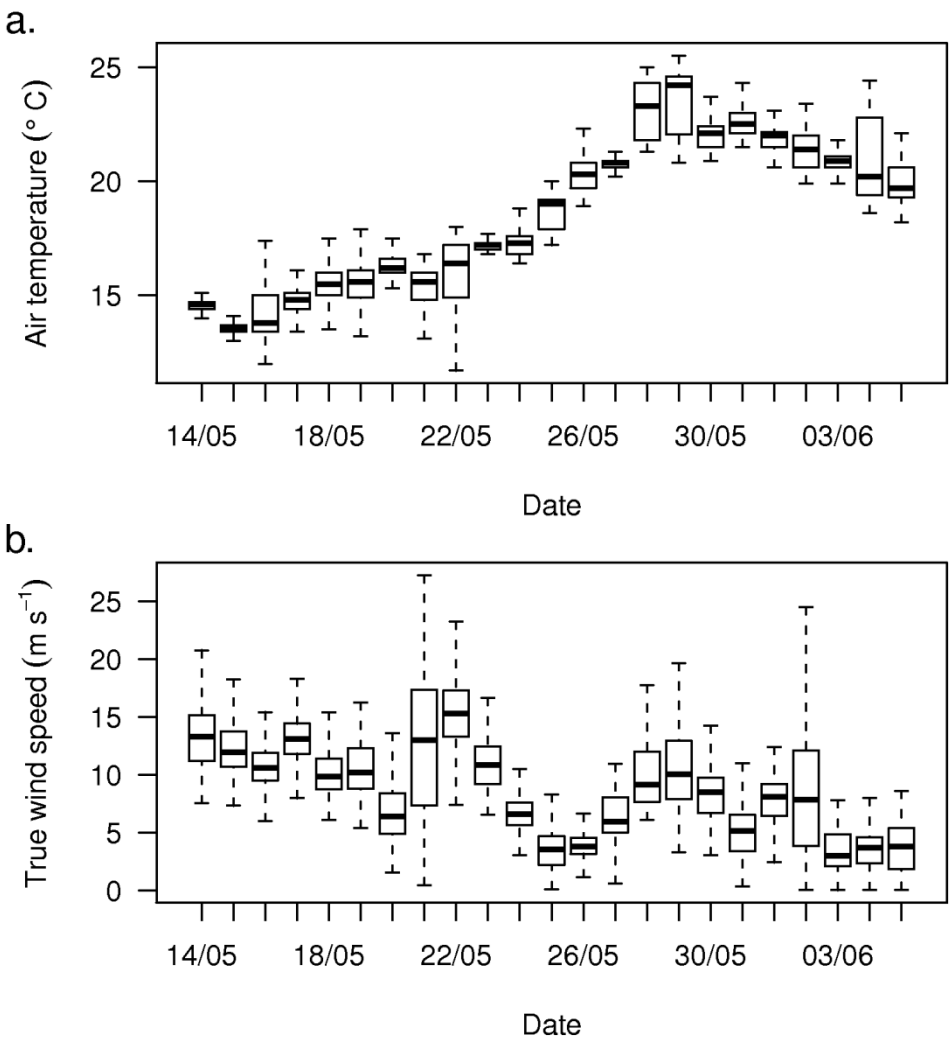

Figure 4. The air temperature (a.) and true wind speed (b.) during 64PE370.

General preliminary results

This paragraph will show the section plots of some of the parameters directly measured on board on a section distance scale in km. To distinguish the different transects the map in Figure 5 shows colour codes for each set of stations that form a roughly straight transect. Parameters measured on board were salinity (from CTD sensor, Figure 6), the nutrients (phosphate, nitrate, nitrite and silicate, Figure 7-10), and other CTD sensor output (e.g. temperature, fluorescence (Figure 11), oxygen, beam attenuation coefficient).

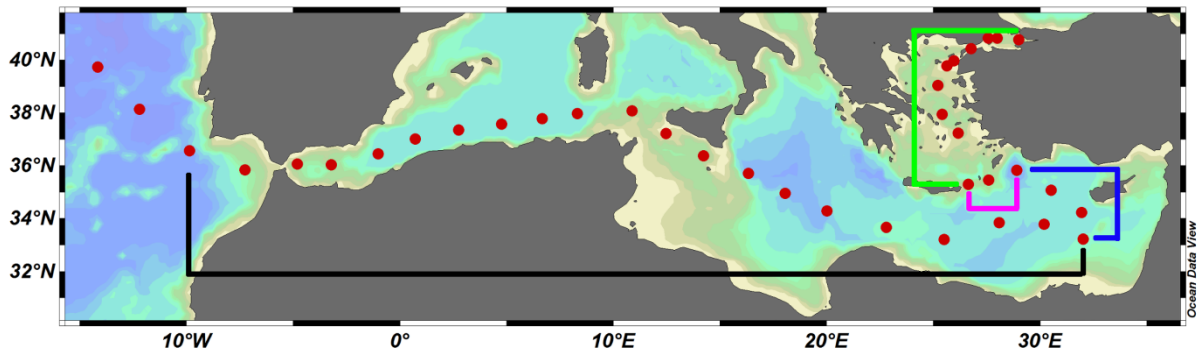

Figure 5. The cruise track of cruise 64PE370 with 4 transects of a set of stations that form more or less a straight line. The black transect contains the stations 1-23, the blue transect contains the stations 23-26, the pink transect contains the stations 26-28, and the green transect contains the stations 28-37.

The salinity section plot shows some clearly recognizable water masses. In the Western and the eastern Mediterranean basin one recognizes the Modified Atlantic Water (MAW) formed by the inflow of Atlantic water which is progressively modified by air-sea interaction and mixing along its path through the both basins (Robinson et al., 1992; Send et al., 1999). In the Western Mediterranean on the Algerian side below the MAW lies the Levantine Intermediate Water (LIW) generated in the eastern Mediterranean basin and below the LIW lies the Western Mediterranean Deep Water (WMDW) (Send et al., 1999). The WMDW is formed via deep convection in the Gulf of Lions, and fills the deeper levels of the western basin (Send et al., 1999).

In the Eastern Mediterranean, deep water formation occurs primarily in the Adriatic Sea, which produces bottom water, the Eastern Mediterranean Deep Water (EMDW) (Robinson et al., 1992). However, Aegean Deep Water (AGDW) also forms, sinking to depths somewhere in the middle of the water column. In the Levantine basin, predominantly in March, LIW is formed during storm events. This new LIW circulates and disperses at depths down to a few hundred meters and may recirculate within the basin or exits beneath the MAW through the Sicily Straits (Robinson et al., 1992).

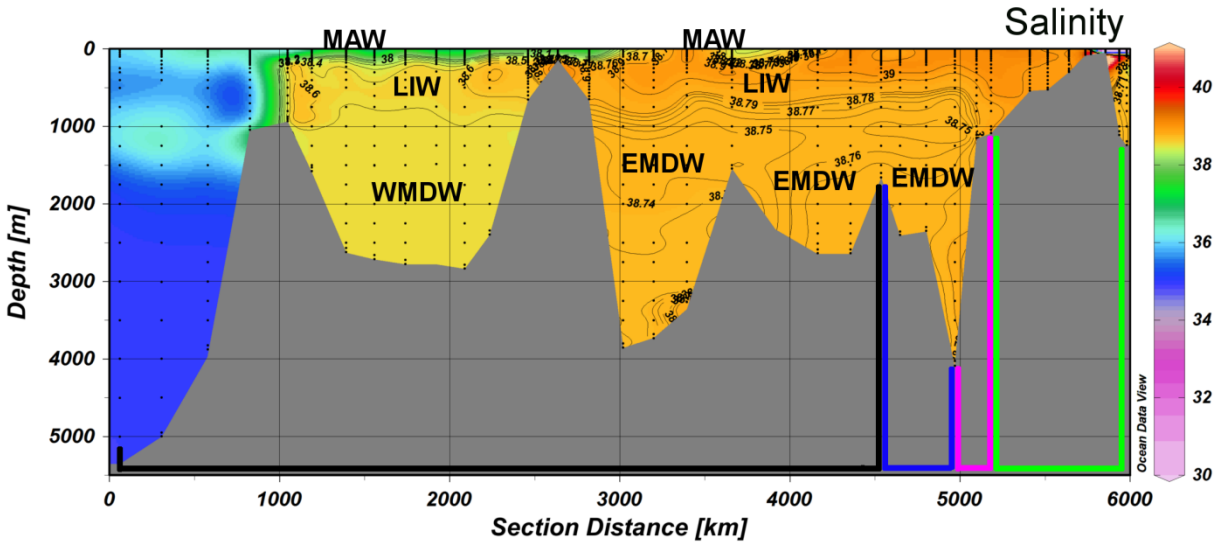

Figure 6. The section plot of preliminary salinity data (UCC sensor data) for the 64PE370 in the Mediterranean Sea. Water masses indicated are the Modified Atlantic Water (MAW), the Levantine Intermediate Water (LIW), the Western Mediterranean Deep Water (WMDW) and Eastern Mediterranean Deep Water (EMWD). Data: Sven Ober and Ruud Groenewegen.

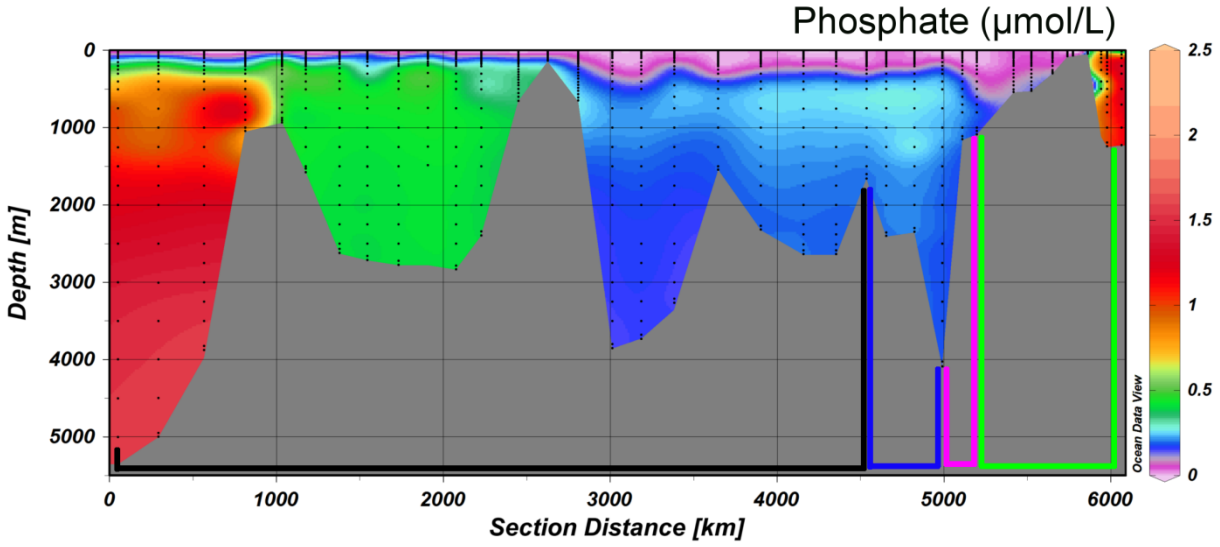

Figure 7. Preliminary phosphate data from the UCC for the 64PE370 in the Mediterranean Sea. Data: Jan van Ooijen

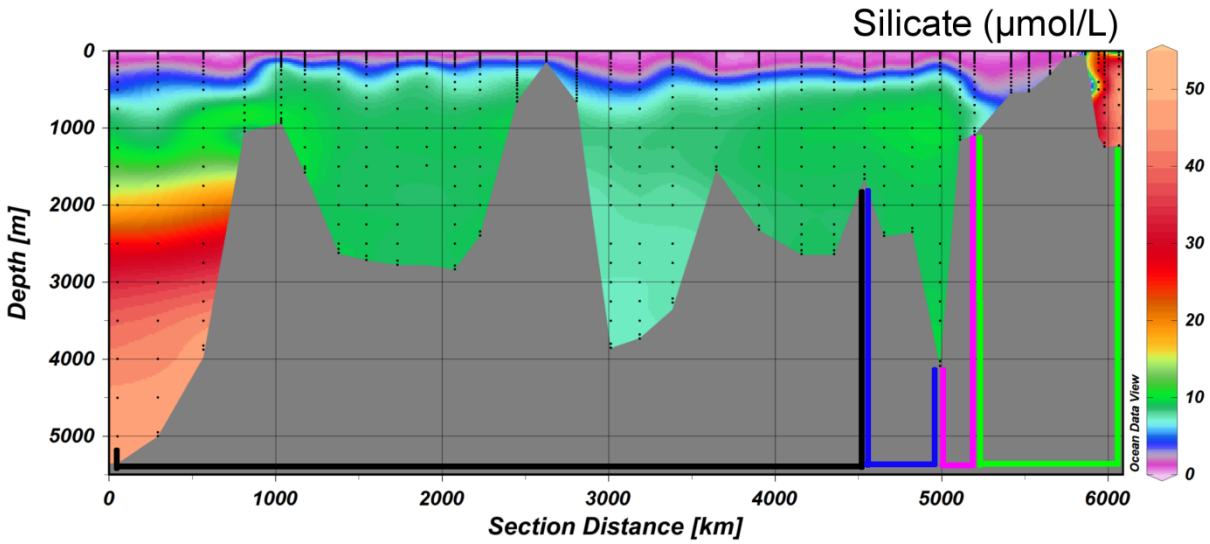

Figure 8. Preliminary silicate data from the UCC for the 64PE370 in the Mediterranean Sea. Data: Jan van Ooijen

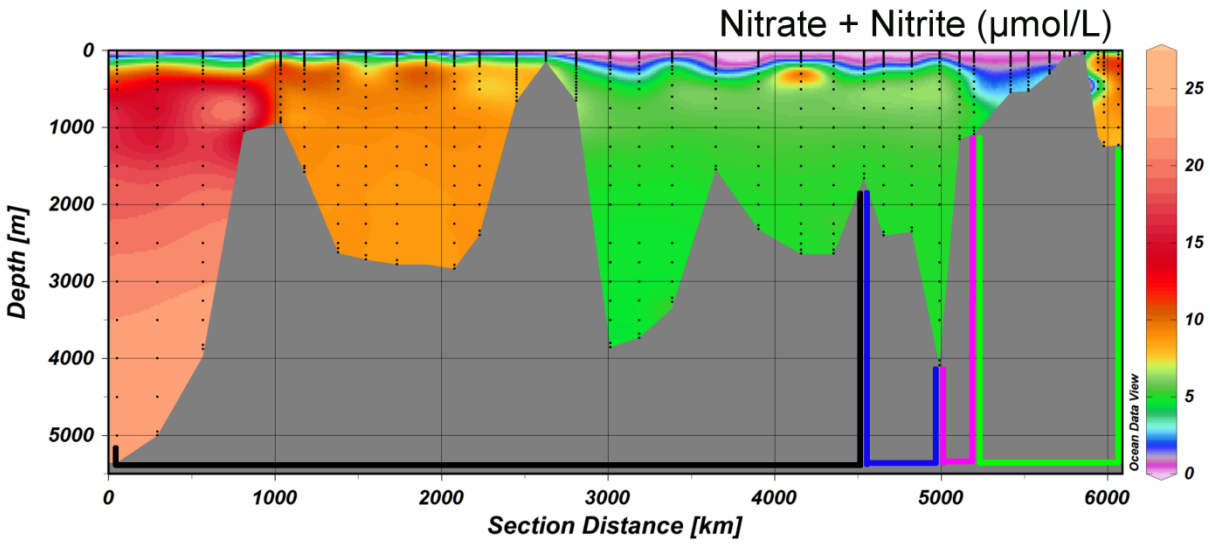

Figure 9. Preliminary nitrate + nitrite data from the UCC for the 64PE370 in the Mediterranean Sea. Data: Jan van Ooijen

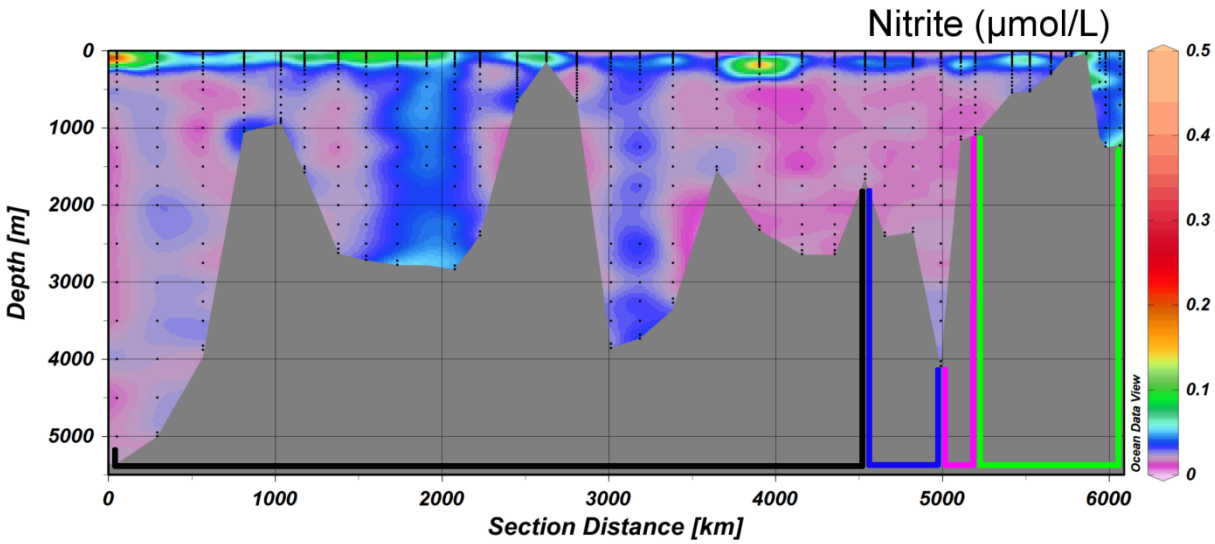

Figure 10. Preliminary nitrite data from the UCC for the 64PE370 in the Mediterranean Sea. Data: Jan van Ooijen

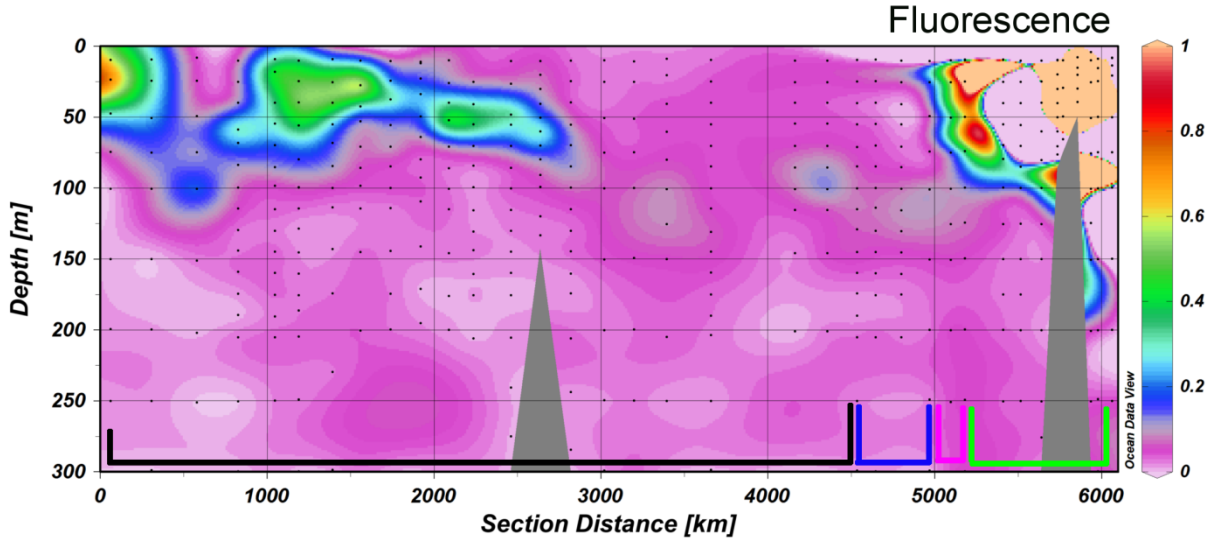

Figure 11. Preliminary fluorescence data from the UCC for the 64PE370 in the Mediterranean Sea. Data: Sven Ober and Ruud Groenewegen

Underway surface data

Figure 12, 13 and 14 show the underway surface seawater data as measured by the ship's Aqua flow system (Chelsea Instruments). The sea surface temperature ranges between 15-25°C and increases in an eastward direction (Figure 12). A similar pattern is visible for the salinity of the surface waters were the seawater coming from the Atlantic Ocean increases in salinity due to ongoing evaporation and mixing (Figure 13). In concert with the nutrient distributions, the underway surface fluorescence decreases in eastward direction (Figure 14).

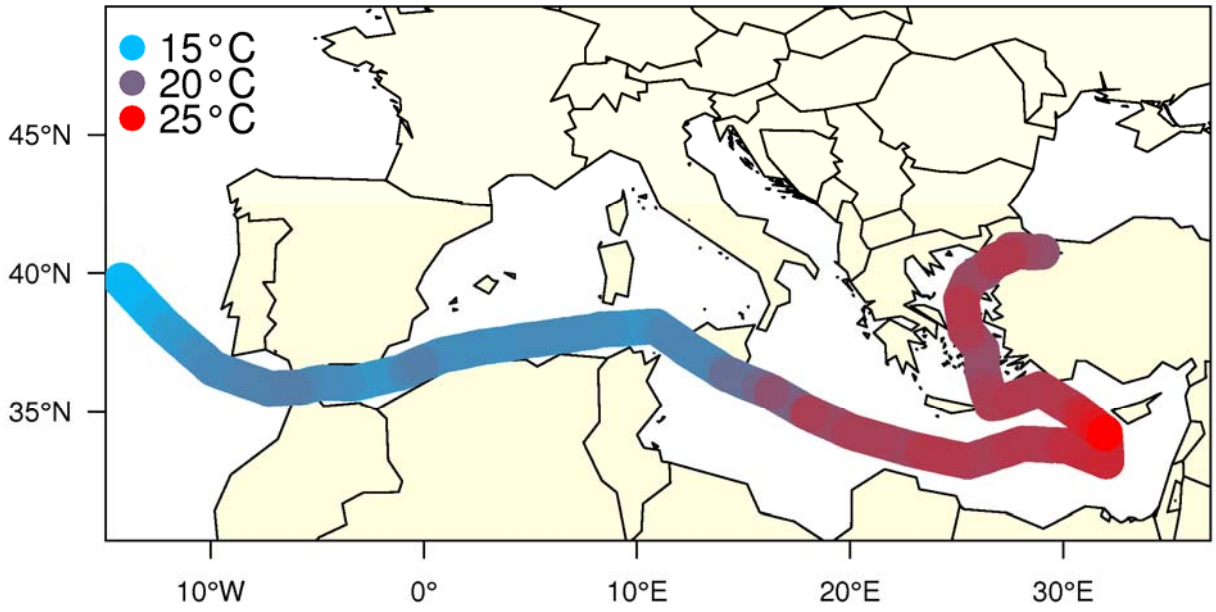

Figure 12. The preliminary sea surface temperature data as measured with the ship's underway system during 64PE370.

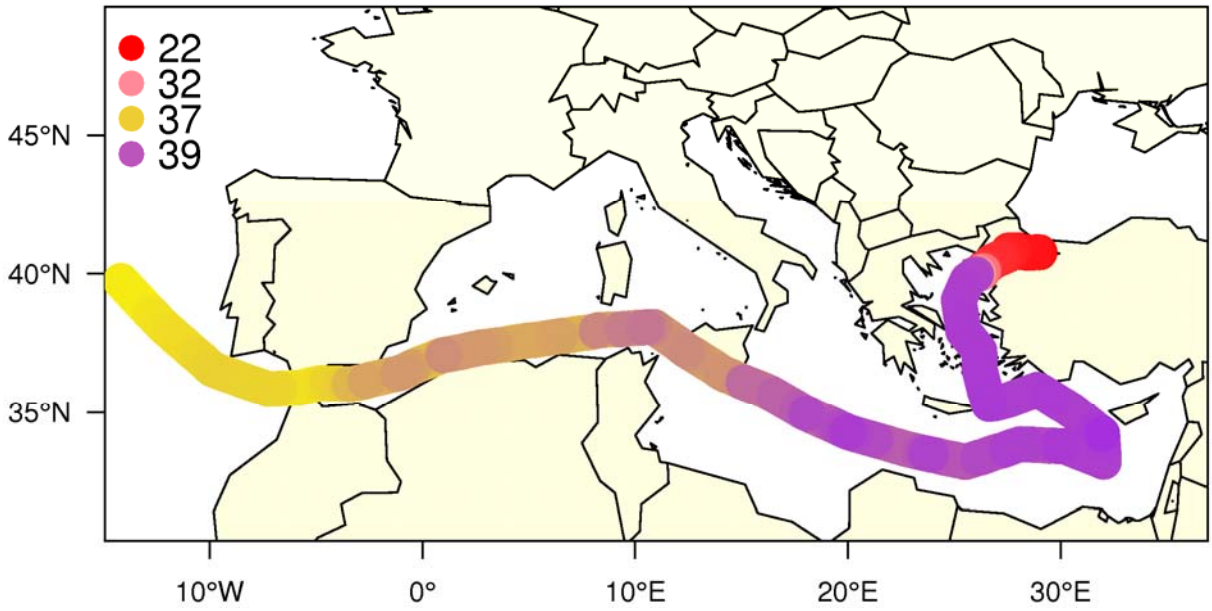

Figure 13. The preliminary sea surface salinity data as measured with the ship's underway system during 64PE370.

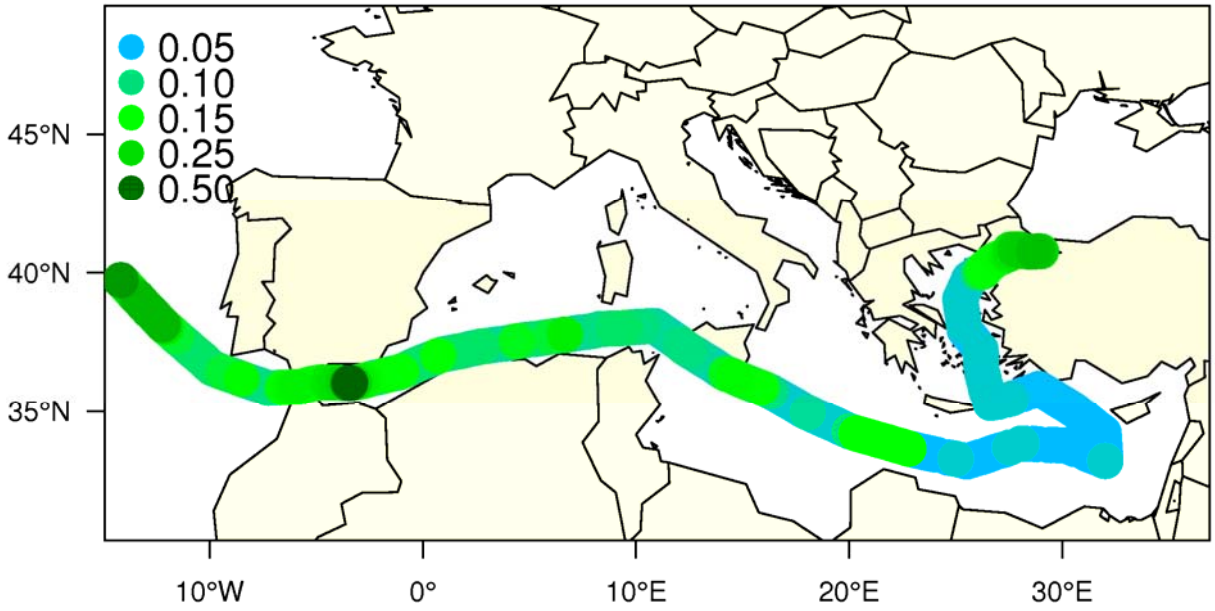

Figure 14. The preliminary sea surface fluorescence data as measured with the ship's underway system during 64PE370.

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 (UltraClean Ctd abbreviated UCC), see Figure 15. A Kley France winch was used to deploy the UCC to deep ocean 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 sample trace metal clean in anoxic and hyper saline environments we use a dedicated plastic-coated frame with GO-FLOW samplers called "the brine frame". Filtered samples were taken under nitrogen pressure on deck. We used plastic bags to shield the sampling from contamination.

To collect non trace metal clean samples a high volume CTD frame of stainless steel was used equipped with 24 water samplers each with a volume of 25 liter manufactured by Ocean Test Equipment.

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.

More details about the CTD frames used can be found at page 25.

Figure 15. The sample equipment used to take trace metal clean and non-trace metal clean water samples during 64PE370.

Concluding

With 37 full depth stations we have completed the first 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. 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 therefore ideal to investigate the effect of dust on the biogeochemical cycles of trace elements and isotopes. We sampled an extensive set of parameters with direct on board measurement of the trace metals Fe and Al, the CO_2 system, nutrients at nanomolar as well as micromolar concentrations, organic speciation and size fractionation 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, Hg, Ba, U, Mo, the rare earth elements, the isotopes of Fe, Cu, Zn, Cd, Pb, Cr, Ni, Nd, Si, ^{15}N, ^{18}O, D, Ra radio nuclides, algae pigments, coccoliths, POC, particulates and other elements.

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2. General introduction 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. 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 therefore 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, 2000a) 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 (Boyle et al., 1985; Thuróczy et al., 2010; Hydes, 1983; 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 (Guerzoni et al., 1999; Ternon et al., 2011; Wagener et al., 2010; Quétel et al., 1993; Bonnet and Guieu, 2006). 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, however, Fe was still 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 (Bonnet and Guieu, 2006; Sarthou and Jaendel, 2001). 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 (Sarthou and Jaendel, 2001; Krom et al., 1999; 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 (Yemenicioglu et al., 2006; Lewis and Landing, 1991). 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; Bonnet and Guieu, 2006; Saydam, 1996; Saager et al., 1993; de Baar et al., 2001; Statham and Hart, 2005; Zeri and Voutsinou-Taliadouri, 2003). 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; BIO-Chemical Oceanography
2	**Marietta Anthoulas**	Helenic Center For Marine Research
3	**Marcel Bakker**	NIOZ; MTEC
4	**Pim Boute**	University of Groningen
5	**Nikki Clargo**	NIOZ; BIO-Chemical Oceanography
6	**Gabriel Dulaquais**	LEMAR IUEM
7	**Ruud Groenewegen**	NIOZ; MRF
8	**Patrick Laan**	NIOZ; BIO-Chemical Oceanography
9	**Rob Middag**	University of Otago
10	**Sven Ober**	NIOZ; FYS
11	**Jan van Ooijen**	NIOZ; MRF
12	**Joaquin Pampin**	NOC, Southampton
13	**John Rolison**	University of Otago
14	**Aymen Saadi**	INSTM Salambôo
15	**Lesley Salt**	NIOZ; BIO-Chemical Oceanography
16	**Nicolas Sanchez**	NTNU Norway
17	**Hans Slagter**	NIOZ; BIO-Chemical Oceanography
18	**Leon Wuis**	NIOZ; MTEC

For complete addresses and email see Appendix 2

Figure 16. Scientists and crew during 64PE370 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) Marietta Anthoulas
2) Hans Slagter
3) Gabriel Dulaquais
4) Nicolas Sanchez
5) Joaquin Pampin
6) Micha Rijkenberg
7) Patrick Laan
8) John Rolison
9) Rob Middag
10) Pim Boute

Figure 17. a) Nicolas and Patrick, b) Marietta and Rob, c) Pim and Hans, d) John, and e) Gabriel sampling in the ultra clean container.

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
Nutrients (µM)	J. van Ooijen	J. van Ooijen
Nutrients (nM)	J. Pampin	J. Pampin, E. Achterberg
Dissolved Fe	M. Rijkenberg	P. Laan, M. Rijkenberg
Fe ultra filtration	M. Rijkenberg	P. Laan, M. Rijkenberg
Fe Speciation	H. Slagter	H. Slagter, L. Gerringa
Fe Speciation	H. Slagter	L. Laglera
Dissolved Al	R. Middag/J. Rolison	R. Middag/J. Rolison
Dissolved Cu	G. Dulaquais	Waeles, Pernet-Coudrier, Riso
Dissolved Ag	M. Rijkenberg/UCC team	E. Achterberg
Dissolved Co	G. Dulaquais	G. Dulaquais, M. Boyé
Co-speciation	G. Dulaquais	G. Dulaquais, M. Boyé
Cu-speciation	G. Dulaquais	Waeles, Pernet-Coudrier, Riso
Co, Zn, Cd ultrafiltration	G. Dulaquais	G. Dulaquais, M. Boyé
Total dissolvable Co, Zn, Cd	G. Dulaquais	G. Dulaquais, M. Boyé
Total dissolvable Cu	G. Dulaquais	Waeles, Pernet-Coudrier, Riso
$^{15}NO_3$	M. Rijkenberg/UCC team	R. Ganeshram
Nd isotopes	M. Rijkenberg/UCC team	C. Jeandel
Nd isotopes	M. Rijkenberg/UCC team	M. Frank
Aerosols (mineral comp)	P. Boute	J.-B. Stuut
Aerosols (major ions, trace metals)	P. Boute	A. Baker
DGT labile Fe	N. Sanchez	N. Sanchez, M. van Ardelan
Size fractionated plankton Fe	N. Sanchez	N. Sanchez, M. van Ardelan
Dissolved Hg	M. Rijkenberg/UCC team	L.-E. Heimburger
Dissolved Mo	H. Slagter/UCC team	J.-M. Godoy
Dissolved Ba	H. Slagter/UCC team	J.-M. Godoy
Dissolved U	H. Slagter/UCC team	J.-M. Godoy
Dissolved ^{18}O	H. Slagter/UCC team	J.-M. Godoy
Deuterium	H. Slagter/UCC team	J.-M. Godoy
Dissolved Fe isotopes	J. Rolison	J. Rolison/C. Stirlinger
Dissolved Zn 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
Dissolved Cu isotopes	G. Dulaquais	O. Rouxel

Pb isotopes	M. Rijkenberg/UCC team	S. Galer, W. Abouchami
Cr isotopes	M. Rijkenberg/UCC team	S. Galer, W. Abouchami
Ni isotopes	M. Rijkenberg/UCC team	S. Galer, W. Abouchami
Dissolved Si isotopes	M. Rijkenberg/UCC team	D. Cardinal
Humic acids	G. Dulaquais	Waeles, Pernet-Coudrier, Riso
Coccoliths	G. Dulaquais	M. Boyé
Coccolith taxonomy	G. Dulaquais	M. Boyé
POC	G. Dulaquais	G. Dulaquais, M. Boyé
Particulate Co (other metals, CTD)	G. Dulaquais	G. Dulaquais, M. Boyé
DOC/CDOM	M. Anthoulas	C. Zeri
DOC/CDOM	M. Anthoulas	C. Santinelli
Salinity	S. Ober/UCC team	S. Ober
25L CTD		
DIC & Alkalinity	N. Clargo, L. Salt	N. Clargo, L. Salt
Phytoplankton pigments	P. Boute	W. van de Poll
Oxygen	P. Boute	L. Salt, J. van Ooijen, S. Ober
Ships underway SW system		
Ra isotopes	M. Rijkenberg	V. Rodellas, J. Garcia-Orellana

[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

Sven Ober and Ruud Groenewegen

Royal Netherlands Institute for Sea Research, Texel, the Netherlands

During the cruise 3 different CTD-systems were deployed.

1) An Ultra Clean CTD-system for ultra clean trace metal sampling (43 casts).
2) A Large Volume CTD for almost all the other sampling like DIC & alkalinity, dissolved oxygen (DO) and phytoplankton (34 casts)
3) For one CTD-cast the so called "Brine-system" was deployed.

All these systems are more or less off-standard and therefore briefly described below.

Description of the UCC-system

The system consists of 3 major modules:

- A box-shaped titanium CTD frame with 24 sampling bottles made of PVDF and titanium
- 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, see Figure 18. To prevent contamination and to keep the UCC safe and secure the UCC was at all times placed inside the clean air container (meeting class 100 clean-room specifications) when not in use during casts. Prior to a cast the frame was prepared inside that container and transported to the CTD-launching spot using a custom made aluminum pallet and a longbedded forklift. After the cast the UCC was immediately returned to the clean air container to avoid 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).

The electronic CTD sensor system consists of a SBE9plus underwater unit, a SBE11plusV2 deck unit, 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 water sampling 24 samplers (24 liter each) were used. These samplers were produced by NIOZ and are made of PVDF and titanium. Due to the butterfly-type closure on both ends of the sampler the opening is maximized resulting in an excellent flow-through. Opening and closing of the samplers are controlled by a hydraulic system. The heart of the sampling system is the NIOZ developed Multivalve. For bottom-detection 2 devices were 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 calibration of the profiling thermometer (SBE3) a high-accuracy reference-thermometer (SBE35) was mounted for about half of the casts.

Figure 18. The UCC CTD deployed in the Sea of Marmara during 64PE370.

Description of the Large Volume CTD-system (LV-CTD or 25L CTD)

The CTD-system consists of a SBE9plus underwater unit, a SBE11plusV2 deck unit, a SBE32 carousel, a SBE3plus thermometer, a SBE 4 conductivity sensor, a SBE5T underwater pump, 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 large volume watersampling 24 watersamplers each with a volume of 25 liter manufactured by Ocean Test Equipment were used. These 25-liter samplers are equipped with a internal stainless steel spring and a horizontally mounted Teflon drain assembly. Via this drain assembly sample-bottles and jerry cans can be filled easily, see Figure 19. For bottom detection 2 devices were installed: A Benthos PSA-916 altimeter and a bottom switch with a weight on a 10 meter rope. The SBE11+ had 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.

Figure 19. Pim Boute sampling oxygen from the 25L CTD during 64PE370.

Description of the Brine-system

The Brine CTD-system was designed to measure and sample in brines, see Figure 20. Brines are a type of highly saline underwater lake like basins on the bottom of the Mediterranean Sea. The system consists of a SBE9plus underwater unit, a SBE11plusV2 deck unit, a GO-carousel, a SBE3plus thermometer, a wide-range SBE4 conductivity sensor, a SBE5T underwater pump and a bottom-switch with a weight on a 10 meter rope for bottom-detection. In this occasion a Benthos PSA-916 altimeter was mounted for extra bottom-detection and to find out whether it is possible to detect the seawater/brine-interface acoustically. In order to sample as clean as possible the frame was plastic-coated and GO-FLOW samplers were used.

Figure 20. John Rolison sampling for metal isotopes from the brine frame deployed in the Bannock basin during 64PE370.

Functioning of the CTD's

A total of 78 casts were carried out and in general the equipment worked good, but some problems had to be solved as well. In the very beginning of the cruise a broken conductor in the termination of the cable caused some delay. The DO-sensor of the UCC-system worked unreliable during the first casts due to contact problems in the bulkhead-connector of the CTD underwater unit. This problem was circumvented by slightly bending of the contact-pins and so enforcing better contact. At one occasion the Multivalve broke during transport of the UCC-frame out of the container. The repair took a couple of hours because spares appeared not to be fully compatible. For the future fully compatible spares will be brought. During the cruise strange RS-232/modem problems occurred sometimes. These problems are still not fully understood or diagnosed. The fluorometer of the UCC showed in the beginning of the cruise a greater sensitivity than the fluorometer of the 25L CTD. However during the cruise its noise-level increased and at the end of the cruise is was decided to exchange it for a spare and send the instrument back to Chelsea for repair, probably under warranty.

For in situ calibrations of the profiling CTD-thermometers (type SBE-3) a Seabird reference-thermometer (type SBE35) was used. A first analysis of the temperature calibration data showed that both profiling thermometers performed well within the specifications: the accuracy is better than 1 mK with st.dev 0.8 mK. For the calibration of the C-sensors (salinity) of the UCC and the 25L CDT samples (Figure 21) were taken and analyzed on board for salinity using a Guildline 8400B Autosal calibrated by a OSIL standard batch P154. A first analysis of the salinity data showed that the conductivity-sensor of the UCC-system performed within the specifications. The difference between the Autosal-salinity and the UCC-salinity was on average smaller than 0.001 with a st.dev of 0.0005. The conductivity-sensor of the 25L CTD showed a small offset of 0.004 in salinity. During the postprocessing the data will be corrected.

After most of the casts of the 25L CTD samples were tapped for Winkler titrations in order to calibrate the DO-sensors. A first analysis of the Winkler results showed that the DO-sensor drifted slowly and linear in time towards less sensitive. After correction for this drift the average difference between Winklers and DO-sensor was 0.1 microM/kg with a st.dev of 1.2 microM/kg

Figure 21. Ruud Groenewegen (left) prepares the UCC for deployment and Sven Ober (right) takes samples for salinity from the 25L CTD frame 64PE370.

4.1.2. Dissolved oxygen

Lesley Salt, Nikki Clargo and Pim Boute

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Dissolved oxygen was measured from three depths from 21 of the Large Volume 25L CTD casts to check the calibration of the oxygen sensor fixed to the CTD frame itself (Ossebaar, 2012). 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. Thus, the yellow colored bottles were used during sampling of this cruise with the correction factor of 1.0345 being used.

Sampling

Samples of seawater were obtained from the CTD sampler from only three depths as a calibration for the oxygen sensor fixed to the CTD frame itself. Seawater was siphoned into the 120 ml oxygen bottles (yellow labeled volume class) 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%). The precise addition of chemicals (A) and (B) is important because they dilute the sample. 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 are needed to be stored under water for at least 2 hours after the second shaking. Samples were measured a few days later. 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 flee was inserted into a bottle, the bottle was immediately covered with parafilm and a dark plastic cylinder. 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. The calibration of the system gave a correlation coefficient of 1.0000 for 4 calibration points, for linear chemistry. Duplicate samples were measured from each station to control both the sampling procedure and the reproducibility of the spectrophotometer. The standard deviation of the difference between all duplicate samples was 0.715 umol L^{-1}. The measured absorbance of the iodine at 460 nm wavelength is linear up to an equivalent of 350 mmol O_2 L^{-1}, which is within the range of open ocean oxygen concentrations.

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4.1.3. Nutrients

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Summary

On this cruise around 1400 samples were analyzed for Phosphate, Silicate, Nitrate and Nitrite. The samples were measured on a Seal Analytical QuAAtro Autoanalyzer connected to an autosampler. The different nutrients were determined colorimetrical as described by Grashof (1983).

Methods

Samples were obtained from an Ultra Clean CTD and from a large volume CTD rosette sampler with bottles of 25 Liter each. All CTD-samples were taken in a polypropylene bottle. The samples were sub-sampled in a 5 ml polyethylene vial. These vials were all stored dark at 4 °C. All CTD-samples were analyzed within 18 hours on a QuAAtro autonalyzer. As a light source the QuAAtro uses a LED instead of a lamp to avoid the noise effect of the movements of the ship on the light source and therefore on the baseline.

Standards were prepared fresh every day by diluting the stock solutions of the different nutrients in nutrient depleted surface ocean water. This water is also used as baseline water. Each run of the system had a correlation coefficient for 9 calibrant points of at least 0.9999. The samples were measured from the lowest to the highest concentration in order to keep the carry over effects as small as possible.

In every run a mixed nutrient standard containing phosphate, silicate and nitrate in a constant and well known concentration was measured as a triplicate. Also a reference standard was measured as a duplicate in several run to check the concentration of the mixed nutrient standard. This reference standard (Lot BU) made by Kanso in Japan, was ready to use and contained a known concentration of phosphate, silicate, nitrate and nitrite.

Chemistry

Phosphate reacts with ammoniummolybdate at pH 1.0, and potassiumantimonyl-tartrate was used as an inhibitor. The yellow phosphate-molybdenum complex was reduced by ascorbic acid and measured at 880 nm (Riley & Murphy, 1962).

Silicate reacts with ammoniummolybdate to a yellow complex, after reduction with ascorbic acid the obtained blue silica-molybdenum complex was measured at 800nm. Oxalic acid was used to prevent formation of the blue phosphate-molybdenum (Strickland & Parsons, 1968).

Nitrate plus nitrite was mixed with a buffer imidazol at pH 7.5 and reduced by a copperized cadmium column to nitrite. This was diazotated with sulphanylamide and naphtylethylenediamine to a pink colored complex and measured at 550 nm. After substracting the value of the nitrite analysis the nitrate value was achieved (Grasshoff et al, 1983).

Nitrite was diazotated with sulphanylamide and naphtylethylenediamine to a pink colored complex and measured at 550nm (Grasshoff et al, 1983).

Statistics of the analysis of this cruise

The standard deviation of the analysis of samples taken from 15 bottles of the Ultra Clean CTD at a depth of 1500 meter analyzed in one run:

PO4	:	0.002 uM
Si	:	0.046 uM
NO3 + NO2	:	0.037 uM
NO2	:	0.003 uM

The standard deviation of mixed nutrient standard between different runs:

PO4	:	0.005 uM
Si	:	0.058 uM
NO3 + NO2	:	0.051 uM
NO2	:	0.009 uM

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4.2. Sampling and analysis of key parameters

A. Metals and isotopes

5.2.A.1. Dissolved Fe

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Work at sea

Dissolved iron (DFe) concentrations of 34 full depth stations were measured directly on board by an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998 (Figure 22). For some selected stations also Fe filtered over a filter cartridge with a pore-size of 0.02µm has been collected and measured directly on board (see 4.2.A.2). In addition, unfiltered samples (every other depth) from all stations were acidified and stored to determine the total dissolvable Fe concentrations in the NIOZ laboratory after 12 months of dissolution.

DFe from filtered (0.2µm Sartobran 300 filter cartridge, Sartorius) and acidified (pH 1.8, 2ml/L 12M Baseline grade Seastar HCl) seawater was concentrated on a column containing the solid phase aminodiacetid acid (IDA). This material binds only transition metals and not the interfering salts. After washing the column with ultrapure water to remove the salts, the column was eluted with diluted hydrochloric acid (0.4 M HCl). After mixing with luminol, peroxide and ammonium, the oxidation of luminol with peroxide is catalyzed by iron and blue light is produced quantitatively 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 triplicate and average DFe concentrations and standard deviations are given. Concentrations of DFe measured during the 64PE370 cruise ranged from 13 pM in the surface waters of the Atlantic Ocean up to 52 nM in the high saline anoxic Bannock basin waters. The standard deviation varied between 0% and 50% (the latter being exceptional), but was on average 3.2% 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 0.033nM 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 0.019nM 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 correct for this 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. For the long term consistency and absolute accuracy a certified SAFe and GEOTRACES reference material (Johnson et al. 2007) was measured at a regular basis.

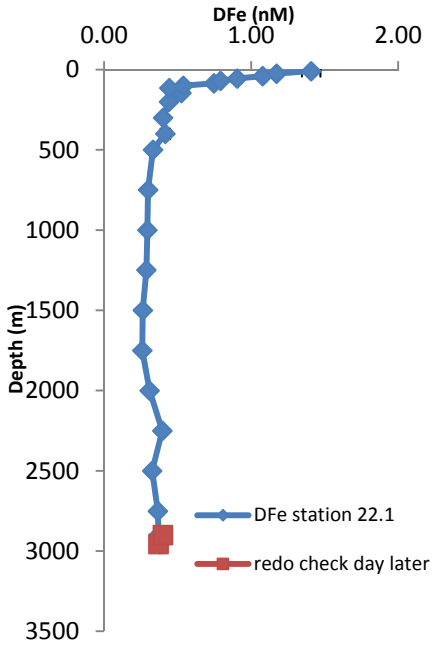

Figure 22) Depth profile of dissolved iron versus depth at station 22.1 of 64PE370.

Preliminary results

The profile from station 22.1 in the western part of the Mediterranean, shows high surface values and decreasing with depth. This is the opposite of what you would expect in the open ocean. Most likely the higher surface values reflects iron input from above dust from the Sahara.

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4.2.A.2. 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 27L 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 23). 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 23. 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 21 the colloidal fraction is highest in the surface waters and appears to become similar to the DFe fraction with depth (Figure 24).

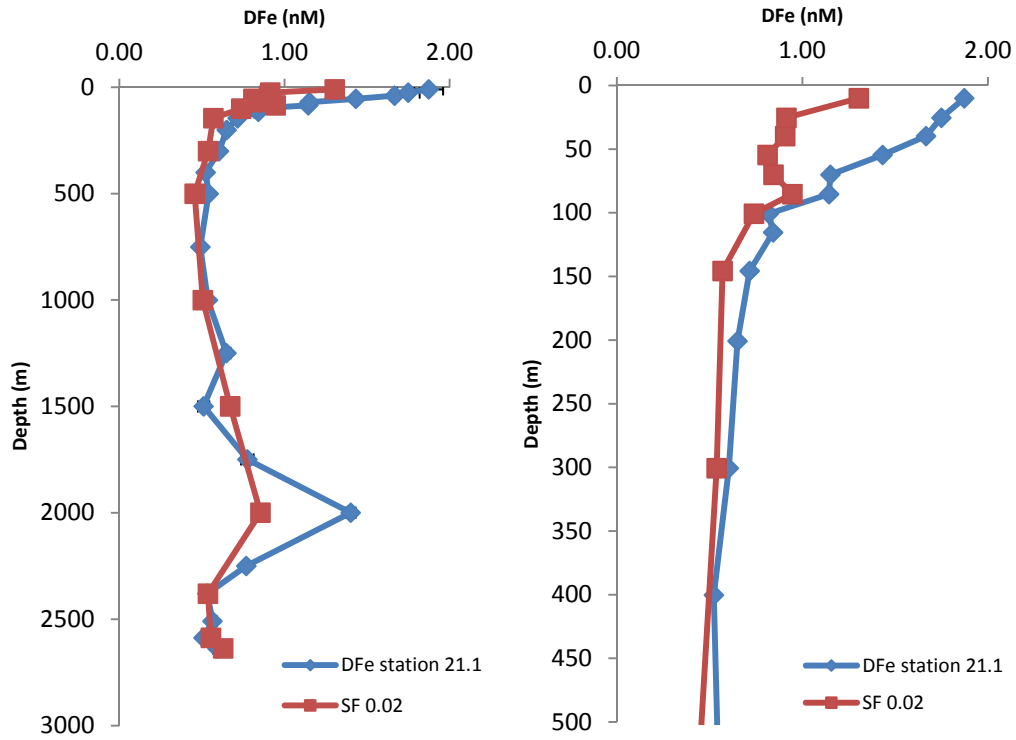

Figure 24) Depth profiles of size fractionated iron (0.2µm and 0.002µm) versus depth from station 21.1.

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4.2.A.3. Organic speciation of Fe

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Objectives

Iron availability controls phytoplankton primary production in 40% of the world's oceans and is in turn influenced by complexation with organic ligands (de Baar et al, 2005; Shaked and Lis, 2012). As part of ongoing research as well as a newly started project, samples were taken from the entire water column during the RV Pelagia cruise 64PE370, making up leg one of MedBlack GEOTRACES 2013. Additionally, large volume allotments (~1 m^3) of surface water were collected during the transit to the first leg start point (64PE369) in the Gulf of Biscay and in the eastern Mediterranean during this cruise (Table 1). A third allotment is to be taken from the western part of the Mediterranean during the third leg of the MedBlack cruise (64PE374), as the weather prevented deployment of the required equipment while passing initially planned stations (between station 10 and 11 of 64PE370). Intercomparison samples for humic-Fe complexation were taken on behalf of L.M. Laglera (University of the Balearic Islands, Palma, Spain) at two stations concurrently with our own samples and frozen. Also taking part in the intercomparison is M. Waeles (University of Brest, France), for who samples for humic acids were taken on board by G. Dulaquais.

Our objective is to measure organic speciation of Fe in the Mediterranean Sea on-board using competing ligand exchange cathodic stripping voltammetry using an added ligand new to us as described in the method below. Start-up problems resulted in the first leg being spent developing the method while freezing profile samples for analysis in the home laboratory (Table 2).

Table 1. Cubic vessels (1 m^3) were filled in the following locations:

Location	**Date**	**From**		**To**	
		Lat	**Lon**	**Lat**	**Lon**
Bay of Biscay	11-05-2013	47°15.5 N	7°8.0 W	46°38.5 N	7°37.0 W
Eastern Mediterranean	29-05-2013	33°22.0 N	26°14.0 E	33°40.1 N	27°25.3 E

Table 2. Organic Fe complexation (FeL) samples were taken as follows:

Sample	**Stations**
FeL	1, 5, 8, 11, 15, 18, 21, 24, 29, 36
FeL-LL	18, 21

Methods and equipment

Filtered ~900 mL FeL samples and ~450 mL FeL-LL (FeL-LL are samples for L. Laglera) samples were taken from the ultra clean CTD (UCC). Samples were filtered over a 0.2 µm Sartobran 300 filter (Sartorius) using N_2 overpressure and stored at -18 °C. Surface water samples were taken using the Fish, a suspended metal torpedo with protruding hose routed back to the UCC sampling container where it connects to a pump and 0.2 µm cartridge filter (NEED DETAILS FILTER) and ultimately to the cubic vessel to be filled.

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.). 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) (Figure 25).

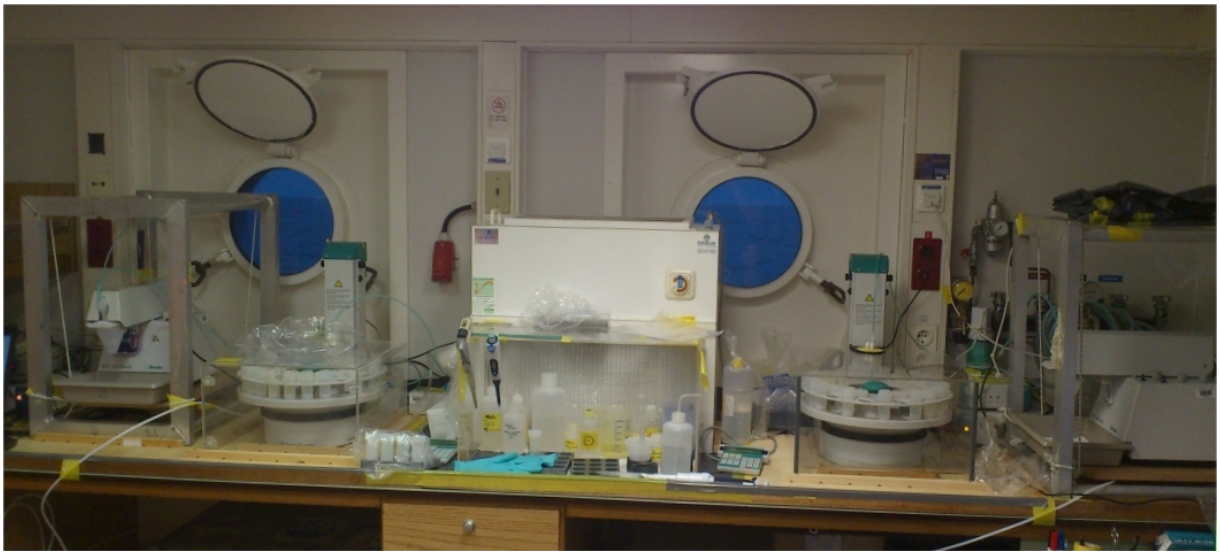

Figure 25) Equipment setup to measure the organic complexation of Fe using voltammetry during 64PE370

In order to measure natural organic ligand characteristics the ligand 2,3-dihydroxynaphthalene (DHN) (van den Berg, 2006; Laglera, 2013) is added to a sample together with a borate buffer and increasing iron concentrations between 0 and 8 nM. Samples were left to equilibrate with the iron additions for 8 hours. After equilibration $KBrO_3$ was added to enhance the voltammetric signal. Samples were then analyzed using CSV yielding a peak signal at the point of Fe-ligand complex disassociation during the scanning step, with the titration subsequently allowing a conversion of the signal into a concentration. This would then enable the ligand concentration and binding strength to be ascertained through non-linear regression of the Langmuir isotherm (Gerringa et al., 1995).

However, during the transit and first leg of the MedBlack GEOTRACES cruise a satisfactory titration curve could not be attained (Figure 26), due to multiple start-up problems plaguing the method. Development continued on-board and issues were narrowed down to non-Fe contaminations disrupting the voltammetric scans and possible lack of buffering strength causing inconsistent returns, as well as a still unexplained high titration baseline which will be addressed in the home laboratory before the second leg.

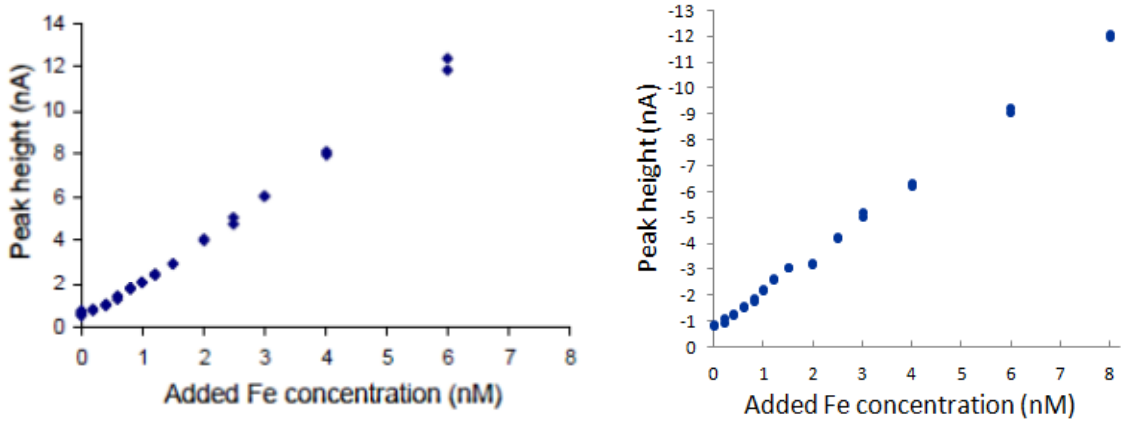

Figure 26) Left: A satisfactory titration plot as derived from similar studies performed using 2-(2-Thiazolylazo)-p-cresol (TAC) as an added ligand during 64PE321 (Source: Cruise Report 64PE321). Right: Best attained however still unsatisfactory titration plot derived from measurement of station 19 subsurface water (85 m) of this cruise 64PE370.

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4.2.A.4. DGT Labile Fe and Size Fractionation of Phytoplankton for Fe content

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Trace elements serve important roles as regulators of ocean processes such as major biogeochemical cycles. Most of these processes are in turn mediated by microorganisms, for which certain trace elements constitute essential micronutrients. However, in the marine environment the concentration of these trace elements can be very low, even at picomolar level. Moreover, the bioavailable fraction of these metals is strongly affected by the nature of the species present due to its interaction with organic and inorganic complexes.

Iron specifically, plays a key role in several processes having effect on major biogeochemical cycles in the marine environment (Morel et al. 1991). Is well known that more than 97% of the dissolved Fe in seawater is complexed with organic ligands (Rue and Bruland 1995), that increase the solubility of Fe but decrease the fraction of inorganic iron. In the other hand, the knowledge of the trace element composition of phytoplankton as it relates to marine biogeochemical cycles, comes from laboratory culture studies generally carried out with a single species of phytoplankton under unrealistically controlled conditions (Cullen and Sherrell 1999), which further adds complexity when linking biological processes to iron chemistry.

In the Mediterranean, with a turnover of 60 years, changes can occur at a relatively fast rate, therefore it is crucial for understanding the role of key processes involved in climate change and further making inferences on other processes occurring also at the global scale. As climate change driven factors may alter the terrestrial inputs into world oceans and so probably altering the Fe-bioavalilability and composition of natural planktonic assemblages, exploring these changes in the different ecosystems constitute a priority.

Methods

Diffusive gradients in thin-films (DGT)

Constitute a technique capable of accumulate dissolved substances in a controlled way, based on Fick's first law of diffusion. For trace metals analysis, it provides an in situ means of quantitatively measuring labile species in aqueous systems (Zhang and Davison 1995). Since both the mechanism of metal assimilation in aquatic organisms and the mode of metal uptake by DGT are governed by labile metal concentrations in solution, a correlation between DGT metal concentrations and the bioavailable fraction would be expected. Each DGT unit consists of 1.) a layer of polyacrylamide hydrogel of known thickness Δg (cm), is backed by 2.) a layer of ion-exchange resin (Chelex-100) of thickness Δr (cm). Between the diffusive gel and the bulk solution there is 3.) a diffusive boundary layer (DBL), of thickness δ, where transport of ions is solely by molecular diffusion (Zhang and Davison 1995).

Samples for the DGT labile iron (Fe_{DGT}), were collected placing three DGT units in acid washed plastic bottles with a volume (~ 2000 mL) of water. Samples were bagged and place in a shaker (65 - 80rpm) inside a temperature controlled container for ~ 48 - 72 hrs. After completing the time period, DGT samplers were taken out of the sample water and stored at low temperature (4ºC) (Ardelan et al. 2009).

Chelex-100

Chelex constitute an ion exchange resin of styrene divinylbenzene copolymers containing paired iminodiacetate ions which act as chelating groups. Has a very strong attraction for transition metals, even in highly concentrated salt solution. It differs from ordinary exchangers because of its high selectivity for metal ions and its much higher bond strength (Bio-Rad Laboratories).

Samples were collected for dissolved (filtered through 0.45 + 0.2 μm Sartorious Sartobran 300) Chelex labile (DFe_{Ch}) and Total (unfiltered) Chelex labile (TFe_{Ch}) iron by adding 0.8 mL of the Chelex-100 solution (Ammonium Acetate buffer) to a 200 ml sample. Afterwards, samples process follows as for DGT (see above). After this period, each sample was transferred to an acid-washed plastic PE column (Bio-Rad Laboratories), where the water was washed out through the column, and the Chelex-100 containing the material was restrained by the resin present at the end of the column. Remains of sample, were washed with Milli-Q water, then after columns were locked and stored at low temperature (4˚C).

Size fraction filtration

Constitute a separation method based on predefined (pore size) criteria that either can be independent simple filtration or sequential. The latter, in which the water sample is filtered sequentially through an in-line system of filters (starting on top from the bigger to the smaller pore size), was employed here. Having sequential filters in an in-line holder rather than performing independent filtrations through each filter vastly simplifies field operations in which many such samples must be collected while minimizing handling and potential contamination of individual filters (Cullen and Sherrell 1999).

To determine concentration and the size-fraction distribution of the particulate iron content within the plankton community ($Fe_{SFPhyto}$), sequential filtration was performed encompassing 3 size classes: 0.8 – 2 μm (picoplankton), 2 - 10 μm (nanoplankton), 10 – 200 μm (microplankton). Filtration was performed using acid washed polycarbonate filters (54 mm diameter) and filterholders, plus a 200 μm pore size Nitex mesh. Filtration volumes ranged from 2000 for the Western Mediterranean up to 3000 mL for the Eastern Mediterranean.

Work at sea

A total of 381 samples (including replicates) were collected at 13 stations of the entire survey area, including 2 in the Atlantic, 2 at the Western Mediterranean, 3 at the Eastern Mediterranean, 5 at the Aegean sea and 1 at the Marmara sea. Samples for Fe_{DGT} and DFe_{Ch} were collected having as main targets the surface, the chlorophyll-a maximum (Chl-max) and below the Chl- max. Also samples at O_2 min and/or near the bottom were included for certain stations. Samples for $Fe_{SFPhyto,}$ as well as for size fraction Chlorophyll and taxonomy, were collected only at the Chl-max for every hyperstation, 1 station in the Atlantic, 1 in the Aegean and 1 in the Marmara sea. In addition, samples for TFe_{Ch} were collected at the surface, the Chl-max and below it (Table 3).

Table 3.) Stations and depths sampled for DGT labile iron (Fe_{DGT}), dissolved Chelex labile (DFe_{Ch}), Total Chelex labile (TFe_{Ch}) iron and the size-fraction particulate iron content ($Fe_{SFPhyto}$), during the first leg of the Geotracers MedBlack cruise.

Station	Depth (m)	Parameters
1	10, 25 ,100, 400	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
4	10, 55, 70, 100, 900	Fe_{DGT}, DFe_{Ch}
5	10, 25, 85, 100, 250, 920	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
11	10, 52, 70, 100, 300, 1500, 2800	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
18	10, 100, 125, 600, 1500, 3000, 3210, 3255	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
21	10, 85, 100, 500, 750, 2500, 2560	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
24	10, 115, 130, 500, 1000	Fe_{DGT}, DFe_{Ch}
26	10, 100, 150, 400	Fe_{DGT}, DFe_{Ch}
27	10, 100, 250, 700	Fe_{DGT}, DFe_{Ch}
29	10, 80, 250, 500	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$
32	10, 75, 80	Fe_{DGT}, DFe_{Ch}
33	10, 30	Fe_{DGT}, DFe_{Ch}
36	10, 25, 400	Fe_{DGT}, DFe_{Ch},TFe_{Ch}, $Fe_{SFPhyto}$

Results

Onboard processing of samples was partially completed for all three types of samples. For both Fe_{DGT} and Chelex samples, this included the deployment of the passive samplers (DGTs) or the addition of the resin in the water sample, put in the shaker and kept in a temperature controlled container for periods of ~ 72 hrs (DGTs) and ~ 48 hrs (Chelex). Further processing for both type of samples will involve acidification for extraction of the metals. $Fe_{SFPhyto}$ samples were frozen and will be processed by acid digestion for metal extraction. Afterwards, all samples will be analyzed by HR-ICP-MS.

Acknowledgements

To the Chief Scientist Micha Rijkenberg, for making everything possible and well executed. To the captain Pieter Kuijt, the technicians and all the crew of the RV Pelagia, for all the assistance and support. To the Dutch GEOTRACERS program and funding institutions. To the Chemistry Department at NTNU in Norway (project nº 81736400) and the Marine Science and technology institute (DEU) in Turkey.

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4.2.A.5. The biogeochemical cycles of cobalt, and copper in the Mediterranean Sea

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LEMAR

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Olivier Rouxel, CII IFREMER - Brest, France

Summary

Our research group at Brest proposes to constrain sources and biogeochemical cycling of key bioessential trace metals (copper and cobalt) along the GEOTRACES-A04N section in the Mediterranean and Black Seas, 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 LEG1 in the Southern Mediterranean Sea, in the water-column in the dissolved, particulate, ultra-filtrated fractions.

Context and main objectives

Many trace elements, especially iron (Fe), 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 in the Mediterranean Sea and Black 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.**

Although focused on Mediterranean Sea and Black Sea, this project will address major questions that pertain to the global ocean, including its benthic and atmospheric oceanic boundaries. As for iron, there is now an increasing debate over the sources of dissolved copper to the deep ocean. Potential inputs include remineralization of sinking particles as well as benthic inputs such as seafloor sediments and also hydrothermal fluids (Sander and Koschinsky, 2011) but the ability to quantify the impact of each of these on the global budget

is extremely difficult. The recent analytical development of metal isotope biogeochemistry (Anbar and Rouxel, 2007; Boyle et al., 2012) may fill the gap in the current knowledge of oceanic metal cycling.

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 TEIs. 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 in ancient deposits such as the Banded Iron Formations that are studied to unravel the redox conditions of the ancient Earth (Rouxel et al., 2005). In addition the climate change is particularly amplified in the Mediterranean Sea, with a temperature increase higher than the global mean (Christensen et al., IPCC 2007) and a faster acidification of the waters (lower pH) than that in the global ocean (Sabine and Tanhua, 2010). It is thus ideal to develop and calibrate new proxies of SST and pH.

Thus far remarkably few measurements and studies exist of trace elements (e.g. Fe, Cu, Zn, Co) in the Mediterranean and Black Seas – and are even more scarce or non-existent for metal isotopes (e.g. Fe, Cu, Cd, Zn). This work will then lead to the first ever high resolution deep sections for traces metals (Cu, Co) and copper stable isotopes. Knowledge gained in the Mediterranean and Black Seas will be applicable for understanding of the biogeochemical cycles of trace elements and isotopes in the global ocean. In particular, results for Cu isotopes will complement ideally on-going work related to metal isotope systematics in deep sea hydrothermal plumes.

Analyses

The analyses will be performed in the home-laboratory 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 analysed 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).

Sampling

Our sampling schedule is summarized in Table 4 and Figure 27.

Table 4 : Inventory of sampling during LEG 1 of the MedBlack cruise.

Team	Dulaquais & Boyé/ Waeles-Pernet-Coudrier-Riso	Dulaquais-Boyé/ Waeles-Riso	Dulaquais-Boyé/	Dulaquais-Boyé/	Waeles-Riso	Rouxel	Dulaquais & Boyé	Dulaquais & Boyé - Planquette	Dulaquais & Boyé	Boyé
Stations	**DCo/DCu/Humics**	**TCo / TCu**	**Sol. Co**	**Orga. Co**	**Orga. Cu**	**Cu-isotopes**	**Taxonomy**	**Particles**	**POC**	**Cocco**
1	16									
2	16									
3	16	16	16	12	10	11		6	6	
4	16	16	16	12	10	9	3	6	12	
5	16	16	16	12	11	13	3	6	12	
6	16						4	6		4
9	16							4		
11	24	16	16	12	10	11	3	6	12	
13							4			4
14	16						2	4	4	
16	16						4	4	8	
17							4			4
18	28	16	16	12	10	10	3	6	12	
19										
21	24	16	16	12	10	10	3	6	12	
23							4			4
24										
26	16						4			4
27	18		8				2	4		
28										
29	18		12							4
30	12						3	6	8	
31	8						4			4
32							4			4
33	4									
35	18									
37	18									

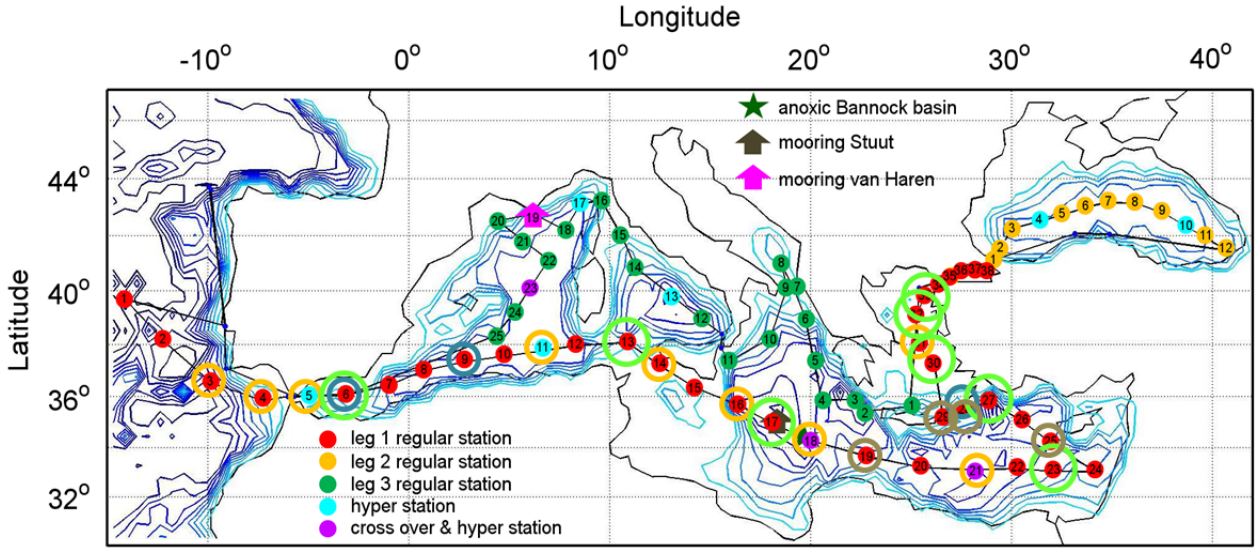

Figure 27: Sampling strategy along LEG1 for particulate material
Stations sampled for:
Particulate trace metals + particulate carbon (x 9)
Particulate trace metals only (x 3)
Coccolithophorides (x 8)

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4.2.A.6. 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 that 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 Sartobran 300 cartridge of Sartorius) seawater is buffered to pH 5.5. The metals are 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) to remove the salts the column is eluted with diluted acid (0.4 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 quantitative 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

Concentrations were low in the surface Atlantic Ocean (~2 nM) and increased with depth. A maximum was observed in the Mediterranean Overflow Water (see Figure 28). Concentrations increased towards the strait of Gibraltar and are in excess of 150 nM in the deep Mediterranean.

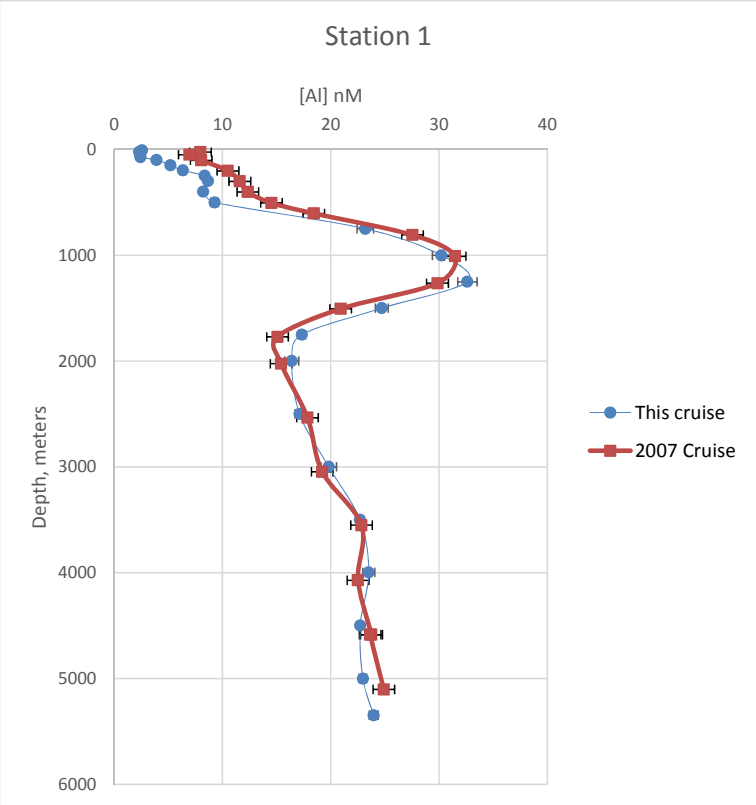

Figure 28) Comparison of dissolved Aluminium at station 1 for this cruise and the average of 5 casts during the 2007 Pelagia Titan test cruise.

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4.2.A.7. 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 HNO3 from dilutions of 1000 ppm SPEX individual element standards. This mixed element standard was then used to make standard additions to acidified 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 HNO3 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.

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4.2.A.8. Dissolved Organic Carbon (DOC) and Chromophoric dissolved Organic Matter (CDOM) Sampling

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During the first leg of the Med Black Geotraces cruise (8/5 – 5/6/13) 50 ml samples were collected for Dissolved Organic Carbon (DOC) and optical parameters in the water column. More specifically, water sampling (~0.3L) was conducted for selected depths from all CTD stations. The samples were filtered through a 0.2 μm cartridge filter (Sartobran 300 cartridge of Sartorius) mounted on the clean CTD bottles. After sealing samples were stored at -18 0C.

DOC and CDOM will be measured in the home laboratories. Dissolved Organic Carbon (DOC) using a high temperature catalytic oxidation (HTCO) method, as described by Sugimura and Suzuki (1988) and Cauwet (1994). Precision and accuracy of the measurements will be tested against Deep Atlantic Seawater Reference Material provided by the DOC-CRM programme, (University of Miami - D.A. Hansell). Another set of samples was taken for chromophoric dissolved organic matter (CDOM) characterization through measurement of absorbance spectra using a UV-vis spectrometer Varian Cary-1E and fluorescence spectra using synchronous emission-excitation Fluorolog 3-21 Jobin –Yvon fluorescence spectrometer.

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4.2.A.9. The isotope intercomparison excersise

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Introduction

More and more laboratories concentrate on the stable isotope composition of radiogenic and natural elements to develop a potential powerful tool for unraveling element sources and their biogeochemical processes in the marine environment. Depending on the element, trace element isotope ratios may provide information about their sources, chemical processes and biological processes that determine their distributions in the oceans. However, development of these methods is difficult as most trace elements occur at picomolar to nanomolar concentrations, and precise stable isotope measurements require 100-1000 times more sample than required for concentration determination (Boyle et al. 2012). This isotope intercomparison excersise is an international intercomparison program for overall accuracy and interlaboratory consistency of isotope ratio values for a range of metal and other isotopes. We took subsamples for determination of the stable isotope systems of Cd (10 laboratories), Cr (3 laboratories), Cu (2 laboratories), Fe (10 laboratories), Mo (2 laboratories), Ni (2 laboratories), Pb (6 laboratories), Si (1 laboratory to be subdivided later), Tl (2 laboratories), Zn (10 laboratories) and a sample for Ba and REE (1 laboratory).

Methods

During 2 separate casts with the UCC CTD at station 1 two large volume seawater samples were taken for the stable isotope intercomparison excersise during 64PE370. The first large volume sample was taken by closing all 24 UCC CTD bottles at 1500 m depth on 15 May station 1 and the second large volume sample was taken by closing all 24 UCC CTD bottles at 25 m depth on 26 May station 1. In both cases the UCC CTD was, after coming back on deck, immediately transported to the class 100 clean room container for filtration and subsampling. Filtration was performed under N_2 pressure using 0.2 µm Sartobran 300 filter cartridges (Sartorius). Sampling differed slightly depending on the isotope system. For Pb isotopes unfiltered and unacidified seawater was collected straight from an UCC CTD bottle into the subsample bottles provided by the different laboratories. Also for Si, Ba and REE were seawater samples filtered and collected straight into the provided subsample bottles/containers. For all other isotope samples seawater was first collected in clean 10L containers (Nalgene) before poored into larger trace metal cleaned containers (50-200L) so that the seawater samples were homogenized before subsampling for the different participating laboratories. The 50L carboys were made of LDPE (Nalgene). The 80L, 100L, 150L and 200L containers were made of transparent polyethylene. All carboys/containers were cleaned overnight with soap (Micro-90 Alkaline Cleaning Solution) and for at least 3 weeks with 1 M HCl in rhowater.

Due to rough weather the larger subsamples were acidified with roughly 1 ml/L ultraclean HCl of Seastar on 18 May. Also the samples for Ba and REE where acidified with 1 ml/L ultraclean HCl of Seastar on 18 May. Further subsampling of the large volume subsamples occurred at:

i) 23 May for Cd isotopes from the 200L container with seawater collected at 25m depth,
ii) 24 May for Fe isotopes from the 150L container with seawater collected at 25m depth,
iii) 25 May for Zn isotopes from the 150L container with seawater collected at 25m depth,

iv) 28 May for Cr, Ni, Cu, Mo, Tl from the same 80L container with seawater collected at 25m depth,
v) 29 May for Cr, Ni, Cu, Mo, Tl from the same 50L container with seawater collected at 1500m depth,
vi) 31 May for Zn isotopes from the 50L container with seawater collected at 1500m depth,
vii) 1 June for Fe isotopes from the 50L container with seawater collected at 1500m depth
viii) 2 June for Cd isotopes from the 100L container with seawater collected at 1500m depth,

A subsample taken while subsampling for Fe isotopes from the 150L container with the large volume seawater sample collected at 25m depth contained 0.14 nM DFe. A subsample taken while subsampling for Fe isotopes from the 50L container with the large volume seawater sample collected at 1500m depth contained 0.71 nM DFe. These values cannot be compared yet with the DFe depthprofile at station 1. However, the DFe concentration of the surface sample of 0.14 nM was close to the surface concentration value of 0.13 nM as reported by Thuroczy et al. (2010) at the same station position. The subsample of the large volume seawater sample from 1500m depth subsampled from the 50L carboy while subsampling for the Fe isotopes was with 0.71 nM slightly higher than the values of about 0.58 as reported by Thuróczy et al. (2010). If we really have slightly enhanced DFe concentrations in the deep sample will only become clear when the depthprofile of station is measured for DFe.

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4.2.B. CO_2

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

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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 (Figure 29), 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. Samples analysis commenced immediately after collection and analysis of profiles was in all cases completed within 12 hours after sampling. 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. Such a report on the treatment of the carbon data will, in due time, be available as a separate report.

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 29. Nikki and Lesley sampling for DIC and alkalinity from the 25L CTD.

4.2.C. Microbial oceanography

4.2.C.1. Algae biomass, algae community structure and algae group specific primary production in the Mediterranean Sea

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Introduction

Since more than 70% of the earth's surface consists of oceans, their impact on our global climate is tremendous. Moreover, the oceans serve as an important food source (FAO, 2010). The basis of this food web is formed by the phytoplankton (Legendre, 1990). Phytoplankton growth is determined mostly by the light conditions and availability of essential micro- and macronutrients such as iron, nitrate and phosphate (Sunda & Huntsman, 1995; Tyrrell, 1999; Morel & Price, 2003; Behrenfeld & Milligan, 2013). Trace elements and nutrients thus serve as important regulators for the oceans' food web and therefore marine ecosystem dynamics (Falkowski *et al.*, 1998). This study investigates the availability of nutrients and trace metals as regulators of the algal biomass, algae community structure and algae group specific primary production and/or vice versa. Knowledge on this subject is important for predicting variability in phytoplankton biomass and composition in future and past changes in oceanographic conditions. This will ultimately serve for mankind to be able to adapt to inescapable future oceanic changes (Hoegh-Guldberg & Bruno, 2010; Rees, 2012).

The Mediterranean Sea is the largest quasi-enclosed sea on the Earth. The size, location, morphology, and external forcing of the Mediterranean Sea provides rich and complex physical dynamics such as unique thermohaline features, distinctive multilayer circulation and topographic gyres. Moreover, the Mediterranean Sea provides a gradient in nutrient concentrations and chlorophyll-a from oligotrophic in the west to ultra-oligotrophic conditions in the eastern part (Azov, 1991; Krom *et al.*, 1991; Antoine *et al.*, 1995; Turley *et al.*, 2000; D'Ortenzio & Ribera d'Alcalá, 2009). In addition there is a gradient in sea surface temperature, increasing from west to east. (Siokou-Frangou *et al.*, 2010). In turbulent water, nutrients are replenished in the surface water for uptake by phytoplankton. However, during the spring and summer in the Mediterranean Sea, major dissolved nutrients such as nitrate and phosphate can be depleted in the surface waters, because strong stratification prevents exchange with colder, nutrient rich water. (Pedrós-Alió *et al.*, 1999; Marty *et al.*, 2002). Under these oligotrophic conditions dust deposition (Saharan dust) can be an important source of trace metals and nutrients such as phosphate in the surface waters (Guerzoni *et al.*, 1997).

During this cruise water samples from four different depths were filtered and will be analysed on shore at the University of Groningen with high-performance liquid chromatography (HPLC) and chlorophyll-a specific absorption in order to make a comparison between the vertical differences in phytoplankton abundance and phytoplankton taxonomic composition. HPLC analysis of phytoplankton pigments will be according to Hooker *et al.*, 2009. Chlorophyll-a concentration will be used as indicator of phytoplankton biomass. Furthermore taxon specific marker pigments will be used to estimate phytoplankton taxonomic composition using the CHEMTAX algorithm (Mackey *et al.*, 1996). Consequently, CTD measurements of PAR attenuation, Chl-a fluorescence and temperature will be combined with phytoplankton biomass and community structure to estimate algae group

specific primary production (carbon fixation per m^2 per day). Potential vertical structure in photoacclimation will be investigated by comparing Chl-a specific absorption from the surface with that from the Chl-a maximum. These data can be used to investigate how the distribution of trace metals and nutrients may affect the algae community and/or how the algae community may affect the distribution of trace metals and nutrients.

Work at Sea

Water samples were taken at all possible stations (stations 1-32 and 36) from the 25L CTD. Four depths were sampled at each station based on the chlorophyll-a fluorescence sensor of the CTD, namely just below the chlorophyll-a maximum, at the Chl-a maximum, just above the chlorophyll-a maximum and from the surface (10 meter). The depth of the chlorophyll-a maximum varied between stations. The samples just below and above the Chl-a max were determined depending on the overall Chl-a profile, mostly varying between 10 and 50 metres from the Chl-a max. From each depth, a maximum of ten litres was sampled for pigment composition analysis (high-performance liquid chromatography, HPLC) in jerry cans. From the Chl-a maximum and at 10 m a maximum of 10 L was sampled for Chl-a specific absorption in jerry cans. The jerry cans were subsequently transported to the wet lab where a filtration set-up was prepared (Figure 30 a,b). The filtration set-up consisted of four 5L PVC tubes connected with tubes to the filtration compartments, which were subsequently connected to glass wastewater bottles. A vacuum varying from 0.2 to 0.6 bar was applied to the entire system. All samples were filtered over 47 mm GF/F filters. Filtered volumes varied between 6 and 10 litres, based on the pace of filtration and the water availability from the 25L CTD. Two forceps were used to remove the filters from their compartments. Consequently, the filters were wrapped in aluminium foil and labelled with their corresponding Station-Cast-Bottle numbers. Filters for the HPLC were folded once, filters for Chl-a specific absorption were not folded. During the filtration procedure, the filters were temporally stored at -20°C and they were stored at - 80°C after all filtrations of a station were finished. The filtration set-up was rinsed with two litres of 70 °C tap water between each station.

Preliminary results

No results can be reported during the cruise due to the fact that all analyses will be performed at the University of Groningen on shore. However, one could notice the less intense colouration of the filters in the Eastern part of the Mediterranean Sea compared to the Atlantic Ocean and the Western Mediterranean Sea (Figure 30 c). This could indicate and reflect that the Eastern Mediterranean is more oligotrophic than the Western part.

Acknowledgements

First of all I would like to thank my supervisor Willem van de Poll. Without him it would not have been possible for me to participate in this cruise in the first place and secondly for his advice and feedback before and during the cruise. Moreover I would like to thank Micha Rijkenberg, the chief scientist of the cruise for the total coordination of this huge project. Furthermore I would like to extend my gratitude to all other scientists, technicians, the captain and all other crewmembers of the R.V. Pelagia for their help and hospitality on the ship and for teaching me all sorts of new things. All participants made my stay on the R.V. Pelagia a very pleasant experience during which I learned a lot and had great times and lots of fun.

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Figure 30) (a) Overview of the filtration system set-up. (b) Pim filtering the sea water in order to capture the phytoplankton. (c) A 47 mm GF/F filter after filtration of 10 L of sea water from the 25L CTD. The colour change from white to green/yellow/ brownish caused by the phytoplankton is clearly visible. White spots can be caused by grazers on the filter, such as salps. The filter can either be used for HPLC analysis or Chl-a absorption measurements.

4.2.C.2. Bacterial communities at the sediment water interface in the Mediterranean Sea

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On Board laboratory work

For biological work we collected deep and superficial seawater from all the station sampled during the cruise. From each station, water collected 1 Liter has been collected to evaluate qualitative microbial community composition and abundance. For those stations located in the Mediterranean Sea, the study of the biological analyses was also applied on water samples collected from each sampling sites in correspondence of the variations of parameters, such as salinity and oxygen concentrations that allow us to recognize more information in water masses origin in eastern and western Mediterranean Sea. For each sample, 1 liter of seawater was immediately filtered on board on sterile 0.20 μm pore-size filters.

4.2.D. Nanomolar nutrients

4.2.D.1 Determination of Nitrate and Phosphate at nanomolar concentrations.

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Introduction

A changing spatial-time distribution of nanomolar concentrations of the nutrients nitrate and phosphate is found across a heterogeneous Mediterranean Sea. The upper Atlantic waters enter through the shallow Strait of Gibraltar, being the first input of nutrients for a young Mediterranean Sea. Nutrients input which is increased by the upwelling in the northern Alboran Sea, transporting nutrient-rich waters from deeper layers by vertical turbulence (Minas et al.1991, and M Estrada, 1996).

The incoming surface waters are also fed by the dust from northern Africa (Herut et al. 1999), and by anthropogenic sources such as agriculture (F.Gomez, 2003). A population of at least 200 million people settles around the Mediterranean Sea, resulting in additional nutrients input via the discharge of large rivers and affecting the nutrients distribution in the different areas. A strong oligotrophic distribution predominates in eastern and northeastern Mediterranean, where phosphate lacks in almost the entire water column. Because of this oligotrophic conditions, an analysis with better accuracy at low concentrations was necessary to determine a more precise distribution of nutrients in the photic zone.

Work at sea

Nitrate and phosphate were measured on board at nanomolar concentrations following the methods described by *Matthew D. Patey et al.2008: Determination of nitrate and phosphate in seawater at nanomolar concentrations*. We used the same chemistry as conventional methods in flow injection analysis, however, we increased sensitivity and therefore the limit of detection by coupling a LWCC as cell (Liquid Waveguide Capillary Cell 220cm) to the system in combination with miniaturized spectrophotometers (Ocean Optics) to read the absorbance.

Theory and Methodology

Phosphate and Nitrate chemistry:

Phosphate

In the ascorbic acid-molybdate method, orthophosphate reacts with molybdate to form phosphomolybdic acid. Phosphomolybdic acid is reduced by ascorbic acid to form a blue complex:

Phosphate + Molybdate -> Phosphomolybdic Acid

Phosphopmolybdic Acid + Ascorbic Acid -> Reduced Phosphomolybdate complex

This blue complex gives a linear response at 700nm wavelength, which will be used for the analysis.

Reagents preparation:

- *Potassium Antimonyl Tartrate stock:*
  3g dissolved in approximately 1L of Milli-Q. Stored protected from light and refrigerated.
- *Amonyum Molybdate 'stock':*
  2.3g AM dissolved in 192mL H_2SO_4 2.5M
  50mL Potassium Antimonyl Tartrate stock
  Diluted to 1L with Milli-Q.
  Refrigerated
- *Ascorbic Acid solution:*
  0,2g Sodium Dodecyl Sulphate
  0,8g Ascorbic Acid
  Dissolved in 100mL Milli-Q
- *Phosphate standards:*
  Phosphate stock solution 1mM. 0,1361 g KH_2PO_4 in 1 L Milli-Q
  Dilutions from stock solution were prepared from 15nM to 450nM.

Nitrate

Samples were buffered with Imidazole pH 8.9. NO_3 is reduced almost quantitatively to nitrite (NO2) in the presence of cadmium (Cd). The produced NO_2 is measured by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a pink complex, which gives a linear response at 540nm wavelength.

Reagents preparation:

- *NEDD stock:*
  0,25g dissolved in approximately 250L of Milli-Q. Stored protected from light and refrigerated.
- *Sulphanilamide 'stock':*
  5g sulphanilamide dissolved in 500mL HCl 10% vv
- *Working Sulphanilamide solution:*
  200 µL Brij 25% added to 100mL sulphanilamide stock.
- *Imidazole Buffer solution:*
  3,4g Imidazole dissolved in 1L Milli-Q
  pH adjusted to 7.8 using HCl 4M.
- *Brij 25 % p v : 25 g Brij in 100mL Milli-Q*

Equipment

The equipment (Figure 31 & 32) consists in a Flow Injection system with 2 channels; each one coupled to a LWCC (Liquid Waveguide Capillary Flow Cell 220cm from *World Precision Instruments*), as the Figure 31shows. The LWCC will be connected by optical fiber to *1.-Source of light (HL-2000-CAL 300-1050nm)* and *2.Ocean optics spectrophotometer (HR4000 for Phosphate and USB2000 for Nitrate).*

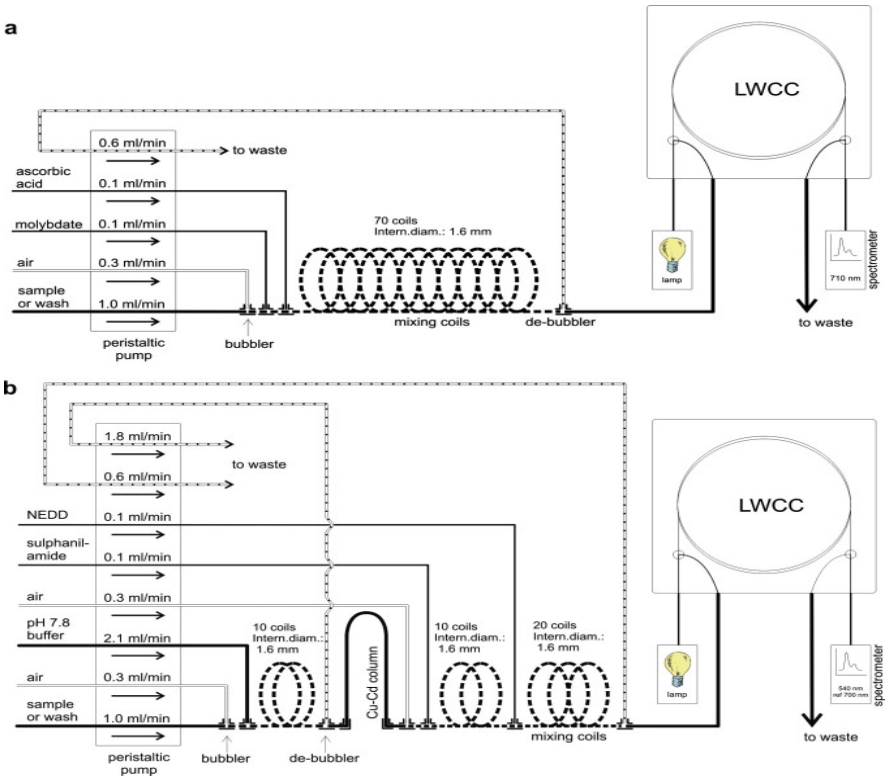

Figure 31. Sketch of FI system, channels for Phosphate (a) and Nitrate (b), with their corresponding flow rates. (*Source: Matthew D. Patey et al.2008).*

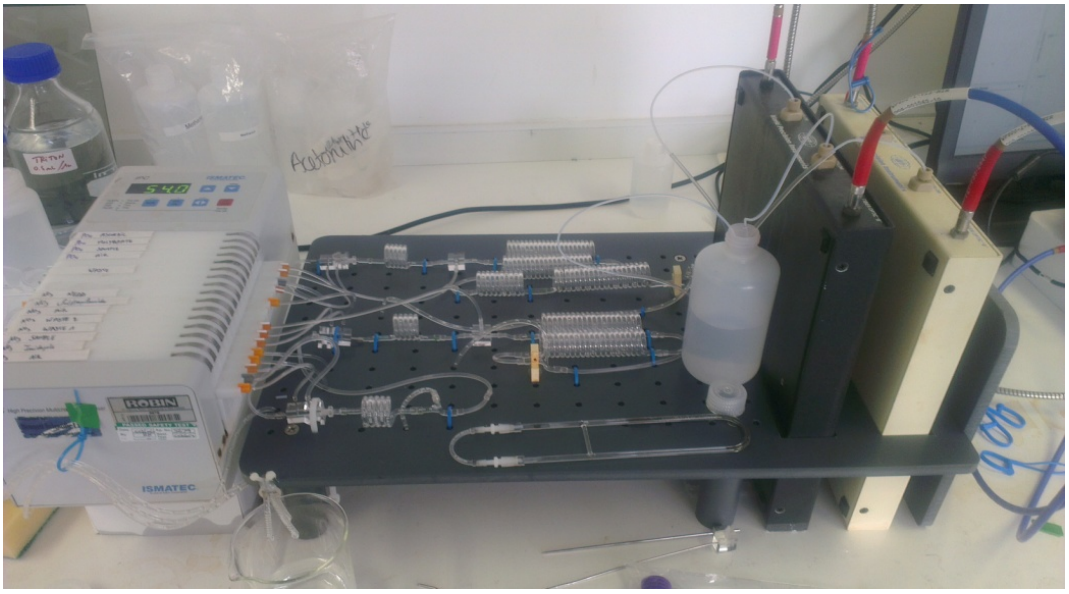

Figure 32. Picture with the equipment set up on board.

Sampling and measuring on board

All the samples were collected in LDPE 60mL bottles, from the ultra-clean CTD. Every bottle was rinsed five times before being filled with the sample. Sample was taken unfiltered, after DIC samples, in case they were also collected from ultra-clean CTD; otherwise they were taken in first position together with nutrients for micromolar determination. By default the whole UCC were sampled, including the 24 bottles. Depending of the results obtained during the analysis, once the concentration reached "high" values (300nM PO4, 1uM NO3), the analysis was stopped.

Samples were measured as soon as possible after collection. When they could not be measured immediately, they were stored in the fridge at 4ºC and analyzed within 4 hours. Prior to the analysis, the samples were left in the dark at room temperature for at least 30 minutes. Although even with the thermal conditioning, sometimes micro-bubbles could appear in the cells, due to the degassing process suffered when temperature increases, affecting to the absorbance reading.

Measuring

Every day the equipment was cleaned with 10%vv HCl and milli Q water for at least 30-40 minutes before and after use. The cells were also carefully cleaned with 25% vv methanol and 10%vv HCl with a rinse of milli Q water in between, ending with an abundant and final rinse of milli Q. After the wash, all the reagents were placed, and run for 50-60 minutes till the baseline became stable.

For the data acquisition, every sample and calibration point was run for *90 seconds*, with *180 seconds* baseline in between. The operational procedure was an initial 6 points calibration (Phosphate: 250nM to 15nM; Nitrate: 400-250nM to 20nM) followed by a blank reference.

As blank references were used:

-Milli Q water in the case of Nitrate

-Phosphate-free seawater obtained by adding 1M NaOH to surface seawater at a ratio 1:40 v/v and letting it settle down overnight. The overlying solution was siphoned off and stored separately.

After the calibration (Figure 33), the samples were run from surface to deeper waters by the same way.

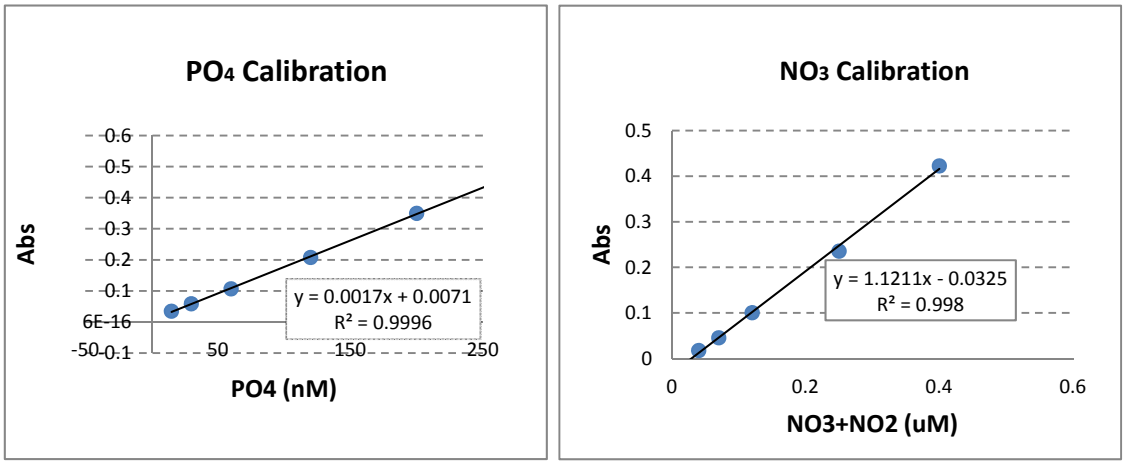

Figure 33. Obtained calibrations previous analysis for Phosphate (left) and Nitrate + Nitrite (right)

Preliminary results:

The preliminary data profiles have been plotted as shown in Figure 34.

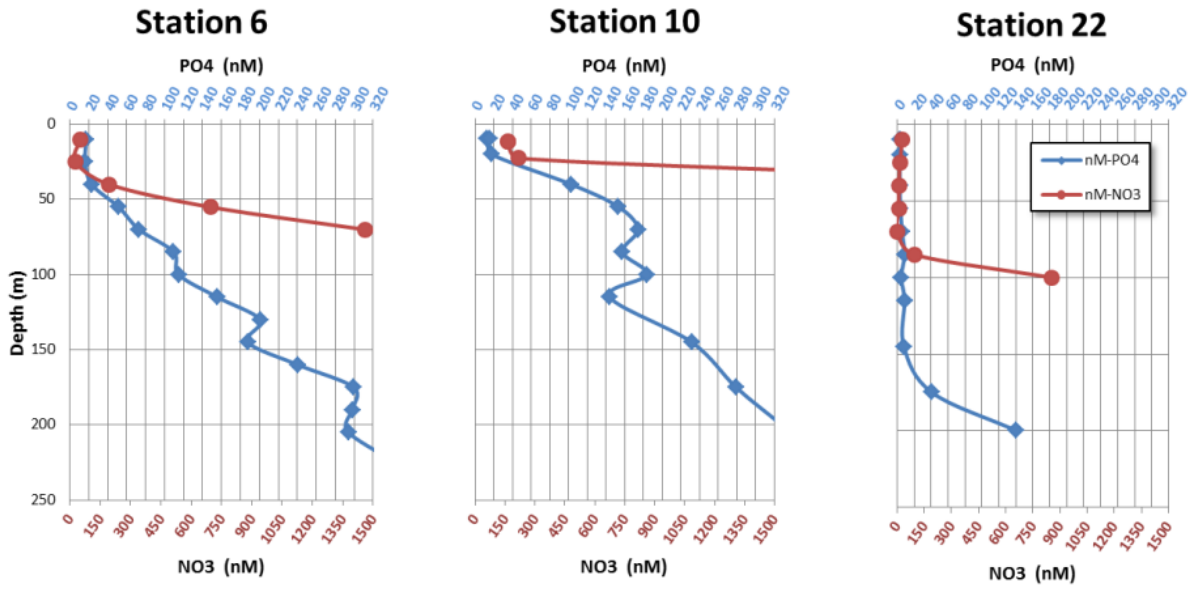

Figure 34. Profiles for Phosphate and Nitrate, in western Mediterranean (Station 6 and 10) and eastern Mediterranean (Station 22)

Sample logger MedBlack Geotraces Leg 1:

A total of 507 samples were collected and measured on board (Table 5).

Table 5. Samples taken for measurement of nanomolar concentrations of phosphate and nitrate.

STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN	STATION	CAST	NISKIN
1	2	17	4	2	15	6	1	7	10	2	7	13	1	24	15	1	17	17	2	13	20	1	18	22	2	1	26	1	23	28	1	4	31	1	15
1	2	16	4	2	14	7	1	24	10	2	6	13	1	23	15	1	16	17	2	12	20	1	17	22	2	2	26	1	22	28	1	3	31	1	14
1	2	15	4	2	13	7	1	23	10	2	5	13	1	22	15	1	15	17	2	11	20	1	16	22	2	3	26	1	21	28	1	2	31	1	13
1	2	14	4	2	12	7	1	22	10	1	1	13	1	21	15	1	14	18	1	24	20	1	15	22	2	4	26	1	20	28	1	1	31	1	12
1	2	13	4	2	11	7	1	21	10	1	2	13	1	20	15	1	13	18	1	23	20	1	14	23	1	24	26	1	19	29	1	18	31	1	11
1	2	12	4	2	10	7	1	20	10	1	3	13	1	19	15	1	12	18	1	22	20	1	13	23	1	23	26	1	18	29	1	17	31	1	10
1	2	11	4	2	9	7	1	19	10	1	4	13	1	18	15	1	11	18	1	21	20	1	12	23	1	22	26	1	17	29	1	16	31	1	9
1	2	10	4	2	8	7	1	18	11	1	24	13	1	17	15	1	10	18	1	20	20	1	11	23	1	21	26	1	16	29	1	15	31	1	8
1	2	9	5	2	24	7	1	17	11	1	23	13	1	16	15	1	9	18	1	19	20	1	10	23	1	20	26	1	15	29	1	14	31	1	7
1	2	8	5	2	23	7	1	16	11	1	22	13	1	15	15	1	8	18	1	18	20	1	9	23	1	19	26	1	14	29	1	13	31	1	6
1	2	7	5	2	22	7	1	15	11	1	21	13	1	14	15	1	7	18	1	17	20	1	8	23	1	18	26	1	13	29	1	12	31	1	5
1	2	6	5	2	21	7	1	14	11	1	20	13	1	13	15	1	6	18	1	16	20	1	7	23	1	17	26	1	12	29	1	11	31	1	4
1	2	5	5	2	20	7	1	13	11	1	19	13	1	12	15	1	5	18	1	15	20	1	6	23	1	16	26	1	11	29	1	10	31	1	3
1	2	4	5	2	19	7	1	12	11	1	18	13	1	11	15	1	4	18	1	14	21	1	24	23	1	15	27	1	18	29	1	9	31	1	2
2	1	24	5	2	18	7	1	11	11	1	17	13	1	10	15	1	3	18	1	13	21	1	23	23	1	14	27	1	17	29	1	8	31	1	1
2	1	23	5	2	17	7	1	10	11	1	16	13	1	9	15	1	2	18	1	12	21	1	22	23	1	13	27	1	16	29	1	7	32	1	8
2	1	22	5	2	16	8	1	24	11	1	15	13	1	8	15	1	1	18	1	11	21	1	21	23	1	12	27	1	15	29	1	6	32	1	7
2	1	21	5	2	15	8	1	23	11	1	14	13	1	7	16	1	24	19	1	24	21	1	20	23	1	11	27	1	14	29	1	5	32	1	6
2	1	20	5	2	14	8	1	22	11	1	13	13	1	6	16	1	23	19	1	23	21	1	19	23	1	10	27	1	13	29	1	4	32	1	5
2	1	19	5	2	13	8	1	21	11	1	12	13	1	5	16	1	22	19	1	22	21	1	18	23	1	9	27	1	12	29	1	3	32	1	4
2	1	18	5	2	12	8	1	20	11	1	11	13	1	4	16	1	21	19	1	21	21	1	17	23	1	8	27	1	11	29	1	2	32	1	3
2	1	17	5	2	11	8	1	19	11	1	10	13	1	3	16	1	20	19	1	20	21	1	16	23	1	7	27	1	10	29	1	1	32	1	2
2	1	16	5	2	10	8	1	18	11	1	9	13	1	2	16	1	19	19	1	19	21	1	15	23	1	6	27	1	9	30	1	18	32	1	1
2	1	15	5	2	9	8	1	17	11	2	5	13	1	1	16	1	18	19	1	18	21	1	14	23	1	5	27	1	8	30	1	17	33	1	4
3	2	24	5	2	8	8	1	16	11	2	4	14	1	12	16	1	17	19	1	17	21	1	13	24	1	24	27	1	7	30	1	16	33	1	3
3	2	23	5	2	7	8	1	15	11	2	3	14	1	11	16	1	16	19	1	16	21	1	12	24	1	23	27	1	6	30	1	15	33	1	2
3	2	22	6	1	24	8	1	14	11	2	2	14	1	10	16	1	15	19	1	15	21	1	11	24	1	22	27	1	5	30	1	14	33	1	1
3	2	21	6	1	23	8	1	13	12	1	24	14	1	9	16	1	14	19	1	14	21	1	10	24	1	21	27	1	4	30	1	13	34	1	5
3	2	20	6	1	22	8	1	12	12	1	23	14	1	8	16	1	13	19	1	13	21	1	9	24	1	20	27	1	3	30	1	12	34	1	4
3	2	19	6	1	21	8	1	11	12	1	22	14	1	7	16	1	12	19	1	12	22	1	24	24	1	19	28	1	18	30	1	11	34	1	3
3	2	18	6	1	20	8	1	10	12	1	21	14	1	6	16	1	11	19	1	11	22	1	23	24	1	18	28	1	17	30	1	10	34	1	2
3	2	17	6	1	19	10	2	19	12	1	20	14	1	5	16	1	10	19	1	10	22	1	22	24	1	17	28	1	16	30	1	9	34	1	1
3	2	16	6	1	18	10	2	18	12	1	19	14	1	4	17	2	24	19	1	9	22	1	21	24	1	16	28	1	15	30	1	8	35	1	18
3	2	15	6	1	17	10	2	17	12	1	18	14	1	3	17	2	23	19	1	8	22	1	20	24	1	15	28	1	14	30	1	7	35	1	17
4	2	24	6	1	16	10	2	16	12	1	17	14	1	2	17	2	22	19	1	7	22	1	19	24	1	14	28	1	13	30	1	6			
4	2	23	6	1	15	10	2	15	12	1	16	14	1	1	17	2	21	19	1	6	22	1	18	24	1	13	28	1	12	30	1	5			
4	2	22	6	1	14	10	2	14	12	1	15	15	1	24	17	2	20	19	1	5	22	1	17	24	1	12	28	1	11	30	1	4			
4	2	21	6	1	13	10	2	13	12	1	14	15	1	23	17	2	19	20	1	24	22	1	16	24	1	11	28	1	10	30	1	3			
4	2	20	6	1	12	10	2	12	12	1	13	15	1	22	17	2	18	20	1	23	22	1	15	24	1	10	28	1	9	30	1	2			
4	2	19	6	1	11	10	2	11	12	1	12	15	1	21	17	2	17	20	1	22	22	1	14	24	1	9	28	1	8	30	1	1			
4	2	18	6	1	10	10	2	10	12	1	11	15	1	20	17	2	16	20	1	21	22	1	13	24	1	8	28	1	7	31	1	18			
4	2	17	6	1	9	10	2	9	12	1	10	15	1	19	17	2	15	20	1	20	22	1	12	24	1	7	28	1	6	31	1	17			
4	2	16	6	1	8	10	2	8	12	1	9	15	1	18	17	2	14	20	1	19	22	1	11	26	1	24	28	1	5	31	1	16			

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Appendix 1. Station list & devices deployment

Station	Cast	Date	Time[1]	Latitude	Longitude	Device name	Action name
1	1	15/05/2013	17:36:52	39.733558	-14.166534	Ultra Clean CTD	Begin
1	1	15/05/2013	17:38:27	39.733654	-14.166419	Ultra Clean CTD	Bottom
1	1	15/05/2013	17:38:28	39.733655	-14.166418	Ultra Clean CTD	End
1	1	15/05/2013	17:59:55	39.733739	-14.166062	Ultra Clean CTD	Begin
1	1	15/05/2013	19:26:36	39.734031	-14.16592	Ultra Clean CTD	Bottom
1	1	15/05/2013	21:15:40	39.732058	-14.165843	Ultra Clean CTD	End
1	2	15/05/2013	22:23:15	39.732927	-14.166849	CTD 25L	Begin
1	2	16/05/2013	00:01:57	39.733724	-14.166243	CTD 25L	Bottom
1	2	16/05/2013	02:19:59	39.73315	-14.166329	CTD 25L	End
1	3	16/05/2013	03:59:08	39.733329	-14.166429	CTD 25L	Begin
1	3	16/05/2013	04:33:22	39.733045	-14.167565	CTD 25L	Bottom
1	3	16/05/2013	05:35:10	39.733352	-14.16904	CTD 25L	End
1	4	16/05/2013	06:35:34	39.7323	-14.165304	Ultra Clean CTD	Begin
1	4	16/05/2013	08:08:02	39.732975	-14.166694	Ultra Clean CTD	Bottom
1	4	16/05/2013	09:59:42	39.732728	-14.166424	Ultra Clean CTD	End
1	5	16/05/2013	13:04:51	39.733355	-14.166478	Ultra Clean CTD	Begin
1	5	16/05/2013	13:18:51	39.733337	-14.166595	Ultra Clean CTD	Bottom
1	5	16/05/2013	13:20:51	39.733412	-14.166425	Ultra Clean CTD	End
2	1	17/05/2013	02:20:22	38.14056	-12.207509	Ultra Clean CTD	Begin
2	1	17/05/2013	03:55:19	38.139998	-12.20853	Ultra Clean CTD	Bottom
2	1	17/05/2013	05:46:50	38.138482	-12.209073	Ultra Clean CTD	End
2	2	17/05/2013	06:14:25	38.140742	-12.207188	CTD 25L	Begin
2	2	17/05/2013	06:20:28	38.140696	-12.206744	CTD 25L	Bottom
2	2	17/05/2013	06:33:24	38.140417	-12.205768	CTD 25L	End
3	1	17/05/2013	21:13:14	36.566592	-9.865774	Ultra Clean CTD	Begin
3	1	17/05/2013	22:22:22	36.566594	-9.866454	Ultra Clean CTD	Bottom
3	1	18/05/2013	00:08:53	36.566254	-9.86608	Ultra Clean CTD	End
3	2	18/05/2013	00:32:17	36.566902	-9.865867	CTD 25L	Begin
3	2	18/05/2013	01:38:21	36.566909	-9.865887	CTD 25L	Bottom
3	2	18/05/2013	03:09:31	36.566554	-9.865972	CTD 25L	End
4	1	18/05/2013	17:58:50	35.839646	-7.254664	Ultra Clean CTD	Begin
4	1	18/05/2013	18:25:48	35.839813	-7.255833	Ultra Clean CTD	Bottom
4	1	18/05/2013	19:19:20	35.841703	-7.255818	Ultra Clean CTD	End
4	2	18/05/2013	19:59:47	35.839452	-7.252941	CTD 25L	Begin
4	2	18/05/2013	20:42:01	35.839881	-7.254919	CTD 25L	Bottom
4	2	18/05/2013	21:30:31	35.842463	-7.256786	CTD 25L	End
5	1	19/05/2013	09:11:59	36.058718	-4.821754	Ultra Clean CTD	Begin
5	1	19/05/2013	09:28:32	36.058779	-4.819439	Ultra Clean CTD	Bottom
5	1	19/05/2013	10:16:04	36.058483	-4.815061	Ultra Clean CTD	End
5	2	19/05/2013	10:39:06	36.057855	-4.828238	CTD 25L	Begin
5	2	19/05/2013	10:57:26	36.058669	-4.825384	CTD 25L	Bottom

5	2	19/05/2013	11:40:02	36.058832	-4.819214	CTD 25L	End
5	3	19/05/2013	12:56:01	36.057789	-4.82647	Ultra Clean CTD	Begin
5	3	19/05/2013	13:14:24	36.058548	-4.822287	Ultra Clean CTD	Bottom
5	3	19/05/2013	14:16:59	36.058488	-4.813997	Ultra Clean CTD	End
6	1	19/05/2013	21:21:55	36.039531	-3.216183	Ultra Clean CTD	Begin
6	1	19/05/2013	21:51:33	36.039332	-3.217345	Ultra Clean CTD	Bottom
6	1	19/05/2013	23:00:08	36.0405	-3.222548	Ultra Clean CTD	End
6	2	19/05/2013	23:31:01	36.040681	-3.213561	CTD 25L	Begin
6	2	20/05/2013	00:00:26	36.039497	-3.216677	CTD 25L	Bottom
6	2	20/05/2013	00:59:34	36.042076	-3.223174	CTD 25L	End
7	1	20/05/2013	11:44:44	36.447824	-1.026669	Ultra Clean CTD	Begin
7	1	20/05/2013	12:35:02	36.448541	-1.022691	Ultra Clean CTD	Bottom
7	1	20/05/2013	13:58:17	36.447508	-1.020401	Ultra Clean CTD	End
7	1	20/05/2013	14:12:53	36.447708	-1.020565	CTD 25L	Begin
7	1	20/05/2013	14:15:23	36.447778	-1.020727	CTD 25L	Bottom
7	1	20/05/2013	14:25:53	36.447682	-1.021317	CTD 25L	End
8	1	21/05/2013	00:10:13	37.009694	0.722603	Ultra Clean CTD	Begin
8	1	21/05/2013	00:59:08	37.010377	0.724668	Ultra Clean CTD	Bottom
8	1	21/05/2013	02:23:22	37.011315	0.728734	Ultra Clean CTD	End
8	2	21/05/2013	02:43:32	37.012915	0.723476	CTD 25L	Begin
8	2	21/05/2013	02:45:40	37.012617	0.723354	CTD 25L	Bottom
8	2	21/05/2013	02:53:46	37.011409	0.722867	CTD 25L	End
9	1	21/05/2013	13:40:14	37.34804	2.749868	Ultra Clean CTD	Begin
9	1	21/05/2013	14:34:06	37.348379	2.750021	Ultra Clean CTD	Bottom
9	1	21/05/2013	16:03:31	37.348824	2.747326	Ultra Clean CTD	End
9	2	21/05/2013	16:12:18	37.348499	2.747736	CTD 25L	Begin
9	2	21/05/2013	16:13:58	37.348585	2.747541	CTD 25L	Bottom
9	2	21/05/2013	16:21:19	37.348571	2.747237	CTD 25L	End
10	1	22/05/2013	07:48:46	37.571076	4.774565	CTD 25L	Begin
10	1	22/05/2013	07:50:42	37.571192	4.774678	CTD 25L	Bottom
10	1	22/05/2013	07:56:28	37.57168	4.774992	CTD 25L	End
10	2	22/05/2013	08:17:46	37.571219	4.77528	Ultra Clean CTD	Begin
10	2	22/05/2013	08:59:35	37.573349	4.77495	Ultra Clean CTD	Bottom
10	2	22/05/2013	09:36:51	37.574608	4.774047	Ultra Clean CTD	End
11	1	22/05/2013	20:08:38	37.772266	6.662278	Ultra Clean CTD	Begin
11	1	22/05/2013	21:01:55	37.774791	6.663301	Ultra Clean CTD	Bottom
11	1	22/05/2013	22:27:22	37.777337	6.663869	Ultra Clean CTD	End
11	2	22/05/2013	22:47:15	37.776429	6.661654	CTD 25L	Begin
11	2	22/05/2013	22:53:13	37.776336	6.661065	CTD 25L	Bottom
11	2	22/05/2013	23:00:32	37.776044	6.660799	CTD 25L	End
11	3	23/05/2013	01:22:47	37.772243	6.660371	Ultra Clean CTD	Begin
11	3	23/05/2013	02:20:58	37.770741	6.659524	Ultra Clean CTD	Bottom
11	3	23/05/2013	03:45:01	37.769241	6.658882	Ultra Clean CTD	End
12	1	23/05/2013	14:48:03	37.971782	8.32113	Ultra Clean CTD	Begin

12	1	23/05/2013	15:32:05	37.971908	8.320094	Ultra Clean CTD	Bottom
12	1	23/05/2013	16:48:42	37.971599	8.317953	Ultra Clean CTD	End
12	2	23/05/2013	17:03:16	37.971562	8.318495	CTD 25L	Begin
12	2	23/05/2013	17:45:06	37.972289	8.317632	CTD 25L	Bottom
12	2	23/05/2013	18:51:05	37.976315	8.31017	CTD 25L	End
13	1	24/05/2013	07:19:24	38.085401	10.881704	Ultra Clean CTD	Begin
13	1	24/05/2013	07:32:12	38.085914	10.881046	Ultra Clean CTD	Bottom
13	1	24/05/2013	08:14:40	38.085129	10.878495	Ultra Clean CTD	End
13	2	24/05/2013	08:33:06	38.084689	10.880121	CTD 25L	Begin
13	2	24/05/2013	08:46:55	38.084742	10.880166	CTD 25L	Bottom
13	2	24/05/2013	09:21:16	38.084304	10.880496	CTD 25L	End
13	3	24/05/2013	10:20:27	38.082337	10.883866	Ultra Clean CTD	Begin
13	3	24/05/2013	10:27:22	38.082336	10.883856	Ultra Clean CTD	Bottom
13	3	24/05/2013	10:42:29	38.081957	10.883312	Ultra Clean CTD	End
14	1	24/05/2013	19:48:12	37.214685	12.467514	Ultra Clean CTD	Begin
14	1	24/05/2013	19:50:28	37.214365	12.467272	Ultra Clean CTD	Bottom
14	1	24/05/2013	20:15:48	37.215417	12.466976	Ultra Clean CTD	End
14	2	24/05/2013	20:36:24	37.215664	12.465713	CTD 25L	Begin
14	2	24/05/2013	20:38:58	37.215488	12.465577	CTD 25L	Bottom
14	2	24/05/2013	20:56:35	37.2161	12.465812	CTD 25L	End
15	1	25/05/2013	07:25:23	36.373333	14.220465	Ultra Clean CTD	Begin
15	1	25/05/2013	07:37:06	36.372821	14.219713	Ultra Clean CTD	Bottom
15	1	25/05/2013	08:16:52	36.372127	14.22052	Ultra Clean CTD	End
15	2	25/05/2013	08:33:02	36.371769	14.220465	CTD 25L	Begin
15	2	25/05/2013	08:44:32	36.371793	14.220278	CTD 25L	Bottom
15	2	25/05/2013	09:20:29	36.37201	14.220277	CTD 25L	End
16	1	25/05/2013	20:11:12	35.711698	16.329457	Ultra Clean CTD	Begin
16	1	25/05/2013	21:16:53	35.712435	16.328313	Ultra Clean CTD	Bottom
16	1	25/05/2013	22:59:47	35.71139	16.327045	Ultra Clean CTD	End
16	2	25/05/2013	23:22:36	35.712183	16.327105	CTD 25L	Begin
16	2	25/05/2013	23:38:35	35.712079	16.327702	CTD 25L	Bottom
16	2	25/05/2013	23:45:18	35.712055	16.328112	CTD 25L	End
17	1	26/05/2013	10:16:48	34.965237	18.039963	Mooring	Deployment
17	2	26/05/2013	10:35:09	34.957969	18.0608	Ultra Clean CTD	Begin
17	2	26/05/2013	11:37:27	34.957972	18.059843	Ultra Clean CTD	Bottom
17	2	26/05/2013	13:23:06	34.959035	18.057768	Ultra Clean CTD	End
17	3	26/05/2013	13:38:58	34.95947	18.057771	CTD 25L	Begin
17	3	26/05/2013	14:40:38	34.959551	18.055712	CTD 25L	Bottom
17	3	26/05/2013	16:08:44	34.960134	18.056526	CTD 25L	End
18	1	27/05/2013	03:21:40	34.283316	20.017285	Ultra Clean CTD	Begin
18	1	27/05/2013	04:16:33	34.283334	20.016917	Ultra Clean CTD	Bottom
18	1	27/05/2013	05:43:18	34.283621	20.016225	Ultra Clean CTD	End
18	2	27/05/2013	05:58:03	34.283304	20.016338	CTD 25L	Begin
18	2	27/05/2013	06:58:35	34.283269	20.016587	CTD 25L	Bottom

18	2	27/05/2013	08:18:55	34.283062	20.01592	CTD 25L	End
18	3	27/05/2013	08:34:14	34.283321	20.016303	CTD Brine	Begin
18	3	27/05/2013	09:34:05	34.283428	20.016129	CTD Brine	Bottom
18	3	27/05/2013	10:52:07	34.284227	20.016551	CTD Brine	End
18	4	27/05/2013	11:07:44	34.283409	20.015551	Ultra Clean CTD	Begin
18	4	27/05/2013	12:01:17	34.284305	20.016019	Ultra Clean CTD	Bottom
18	4	27/05/2013	13:29:10	34.28737	20.013611	Ultra Clean CTD	End
19	1	28/05/2013	04:39:17	33.663667	22.788197	Ultra Clean CTD	Begin
19	1	28/05/2013	05:10:04	33.663542	22.787538	Ultra Clean CTD	Bottom
19	1	28/05/2013	06:07:02	33.663603	22.787864	Ultra Clean CTD	End
19	2	28/05/2013	06:28:31	33.66362	22.787861	CTD 25L	Begin
19	2	28/05/2013	06:53:51	33.663609	22.787758	CTD 25L	Bottom
19	2	28/05/2013	07:42:48	33.663576	22.787975	CTD 25L	End
20	1	28/05/2013	22:15:16	33.206735	25.504579	Ultra Clean CTD	Begin
20	1	28/05/2013	22:59:31	33.205826	25.50626	Ultra Clean CTD	Bottom
20	1	29/05/2013	00:33:23	33.207643	25.504597	Ultra Clean CTD	End
20	2	29/05/2013	00:46:24	33.206355	25.505196	CTD 25L	Begin
20	2	29/05/2013	01:30:27	33.206936	25.504953	CTD 25L	Bottom
20	2	29/05/2013	02:36:55	33.207441	25.506094	CTD 25L	End
21	1	29/05/2013	16:30:08	33.842545	28.082809	Ultra Clean CTD	Begin
21	1	29/05/2013	17:14:36	33.842346	28.081498	Ultra Clean CTD	Bottom
21	1	29/05/2013	18:31:34	33.842525	28.082424	Ultra Clean CTD	End
21	2	29/05/2013	18:46:45	33.842614	28.082006	CTD 25L	Begin
21	2	29/05/2013	19:29:20	33.842332	28.082233	CTD 25L	Bottom
21	2	29/05/2013	20:31:31	33.842144	28.081775	CTD 25L	End
21	3	29/05/2013	20:57:23	33.842054	28.083657	CTD 25L	Begin
21	3	29/05/2013	20:59:49	33.841805	28.083501	CTD 25L	Bottom
21	3	29/05/2013	21:14:06	33.841443	28.083053	CTD 25L	End
21	4	29/05/2013	21:32:34	33.842832	28.082565	Ultra Clean CTD	Begin
21	4	29/05/2013	22:26:56	33.844028	28.083299	Ultra Clean CTD	Bottom
21	4	29/05/2013	23:42:21	33.845715	28.080486	Ultra Clean CTD	End
22	1	30/05/2013	10:16:35	33.781896	30.197019	Ultra Clean CTD	Begin
22	1	30/05/2013	11:05:10	33.782616	30.196997	Ultra Clean CTD	Bottom
22	1	30/05/2013	12:21:21	33.783016	30.197021	Ultra Clean CTD	End
22	2	30/05/2013	12:37:59	33.78261	30.19736	CTD 25L	Begin
22	2	30/05/2013	12:45:58	33.782466	30.196931	CTD 25L	Bottom
22	2	30/05/2013	12:55:36	33.782518	30.196791	CTD 25L	End
23	1	30/05/2013	22:44:14	33.220574	32.018978	Ultra Clean CTD	Begin
23	1	30/05/2013	23:16:51	33.220987	32.017599	Ultra Clean CTD	Bottom
23	1	31/05/2013	00:18:31	33.221123	32.017595	Ultra Clean CTD	End
23	2	31/05/2013	00:37:21	33.221418	32.017248	CTD 25L	Begin
23	2	31/05/2013	01:06:58	33.222463	32.016955	CTD 25L	Bottom
23	2	31/05/2013	02:04:48	33.224696	32.017388	CTD 25L	End
24	1	31/05/2013	08:14:48	34.222806	31.942165	Ultra Clean CTD	Begin

24	1	31/05/2013	08:54:47	34.222235	31.941315	Ultra Clean CTD	Bottom
24	1	31/05/2013	10:07:31	34.221883	31.940565	Ultra Clean CTD	End
24	2	31/05/2013	10:21:50	34.222408	31.941237	CTD 25L	Begin
24	2	31/05/2013	11:01:12	34.222106	31.94256	CTD 25L	Bottom
24	2	31/05/2013	12:10:11	34.22195	31.942453	CTD 25L	End
25	1	31/05/2013	22:30:25	35.069867	30.514287	CTD 25L	Begin
25	1	31/05/2013	23:14:11	35.069954	30.514415	CTD 25L	Bottom
25	1	01/06/2013	00:33:50	35.069724	30.514087	CTD 25L	End
26	1	01/06/2013	13:04:54	35.826172	28.909937	Ultra Clean CTD	Begin
26	1	01/06/2013	14:12:31	35.826301	28.908992	Ultra Clean CTD	Bottom
26	1	01/06/2013	15:49:31	35.825811	28.909595	Ultra Clean CTD	End
26	2	01/06/2013	16:04:13	35.825949	28.909389	CTD 25L	Begin
26	2	01/06/2013	17:16:13	35.826044	28.909659	CTD 25L	Bottom
26	2	01/06/2013	19:02:45	35.826034	28.909907	CTD 25L	End
27	1	02/06/2013	01:51:53	35.452989	27.585629	Ultra Clean CTD	Begin
27	1	02/06/2013	02:14:33	35.453116	27.58666	Ultra Clean CTD	Bottom
27	1	02/06/2013	02:56:53	35.452906	27.586141	Ultra Clean CTD	End
27	2	02/06/2013	03:13:46	35.453241	27.586348	CTD 25L	Begin
27	2	02/06/2013	03:29:57	35.453049	27.586388	CTD 25L	Bottom
27	2	02/06/2013	04:10:18	35.453625	27.586464	CTD 25L	End
28	1	02/06/2013	09:13:51	35.296458	26.640418	Ultra Clean CTD	Begin
28	1	02/06/2013	09:34:22	35.296334	26.640664	Ultra Clean CTD	Bottom
28	1	02/06/2013	10:15:51	35.296331	26.640793	Ultra Clean CTD	End
28	2	02/06/2013	10:26:47	35.296279	26.640209	CTD 25L	Begin
28	2	02/06/2013	10:47:19	35.295524	26.639841	CTD 25L	Bottom
28	2	02/06/2013	11:26:51	35.295479	26.639675	CTD 25L	End
29	1	03/06/2013	05:16:09	37.23707	26.166341	Ultra Clean CTD	Begin
29	1	03/06/2013	05:26:13	37.237128	26.166692	Ultra Clean CTD	Bottom
29	1	03/06/2013	06:03:07	37.23748	26.166326	Ultra Clean CTD	End
29	2	03/06/2013	06:16:55	37.237274	26.166269	CTD 25L	Begin
29	2	03/06/2013	06:26:03	37.237307	26.165978	CTD 25L	Bottom
29	2	03/06/2013	06:55:27	37.237425	26.166287	CTD 25L	End
30	1	03/06/2013	12:26:46	37.941384	25.420701	Ultra Clean CTD	Begin
30	1	03/06/2013	12:37:56	37.941495	25.42049	Ultra Clean CTD	Bottom
30	1	03/06/2013	13:12:44	37.941198	25.420211	Ultra Clean CTD	End
30	2	03/06/2013	13:29:11	37.94162	25.42014	CTD 25L	Begin
30	2	03/06/2013	13:37:13	37.941576	25.420032	CTD 25L	Bottom
30	2	03/06/2013	14:09:45	37.94126	25.420063	CTD 25L	End
31	1	03/06/2013	20:48:18	39.048084	25.210623	Ultra Clean CTD	Begin
31	1	03/06/2013	20:55:59	39.048433	25.210404	Ultra Clean CTD	Bottom
31	1	03/06/2013	21:23:20	39.04773	25.210359	Ultra Clean CTD	End
31	2	03/06/2013	21:36:50	39.047665	25.210582	CTD 25L	Begin
31	2	03/06/2013	21:44:48	39.047459	25.210458	CTD 25L	Bottom
31	2	03/06/2013	22:05:05	39.047431	25.209949	CTD 25L	End

32	1	04/06/2013	02:50:36	39.782716	25.639785	Ultra Clean CTD	Begin
32	1	04/06/2013	02:55:06	39.782853	25.639846	Ultra Clean CTD	Bottom
32	1	04/06/2013	03:10:27	39.782794	25.640346	Ultra Clean CTD	End
32	2	04/06/2013	03:22:32	39.782449	25.639801	CTD 25L	Begin
32	2	04/06/2013	03:23:58	39.782499	25.639885	CTD 25L	Bottom
32	2	04/06/2013	03:35:13	39.782765	25.63964	CTD 25L	End
33	1	04/06/2013	06:42:40	39.967505	25.95773	Ultra Clean CTD	Begin
33	1	04/06/2013	06:44:20	39.967624	25.957714	Ultra Clean CTD	Bottom
33	1	04/06/2013	06:54:16	39.967699	25.957398	Ultra Clean CTD	End
34	1	04/06/2013	12:52:37	40.428539	26.774062	Ultra Clean CTD	Begin
34	1	04/06/2013	12:59:31	40.428627	26.774325	Ultra Clean CTD	Bottom
34	1	04/06/2013	13:11:27	40.428457	26.77417	Ultra Clean CTD	End
35	1	04/06/2013	18:31:22	40.832994	27.565466	Ultra Clean CTD	Begin
35	1	04/06/2013	18:49:44	40.833055	27.565544	Ultra Clean CTD	Bottom
35	1	04/06/2013	19:42:58	40.833415	27.566549	Ultra Clean CTD	End
36	1	04/06/2013	21:55:07	40.839986	27.998746	Ultra Clean CTD	Begin
36	1	04/06/2013	22:19:45	40.839767	27.998606	Ultra Clean CTD	Bottom
36	1	04/06/2013	23:10:55	40.840033	27.998589	Ultra Clean CTD	End
36	2	04/06/2013	23:25:18	40.839952	27.998687	CTD 25L	Begin
36	2	04/06/2013	23:48:19	40.839943	27.998654	CTD 25L	Bottom
36	2	05/06/2013	00:18:48	40.839917	27.998664	CTD 25L	End
37	1	05/06/2013	05:24:43	40.767006	28.999944	Ultra Clean CTD	Begin
37	1	05/06/2013	05:48:24	40.767177	28.999985	Ultra Clean CTD	Bottom
37	1	05/06/2013	06:33:44	40.766876	29.000202	Ultra Clean CTD	End

[1] Time in UTC

Appendix 2.

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