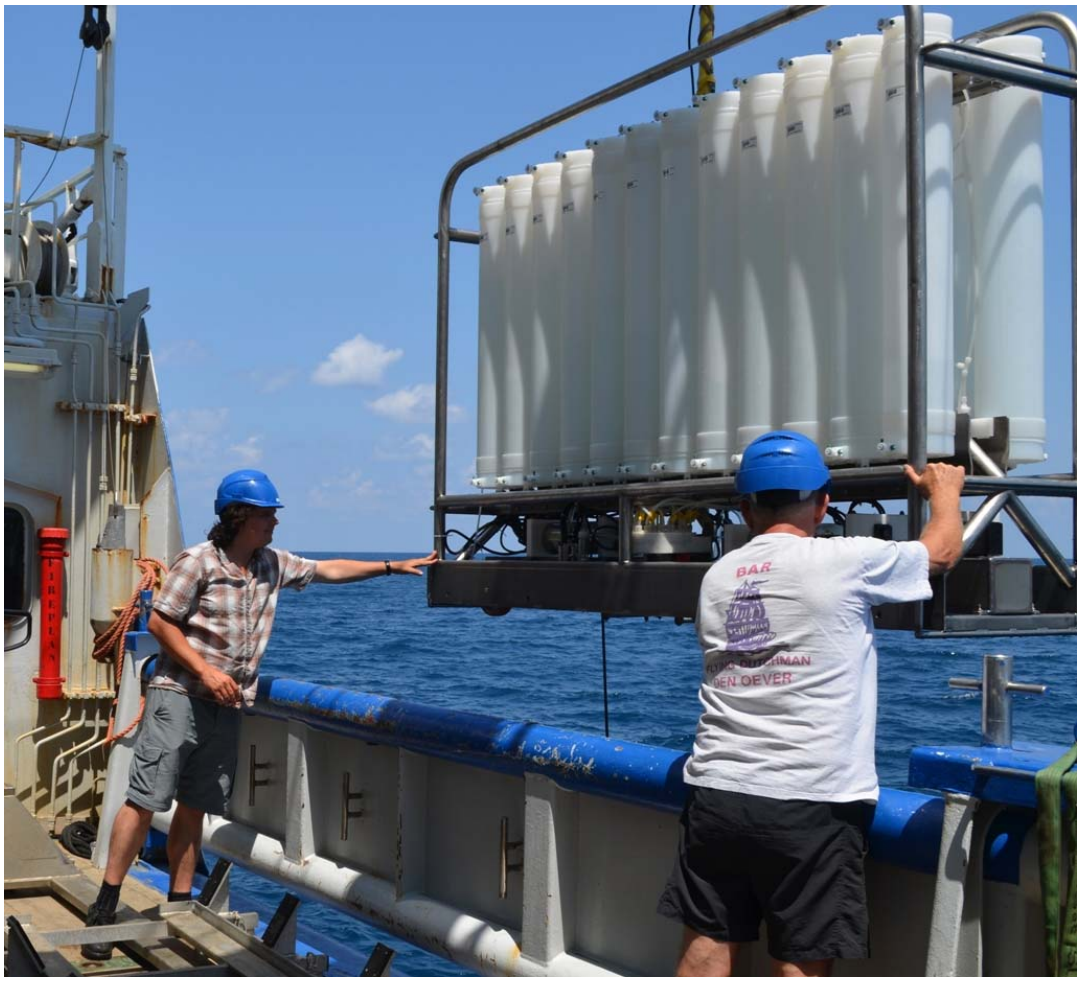
Cruise report 64PE373 on RV Pelagia

MedBlack GEOTRACES leg 2

Istanbul (Turkey) 13-07-2013 to Istanbul (Turkey) 25-07-2013

Micha J.A. Rijkenberg

With contributions of participants



Royal Netherlands Institute for Sea Research

Acknowledgements

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

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

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Cruise summary

Research cruise
The MedBlack GEOTRACES leg 2 (64PE373) on RV *Pelagia* departed 13 July 2013 from Istanbul (Turkey) and arrived 25 July 2013 back in Istanbul (Turkey) with Micha Rijkenberg and Loes Gerringa (Royal NIOZ) as chief scientists.

Stations
During cruise 64PE373 we occupied a total of 12 full depth stations (Figure 1). Typically at each station we did two casts to the bottom starting with the ultraclean CTD (UCC) followed by the high volume CTD (25L CTD). In addition, at each station, the full depth casts would be followed by a shallow cast with the UCC and a cast with 3 in situ pumps, both over the oxic-anoxic interface. The demand for ultraclean seawater samples was high at the hyper stations 2 and 5 and an extra cast with the UCC was taken at station 10. Details like the date, time and position of the actual deployments at each station can be found in Appendix 1. Note that the actual station numbering is different from the original planned station numbering.

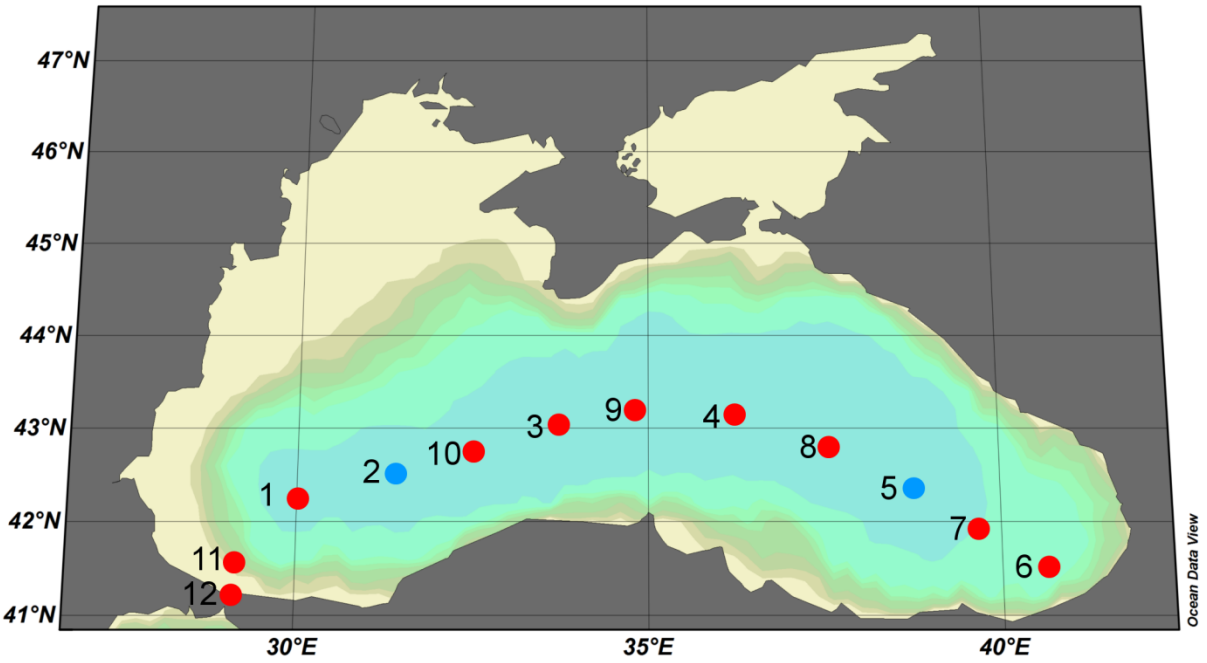

Figure 1. Cruise track of research cruise 64PE373 on the RV Pelagia in July 2013. Red dots represent normal stations with typically one full depth UCC cast, a full depth 25L CTD, a UCC cast over the oxic-anoxic interface, and a cast with in situ pumps over the oxic-anoxic interface. Blue dots represent hyper stations with 2 full depth UCC casts, 1 full depth 25L CTD cast, a UCC cast over the oxic-anoxic interface, and and a cast with in situ pumps over the oxic-anoxic interface.

Cruise narrative
The participants boarded the RV Pelagia at 09:00 am on 13 July 2013. The Pelagia was ready to go at 15:00 and at 21:00 we joined a convoy from Istanbul through the Bosporus into the Black Sea to start leg 2 of the MedBlack GEOTRACES cruises. To allow all participants to set up their equipment the first station was planned at 08:00 am on 14 July. All CTD's and the in situ pumps worked well at station 1 and also at all other stations. We arrived at station 2 at

00:15 am on 15 July. Station 2 was a hyper station where we used an extra UCC cast to collect water for the isotope intercomparison excercise and an extra UCC cast to collect water for mercury (Hg) isotopes and particulate cobalt (Co). After station 2 we started to alternate the planned stations (Figure 1). Alternating the stations allowed for more time in between stations to finish sampling and perform measurements. At hyper station 5 an extra UCC cast was executed. Also at station 10 an extra UCC cast was executed to collect a second batch of water for the isotope intercomparison excercise. The last 2 stations 11 and 12 were close to the entrance of the Bosporus. At station 11 we tried 2 times to sample the Mediterranean outflow intrusion through a canyon into the Black Sea (Ozsoy et al., 2001) but we didn't succeed. This is why at station 11 three casts were recorded, however, only cast 2 (UCC) and cast 3 (25L CTD) were sampled. At station 12 we also tried to find the Mediterranean outflow. We did not succeed at our first location but instead of a second cast we manoeuvered the ship slowly to deeper waters in the Bosporus where we did find the Mediterranean outflow. We entered the Bosporus at 04:30 on 24 July and were around 06:00 back into the harbour of Istanbul.

Ship's clock

The ship left the harbour of Istanbul on 13 July 2013 with the ship's time set on Turkish local time (UTC+3). The ship's time stayed on UTC+3 throughout the expedition.

Weather

The weather conditions were excellent during the whole expedition (Figure 2).

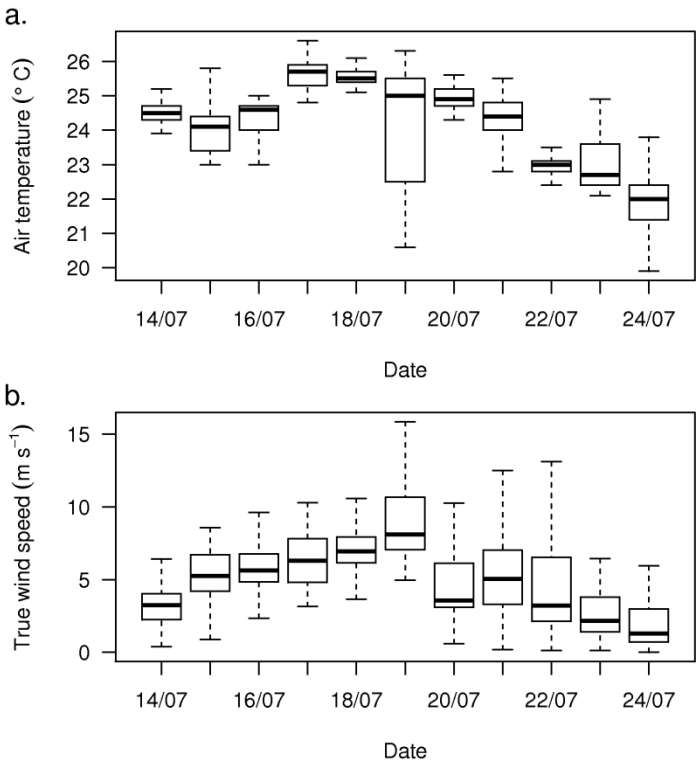

Figure 2. The air temperature (a.) and wind speed (b.) during 64PE373.

General preliminary results

This paragraph will show the section plots of some of the parameters which were measured on board. Parameters measured on board were salinity and oxygen (from the CTD sensor, Figure 3 and 4), hydrogen sulphide (Figure 5), the nutrients (phosphate, silicate, nitrate, nitrite and ammonium Figure 6-10) and fluorescence (Figure 11).

The salinity section plot shows that the salinity increases rapidly with depth. There is a relatively homogenous benthic bottom layer that extends from about 1700 m to the bottom (Murray et al., 1991). Relatively saline water enters the Black Sea via the Bosporus (e.g. Ozsoy et al. 2001). Black Sea surface waters are less saline due to riverine freshwater input by rivers like the Danube, Dnieper, Don, Rioni, Kuban, Dniester, Coruh, Kizil Irmak, Sakarya, and Yesil Irmak rivers, which together are responsible for about 85% of the riverine freshwater input (Ludwig et al. 2009).

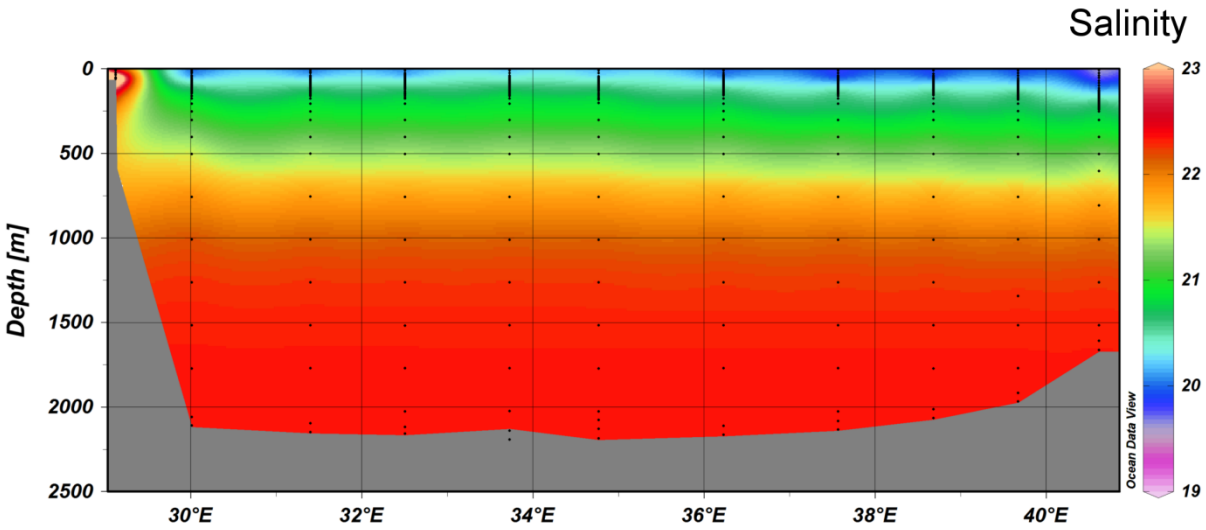

Figure 3. The section plot of preliminary salinity data (UCC sensor data) for cruise 64PE373 in the Black Sea. Data: Sven Ober and Frank van Maarseveen.

An oxygen-rich layer above the permanent halocline at depths lying between 50 and 120 m is the result of winter mixing (e.g. Pakhomova et al. 2013). The vertical diffusive flux of oxygen is insufficient to meet the oxygen consumption demands for the degradation of sinking organic material. As a consequence, the strong vertical stratification results in a well oxygenated surface layer (from 0 to 50-200 m), a suboxic zone, and a permanently anoxic deeper layer (from 70-200 to >2000 m) containing high sulphide concentrations (e.g. Pakhomova et al. 2013) (Figure 4 and 5).

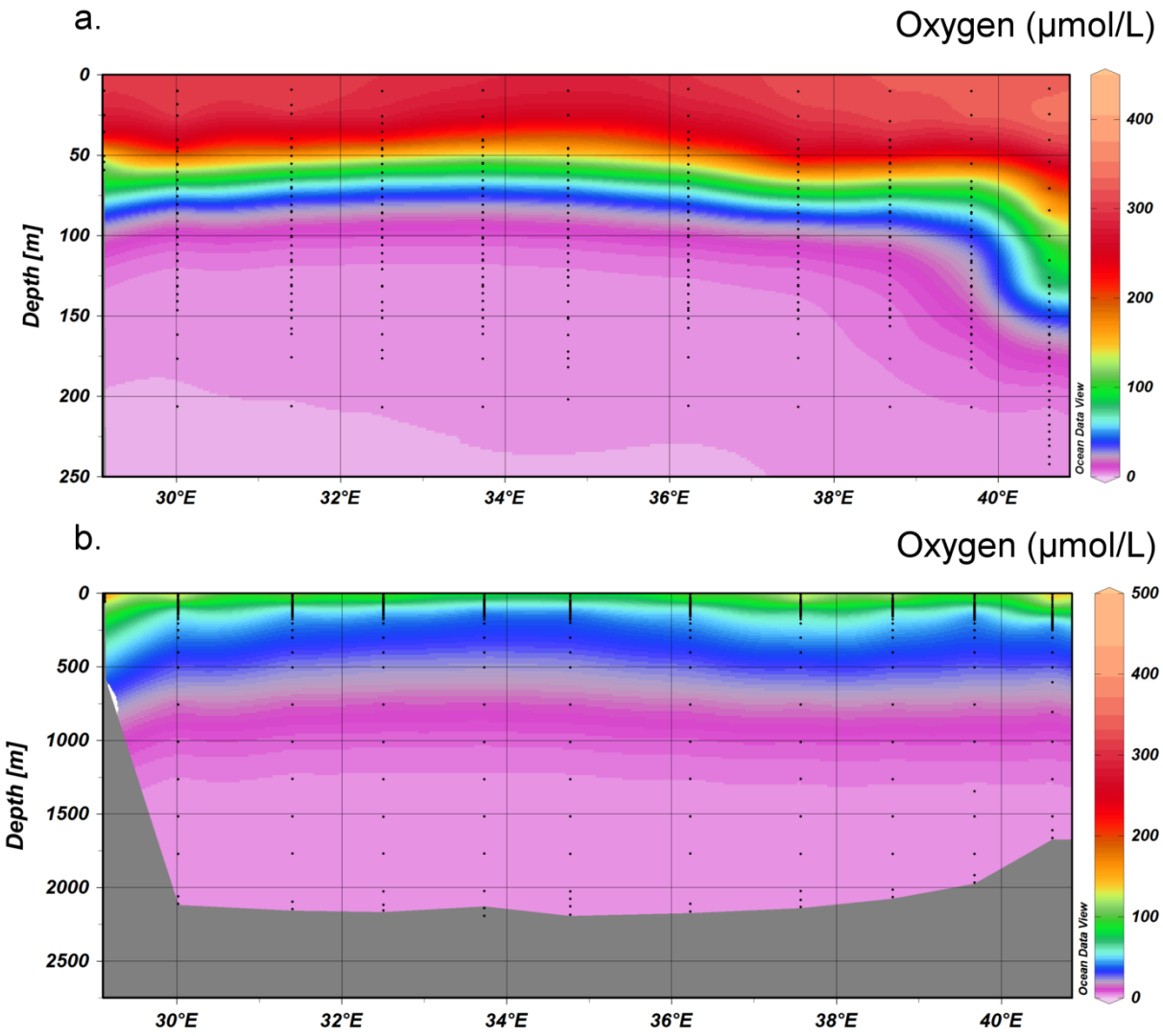

Figure 4. Section plots of preliminary oxygen data (UCC sensor data) for cruise 64PE373 in the Black Sea with a) the upper 250 m of the water column, and b) the full water column. Data: Sven Ober and Frank van Maarseveen

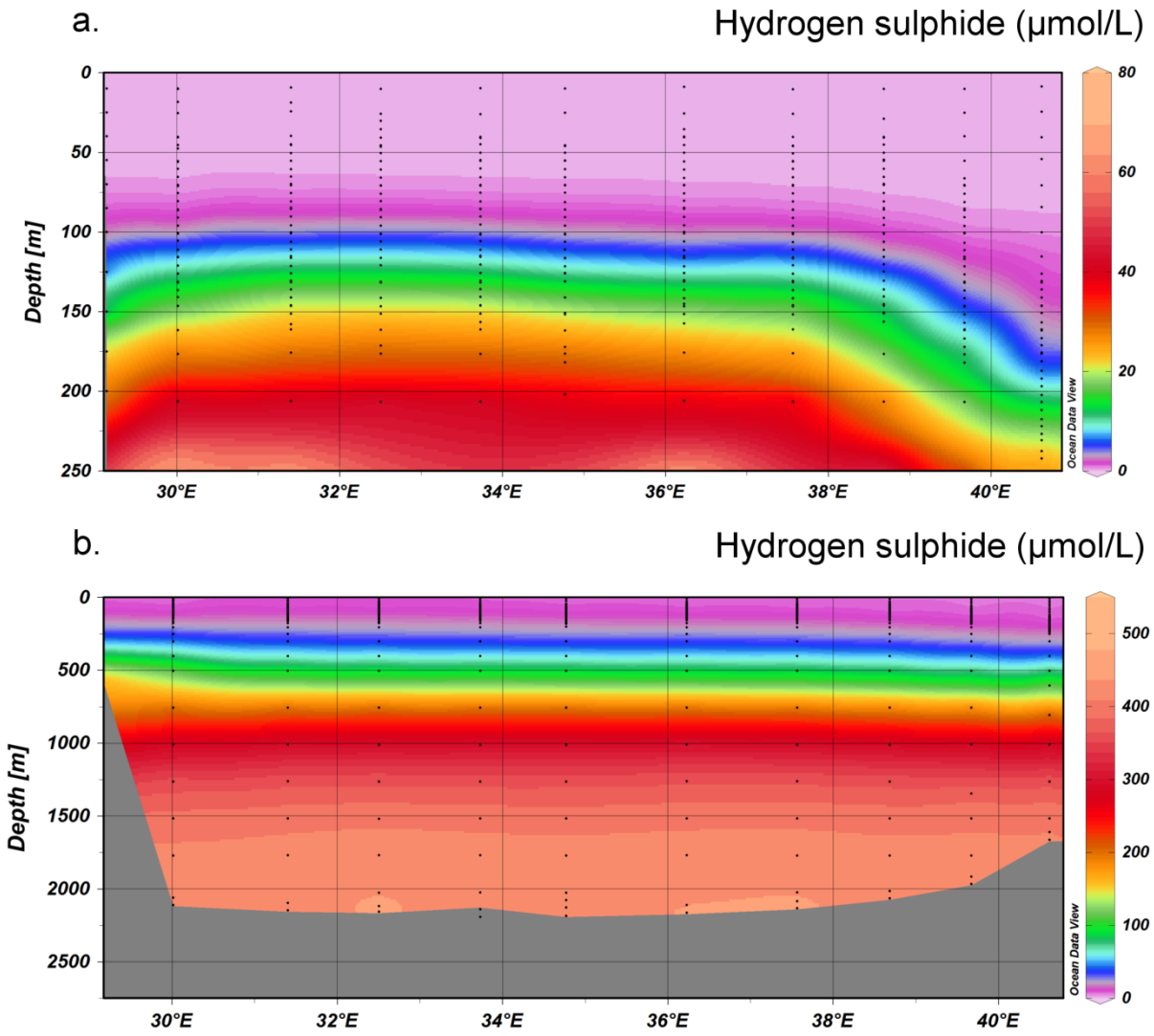

Figure 5. Preliminary hydrogen sulphide data from the UCC for cruise 64PE373 in the Black Sea with a) the upper 250 m of the water column, and b) the full water column. Data: Jan van Ooijen and Sharyn Ossebaar

The nutrient dynamics in the Black Sea upper water column are the result of climate-induced fluctuations and eutrophication. Cold winter conditions typically correspond to increased nutrient conditions whilst mild winters correspond to decreased nutrient concentrations (Pakhomova et al. 2013). Phosphate and silicate increase in concentration with depth (Figure 6 and 7).

Relatively high nitrate and nitrite concentrations can be found between 50-100 m where oxygen starts to decrease and hydrogen sulphide slowly starts to increase (Figure 8 and 9). In the suboxic zone where oxygen has almost disappeared nitrate concentrations undergo a fast decrease to trace values. Below the suboxic zone high concentrations of hydrogen sulphide and ammonium occur (Figure 5 and 10). Nitrate in the euphotic zone between 0-50 m is depleted due to uptake by phytoplankton as also indicated by high fluorescence (e.g. Oguz et al. 2000) (Figure 11).

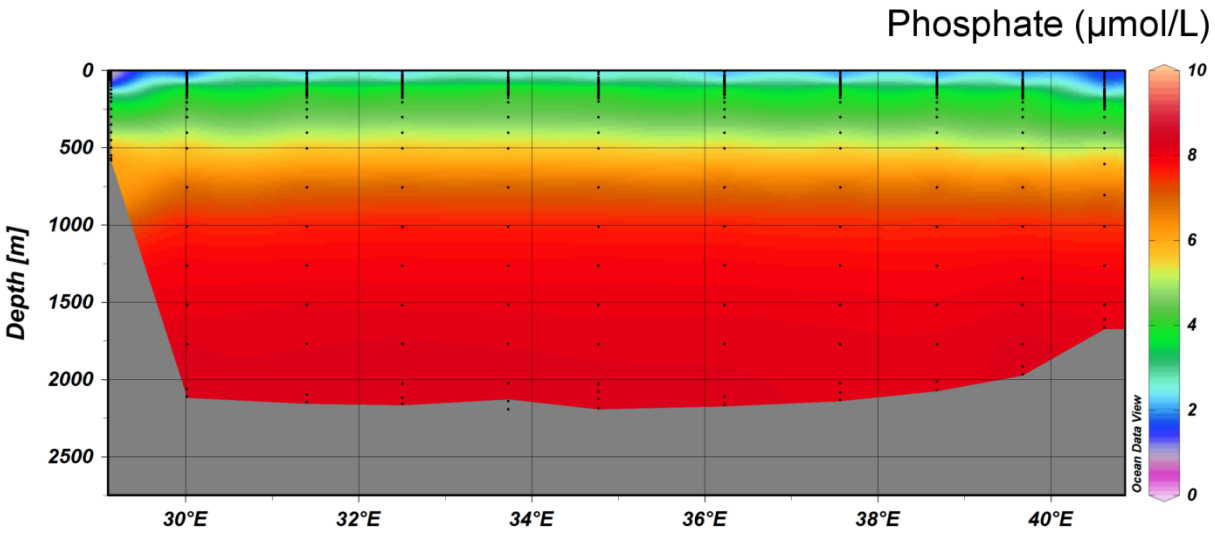

Figure 6. Preliminary phosphate data from the UCC for cruise 64PE373 in the Black Sea. Data: Jan van Ooijen and Sharyn Ossebaar

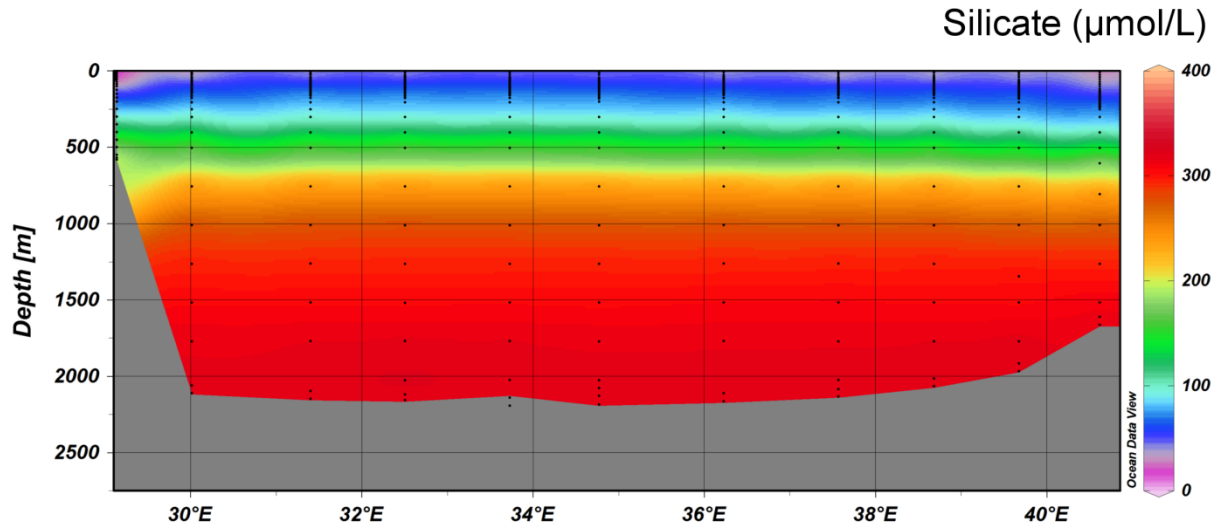

Figure 7. Preliminary silicate data from the UCC for cruise 64PE373 in the Black Sea. Data: Jan van Ooijen and Sharyn Ossebaar

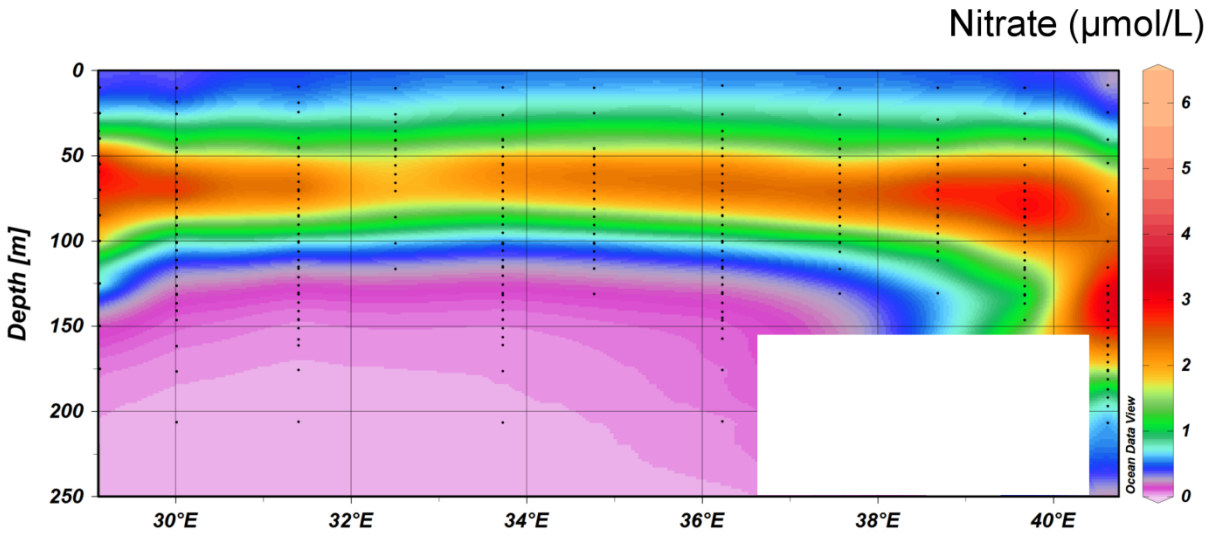

Figure 8. Preliminary nitrate data from the UCC for cruise 64PE373 in the Black Sea. The white block depicts an area without data. Data: Jan van Ooijen and Sharyn Ossebaar

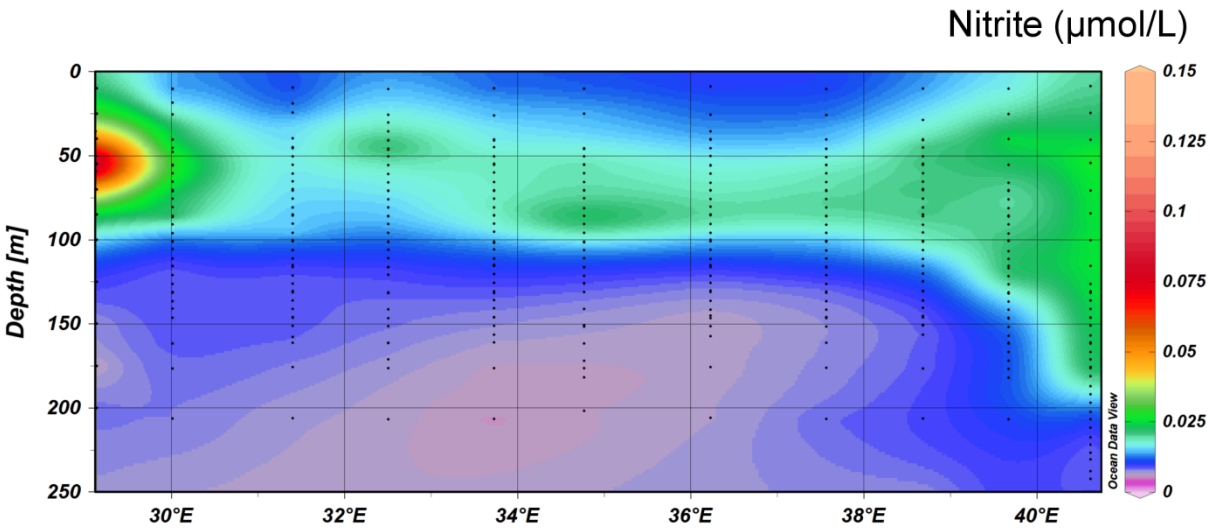

Figure 9. Preliminary nitrite data from the UCC for cruise 64PE373 in the Black Sea. Data: Jan van Ooijen and Sharyn Ossebaar

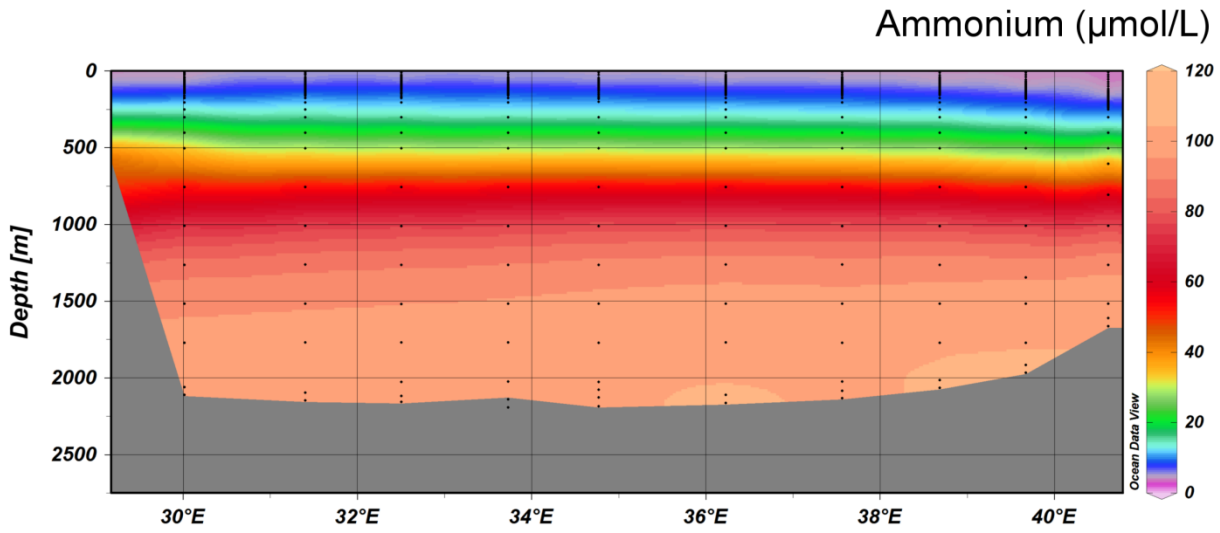

Figure 10. Preliminary ammonium (NH_4^+) data from the UCC for cruise 64PE373 in the Black. Data: Jan van Ooijen and Sharyn Ossebaar

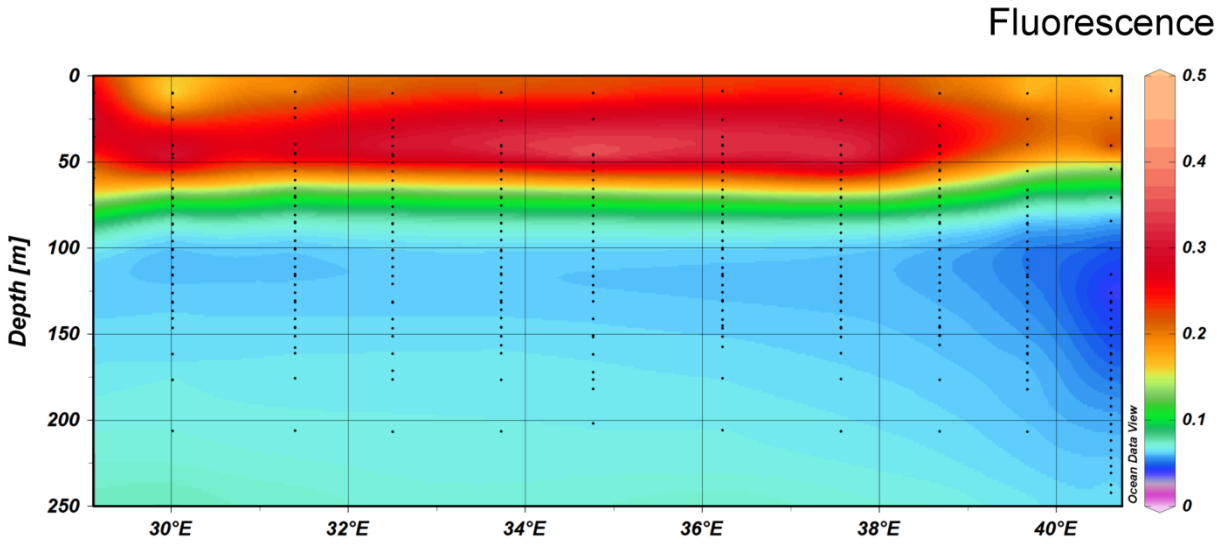

Figure 11. Preliminary fluorescence data for the upper 250 m of the water column from the UCC for cruise 64PE373 in the Black. Data: Sven Ober and Frank van Maarseveen

Underway surface data

Figures 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 19-27°C and increases in an eastward direction (Figure 12). The sea surface salinity varied between 16 and 22 (Figure 13) and the fluorescence varied between 0 and 0.11 (Figure 14).

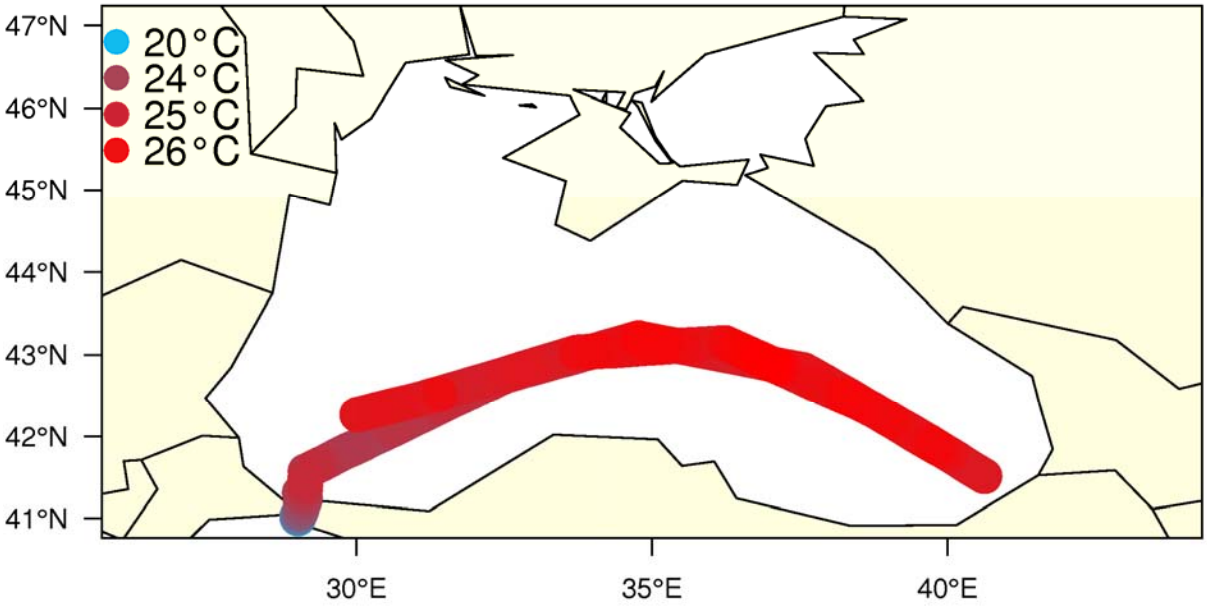

Figure 12. The preliminary sea surface temperature data as measured with the ship's underway system during 64PE373.

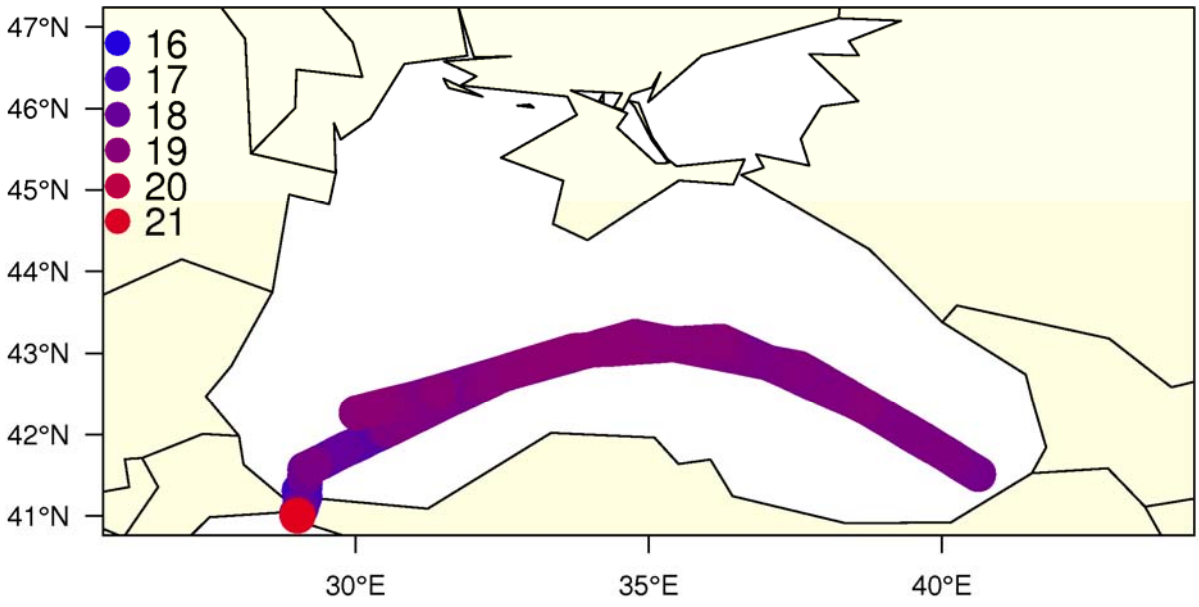

Figure 13. The preliminary sea surface salinity data as measured with the ship's underway system during 64PE373.

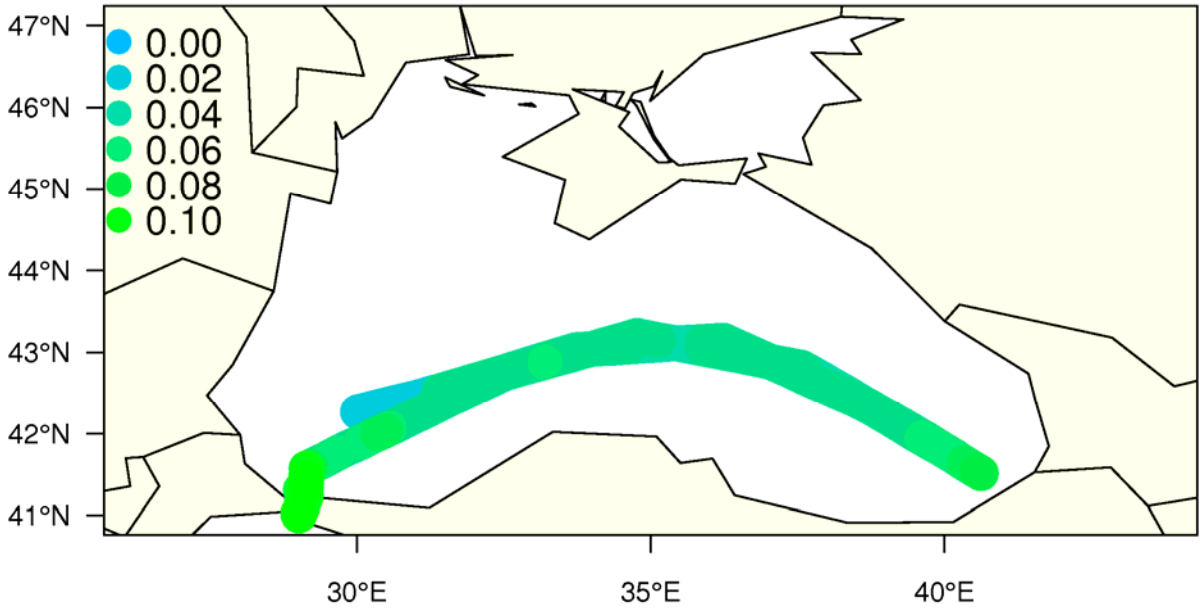

Figure 14. The preliminary sea surface fluorescence data as measured with the ship's underway system during 64PE373.

Description of sample equipment and deployment

We used a system for ultra clean trace metal sampling consisting of an all-titanium frame with 24 sample bottles of 27 L each made of PVDF plastic (abbreviated UCC), see Figure 15. A Kley France winch was used to deploy the UCC to deep waters by a 17.7 mm diameter Kevlar hydrowire with seven independent internal signal/conductor cables (Cousin Trestec S.A.). Sampling of the UCC occurred in a class 100 clean-room container (de Baar et al., 2008). Filtered samples were directly filtered from the UCC sample bottles under nitrogen pressure using 0.2 µm Sartobran 300 cartridges (Sartorius).

To collect non trace metal clean samples a 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. More details about the CTD frames used can be found at page 25.

To collect large volumes of 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.

Trace metal clean particles were collected in the anoxic, the suboxic and the oxic part of the Black Sea water column using 3 SAPS (Challenger in situ pumps, from NOC Southampton).

Figure 15. The sample equipment used to take trace metal clean and non-trace metal clean water samples and particles during 64PE373.

Concluding

With 12 full depth stations we have completed the second 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. 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). We sampled an extensive set of parameters with direct on board measurement of the trace metals Fe and Al, the CO_2 system, nutrients and the organic speciation of Fe. We also sampled a large set of parameters for the international community including labile Fe, Co and Co speciation, Ag, Cu, Zn, Cd, Mn, 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, 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. As dust is a main transport pathway of bio-essential trace elements to the surface of the open ocean the heavy Saharan dust impact on the Mediterranean Sea is ideal to investigate the effect of dust on the biogeochemical cycles of trace elements and isotopes. The Black Sea is the largest anoxic basin of the world and forms an ideal natural laboratory to unravel the microbial driven reduction and oxidation reactions of trace elements and isotopes. For example, here results will have major implications for the isotope systematics of Fe and sulphur in ancient deposits such as the Banded Iron Formations that are studied to unravel the redox conditions of the ancient Earth.

GEOTRACES Mediterranean Sea and Black Sea

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

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

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

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

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3. Participants and parameters

3.1. List of participants

1	**Micha Rijkenberg PI**	NIOZ; Biological Oceanography
2	**Loes Gerringa PI**	NIOZ; Biological Oceanography
3	**Morten Andersen**	ETH Zürich
4	**Kemal Can Bizsel**	IMST-DEU
5	**Lorendz Boom**	NIOZ; MTEC
6	**Johann Bown**	NIOZ; Biological Oceanography
7	**Marie Boyé**	LEMAR IUEM
8	**Nikki Clargo**	NIOZ; Biological Oceanography
9	**Lars-Eric Heimburger**	CNRS-OMP-GET
10	**Patrick Laan**	NIOZ; Biological Oceanography
11	**Frank van Maarseveen**	NIOZ; MRF
12	**Sven Ober**	NIOZ; FYS
13	**Jan van Ooijen**	NIOZ; MRF
14	**Sharyn Ossebaar**	NIOZ; MRF
15	**Matt Patey**	NOC, Southampton
16	**John Rolison**	University of Otago
17	**Lesley Salt**	NIOZ; Biological Oceanography
18	**Jack Schilling**	NIOZ; MTEC
19	**Jeroen Sonke**	CNRS-OMP-GET

For complete addresses and email see Appendix 2

Figure 16. Scientists and crew during 64PE373 on the RV Pelagia in the Black Sea.

3.2. UCC Sample Team

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

1) Morten Andersen
2) Johann Bown
3) Micha Rijkenberg
4) Kemal Can Bizsel
5) Jeroen Sonke
6) Lars-Eric Heimburger
7) Marie Boyé
8) Patrick Laan

Figure 17. a) Jeroen, b) Johann, c) Lars-Eric and Johann, d) Patrick, e) Morten and Micha, and f) Marie 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
Nitrate/Nitrite/Ammonium	J. van Ooijen	J. van Ooijen
Hydrogen sulphide	J. van Ooijen	J. van Ooijen
Phosphate/Silicate	S. Ossebaar	S. Ossebaar
Dissolved Fe	M. Rijkenberg	P. Laan/M. Rijkenberg
Fe Speciation	L. Gerringa	L. Gerringa
Dissolved Al	J. Rolison	R. Middag/J. Rolison
Dissolved Cu	M. Boyé	Waeles/Pernet-Coudrier/Riso
Dissolved Ag	M. Rijkenberg/M. Patey	E. Achterberg
Dissolved Co	M. Boyé	G. Dulaquais/M. Boyé
Co-speciation	M. Boyé	G. Dulaquais/M. Boyé
Cu-speciation	M. Boyé	Waeles/Pernet-Coudrier/Riso
Co, Zn, Cd ultrafiltration	M. Boyé/M. Rijkenberg	G. Dulaquais/M. Boyé
Total dissolvable Co, Zn, Cd	M. Boyé	G. Dulaquais/M. Boyé
Total dissolvable Cu	M. Boyé	Waeles/Pernet-Coudrier/Riso
$^{15}NO_3/N^{18}O_3/^{15}NH_4$	M. Rijkenberg/UCC team	R. Ganeshram
Aerosols (mineral comp)	M. Andersen	J.-B. Stuut
Aerosols (major ions, trace metals)	M. Andersen	A. Baker
DGT labile Fe	C. Bizsel	C. Bizsel/N. Sanchez/M. van Ardelan
Size fractionated plankton Fe	C. Bizsel	C. Bizsel/N. Sanchez/M. van Ardelan
inorganic dissolved Hg	L.-E. Heimburger/J. Sonke	L.-E. Heimburger
Dissolved methyl-Hg	L.-E. Heimburger/J. Sonke	L.-E. Heimburger
Total Hg	L.-E. Heimburger/J. Sonke	L.-E. Heimburger
Dissolved Mo	L. Gerringa/UCC team	J.-M. Godoy
Dissolved Ba	L. Gerringa/UCC team	J.-M. Godoy
Dissolved U	L. Gerringa/UCC team	J.-M. Godoy
Dissolved ^{18}O	L. Gerringa/UCC team	J.-M. Godoy
Deuterium	L. Gerringa/UCC team	J.-M. Godoy
Hg isotopes	L.-E. Heimburger/J. Sonke	L.-E. Heimburger
Dissolved Fe isotopes	J. Rolison	J. Rolison/C. Stirlinger
Dissolved Cd isotopes	J. Rolison	J. Rolison/C. Stirlinger
Dissolved $^{238}U/^{235}U$	J. Rolison	J. Rolison/C. Stirlinger
Pb isotopes	M. Rijkenberg/UCC team	S. Galer/W. Abouchami
Cr isotopes	M. Rijkenberg/UCC team	S. Galer/W. Abouchami

Dissolved Cu isotopes	M. Andersen	D. Vance/S. Little
Dissolved Zn isotopes	M. Andersen	D. Vance/S. Little
Ni isotopes	M. Andersen	D. Vance/S. Little
$^{230}Th/^{231}Pa$	M. Rijkenberg	M. Fleisher/B. Anderson
Dissolved Si isotopes	M. Rijkenberg/UCC team	D. Cardinal
Humic acids	M. Boyé	Waeles/Pernet-Coudrier/Riso
Coccoliths	M. Boyé	M. Boyé
Coccolith taxonomy	M. Boyé	M. Boyé
POC	M. Boyé	G. Dulaquais/M. Boyé
Particulate Co (other metals, CTD)	M. Boyé	G. Dulaquais/M. Boyé
DOC/CDOM	M. Rijkenberg	D. Hansell
Salinity	S. Ober/UCC team	S. Ober
25L CTD		
DIC & Alkalinity	N. Clargo/L. Salt	N. Clargo/L. Salt
Oxygen	N. Clargo/L. Salt	L. Salt/J. van Ooijen/S. Ober
Challenger in situ pumps		
Particulate metals	M. Patey	E. Achterberg
Particulate Hg	M. Patey	L.-E. Heimburger
Ships underway SW system		
Ra isotopes	M. Rijkenberg	V. Rodellas/J. Garcia-Orellana
gaseous elemental Hg	L.-E. Heimburger/J. Sonke	L.-E. Heimburger

[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 Frank van Maarseveeen

Royal Netherlands Institute for Sea Research, Texel, the Netherlands

During the cruise 2 different CTD-systems were deployed:

1) An Ultra Clean CTD-system for ultra clean trace metal sampling (30 casts), Figure 18.
2) A Large Volume CTD for almost all the other sampling like CO_2, dissolved oxygen (DO) and phytoplankton (11 casts)

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
- The Kley France, 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.

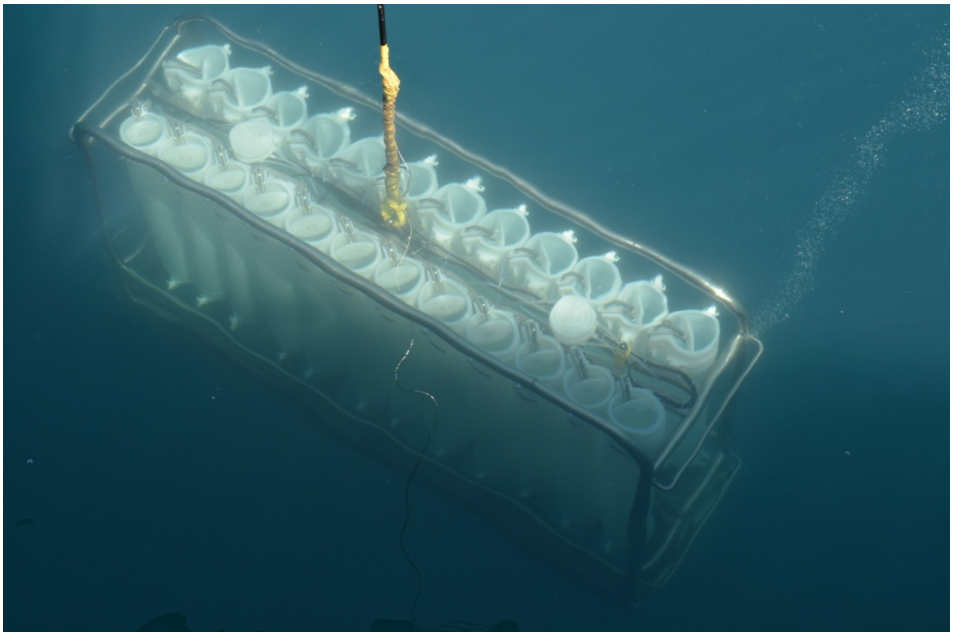

Figure 18. The UCC CTD deployed in the Black Sea during 64PE373.

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 an internal stainless steel spring and a horizontally mounted Teflon drain assembly. Via this drain assembly sample-bottles and jerry cans can be filled easily. 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.

Functioning of the CTD's

A total of 41 casts were executed. In general the equipment worked very good, but in 2 occasions some strange RS-232 communication problems had to be solved. These problems are still not fully understood or diagnosed, but repeated resetting appeared to be the temporary cure. 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 of the UCC and the LV-CTD salinity-samples were tapped and analyzed on board with a Guildline 8400B Autosal using OSIL standardwater batch P155. A first analysis of the salinity data showed that the conductivity-sensor of the UCC-system performed nicely within specifications. The difference between the Autosal-salinity and the UCC-salinity was on average smaller than 0.001 with a st.dev 0.0005. The conductivity-sensor of the LV-CTD showed a small offset of 0.004 in salinity. During the postprocessing the data will be corrected.

From most LV-CTD casts samples were taken for oxygen determination using Winkler titrations in order to calibrate the DO-sensors. With the titration results the DO-sensors of both CTD-systems will be calibrated. It will be a challenge to do so, because only in the high-gradient upper layer of the Black Sea contains DO.

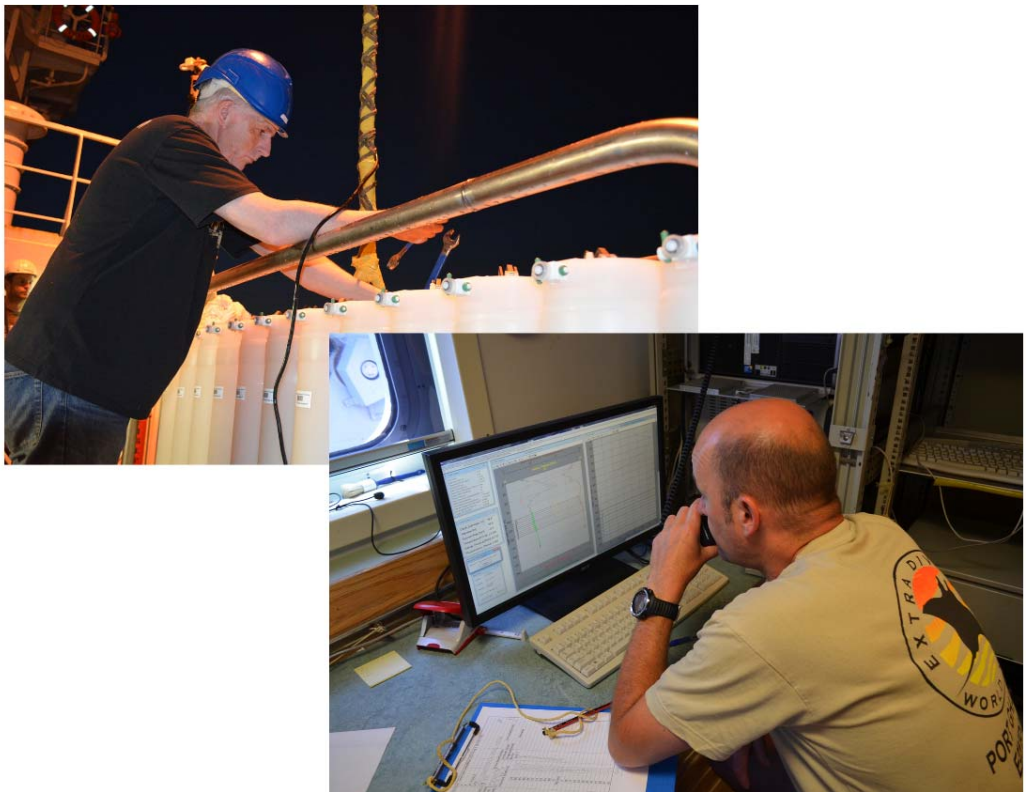

Figure 19. Sven Ober (left) prepares the UCC for deployment and Frank van Maarseveen (right) coordinates its deployment during 64PE373.

4.1.2. Dissolved oxygen

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Dissolved oxygen was measured from three depths from all 11 of the Large Volume 25L CTD casts to check the calibration of the oxygen sensor fixed to the CTD frame itself. A refined protocol of the spectrophotometric Winkler approach was conducted, where a continuous-flow analyzer is coupled with a custom-made autosampler holding up to 30 oxygen bottles (Reinthaler et al. 2006). The time required for analysis is 2 min per sample, and the precision is 0.05% at ~200 mmol O_2 m^{-3}. Dissolved oxygen was analysed in a thermostated lab container equipped with a Traacs 880 auto-analyser spectrophotometer measuring the intense yellow colour of the samples produced from the formation of iodine after the addition of acid. All measurements were calibrated with standards diluted in oxygen saturated surface sea water in the salinity range of the Atlantic Ocean stations.

Theory and Method

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

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

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

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

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

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

Equipment

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

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

Chemicals

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

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

Glass bottles

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

Sampling

Samples of seawater were obtained 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 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 at the end of the cruise. 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. Duplicate samples were measured from each station to control both the sampling procedure and the reproducibility of the spectrophotometer.

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4.1.3. Nutrients

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Summary
Nutrients were analysed in two thermostated lab containers equipped with QuAAtro Gas Segmented Continuous Flow Analysers, measuring approximately 2600 samples during the cruise for the different parameters. Measurements were made simultaneously on three channels for Ammonium, Nitrite, and Nitrate with Nitrite together. In the other lab container, Phosphate and Silicate were simultaneously analysed, and Dissolved Inorganic Carbon (DIC) and Sulphide were each separately measured. All measurements were calibrated with standards diluted in low nutrient seawater (LNSW) in the salinity range of the stations of the Black Sea at approximately $21^{o}/_{oo}$ to ensure that analysis remained within the same ionic strength.

Equipment and Methods
Sample Handling
The oxic and anoxic samples were collected in 60ml high-density polyethylene syringes with a three way valve to make it possible to sample air free water from the Niskin bottles of the Rosette. The syringes with a three way valve were first rinsed three times with a small amount of the sample taken directly from either the Ultra-clean or the normal CTD-rosette bottles before being completely filled. After sampling on deck, the samples were processed immediately in the lab; samples were filtered over 0.2µm and instantly sub-sampled for Sulphide in a glass vial already containing 40µl 1N NaOH and filled with a round meniscus before being capped and stored upside down in a refrigerator and typically analysed within 8 hours. Two more vials made out of high density polyethylene, also known as 'pony-vials', were used for storing NH_4 and NO_3 plus NO_2 as one sample and the other containing 15µl 5N HCl for storing the PO_4 combined with Si sample. The NH_4 and NO_3 plus NO_2 samples were simultaneously measured in the other lab container within 12 hours of sub sampling. DIC was only sampled from the normal CTD for a comparison for the CO_2 group also doing DIC analysis onboard. These samples were also sub-sampled into pony-vials and were usually measured within 4 hours. All samples were stored in a refrigerator at 4^{o}C. Prior to analysis, all samples were brought to lab temperature in about one to two hours. To avoid gas exchange and evaporation during the runs with Sulphide, DIC and NH_4 analysis, all vials including the calibration standards were covered with 'parafilm' under tension before being placed into the auto-sampler, so that the sharpened sample needle easily penetrated through the film leaving only a small hole. The QuAAtro uses an LED instead of a lamp as a light source as it is not affected by the movement of the ship giving a stable reading. The typical sampler rate of 60 samples per hour was used. Calibration standards were diluted from stock solutions of the different nutrients in 0.2µm filtered LNSW diluted with de-ionised water to obtain approximately the same salinity as the samples and were freshly prepared every day. This diluted LNSW was also used as the baseline water for the analysis in between the samples. The LNSW is surface seawater depleted of most nutrients. Each run of the system had a correlation coefficient of at least 0.9999 for 10 calibration points, but typical 1.0000 for linear chemistry, however the DIC and HS^- were fitted using a quadratic calibration curve. The samples were measured from the lowest to the highest concentration in order to keep carry-

over effects as small as possible, i.e. from surface to deep waters. Concentrations were recorded in 'µmol per liter' (µM) at the container temperature of 21.5°C. During the cruise, a freshly diluted mixed nutrient standard, containing silicate, phosphate and nitrate (a so-called nutrient cocktail), was occasionally measured. The cocktail sample was used as a guide to monitor the performance of the standards.

Analytical Methods
The colorimetric methods used are as follows:

Ortho-Phosphate (PO_4) reacts with ammonium molybdate at pH 1.0, and potassium antimonyltartrate is used as a catalyst. The yellow phosphate-molybdenum complex is reduced by ascorbic acid and forms a blue reduced molybdophosphate-complex which is measured at 880nm (Murphy & Riley, 1962).

Ammonium (NH_4) reacts with phenol and sodiumhypochlorite at pH 10.5 to form an indo-phenolblue complex. Citrate is used as a buffer and complexant for calcium and magnesium at this pH. The blue color is measured at 630nm (Koroleff, 1969 and optimized by W. Helder and R. de Vries, 1979).

Nitrate plus Nitrite (NO_3+NO_2) is mixed with an imidazol buffer at pH 7.5 and reduced by a copperized cadmium column to Nitrite. The Nitrite is diazotated with sulphanylamide and naphtylethylene-diamine to a pink colored complex and measured at 550nm. Nitrate is calculated by subtracting the Nitrite value of the Nitrite channel from the 'NO3+NO2' value. (Grasshoff et al, 1983).

Nitrite (NO_2) is diazotated with sulphanylamide and naphtylethylene-diamine to form a pink colored complex and measured at 550nm (Grasshoff et al, 1983).

Silicate (Si) reacts with ammonium molybdate to a yellow complex and after reduction with ascorbic acid, the obtained blue silica-molybdenum complex is measured at 820nm. Oxalic acid is added to prevent formation of the blue phosphate-molybdenum (Strickland & Parsons, 1968).

H_2S:
To keep the samples in the S_2^- form under alkaline conditions, a small aliquot of NaOH is added. The Hydrogen Sulphide in the sample reacts with para-aminodimethylaniline and ferric chloride to yield methylene blue which is measured at 660nm as described by Grasshof, K., 1969.

Dissolved Inorganic Carbon (DIC):
Samples are acidified online after being oxidised by H_2O_2 to prevent H_2S being released before entering the silicon dialyser whereby the formed CO_2 is dialysed to a secondary flow. This secondary flow contains a slightly alkaline phenolphthalein solution giving a pink colour. The more CO_2 that is dialysed, the lower the pH and therefore some discolouration of the pink reagent is observed. This decolouring is measured at 520nm and is an inverse chemistry spectrophotometer method described by Stoll, Bakker, Nobbe and Haesse, 2001.

Calibration and Standards

Nutrient primary stock standards were prepared at the NIOZ as follows:
Phosphate: by weighing Potassium dihydrogen phosphate in a calibrated volumetric PP flask to make a 1mM PO4 stock solution.
Silicate: by weighing Na_2SiF_6 in a calibrated volumetric PP flask to 19.84mM Si stock solution.
Ammonium: by weighing Ammonium Chloride in a calibrated volumetric PP flask to make 1mM NH4 stock solution.
Nitrate: by weighing Potassium nitrate in a calibrated volumetric PP flask set to make a 10mM NO_3 stock solution.
Nitrite: by weighing Sodium nitrite in a calibrated volumetric PP flask set to make a 0.5mM NO_2 stock solution.
DIC: by weighing Na_2CO_3 stock in a calibrated volumetric PP flask set to make a 200mM stock solution.
S_2^- : by weighing Na_2S in 0.5N NaOH set to make a 50mM Sulphide stock solution.

All standards were stored at room temperature in a 100% humidified box apart from the S_2^- standard which was stored in the refrigerator. The calibration standards were prepared daily by diluting the separate stock standards, using three electronic pipettes, into four 100ml PP volumetric flasks (calibrated at the NIOZ) filled with diluted LNSW. The blank values of the diluted LNSW were measured onboard and added to the calibration values to get the absolute nutrient values. In the case of Sulphide, calibration standards were made using anoxic demineralised-water with an addition of 0.8ml 1N NaOH/100ml to keep the Sulphide under alkaline conditions.

Statistics

Quality Control

Our standards have already been proven by inter-calibration exercises from ICES and Quasimeme, and last year the RMNS exercise organised by MRI, Japan. Our cocktail standard was regularly measured and its value remained stable for all nutrient measurements during the cruise.

Mean Detection Limits

The method detection limit was calculated during the cruise using the standard deviation of ten samples containing 2% of the highest standard used for the calibration curve and multiplied with the student's value for n=10, thus being 2.82. (M.D.L = Std Dev of 10 samples x 2.82)

	µM/l	Used measuring ranges µM/l:
PO4	0.008	3
SiO2	0.014	80
NH4	0.031	5
NO3+NO2	0.011	17.0
NO2	0.007	1.00
HS-	0.263	400

Further Remarks

It is suggested that through diluting the samples by means of electronic pipettes, one for the sample and one for the dilution water, a small error of maximum 1.0% could be introduced.

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4.2. Sampling and analysis of key parameters

A. Metals and isotopes

4.2.A.1. Dissolved Fe

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Work at sea

Due to the presence of hydrogen sulphide in the anoxic samples dissolved iron (DFe) concentrations were only measured on board in 2 full depth stations (stations 2 and 5) using an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998 (Figure 20). The anoxic samples contained such high DFe it has been decided that these samples could be measured best in the home laboratory by ICPMS. From all other stations only the oxic samples (upper 6 bottles per cast) were measured on board using FIA. 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 at least 12 months of dissolution.

Filtered (0.2µm, Sartorius Sartobran 300) and acidified (pH 1.8, 2ml/L 12M Baseline grade Seastar HCl) seawater was concentrated on a column containing aminodiacetid acid (IDA).This material binds only transition metals and not the interfering salts. After washing the column with ultrapure water, the column is eluted with diluted hydrochloric acid. After mixing with luminol, peroxide and ammonium, the oxidation of luminol with peroxide is catalyzed by iron and a blue light is produced and detected with a photon counter. The amount of iron is calculated using a standard calibration line, where a known amount of iron is added to low iron containing seawater. Using this calibration line a number of counts per nM iron is obtained. Samples were analyzed in triplicate and average DFe concentrations and standard deviation are given. Concentrations of DFe measured during the 64PE372 cruise ranged from 85 pM in the surface waters up to 429 nM just below the maximum of the sulphite concentration. All samples above 5nM were diluted and measured with different loading times and calibration lines. The standard deviation varied between 0% and 17% (the latter being exceptional), but was on average 1.5% and generally < 3% 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 certified SAFe and GEOTRACES reference material (Johnson et al. 2007) was measured at a regular basis.

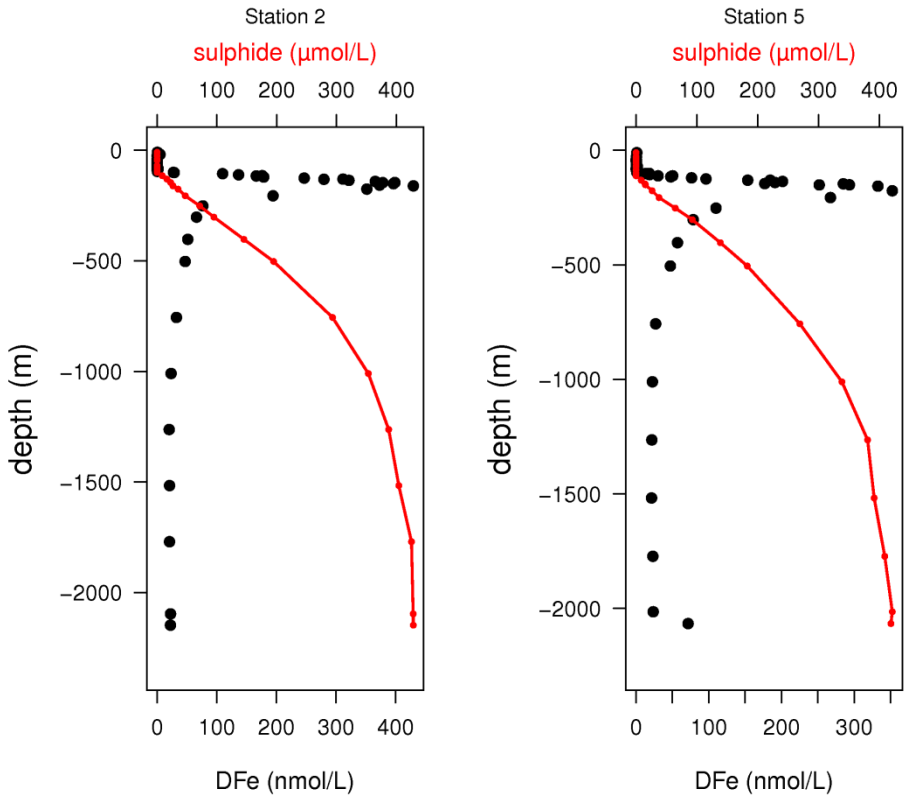

Figure 20. Full depth profiles of dissolved iron (DFe) and hydrogen sulphite versus depth from station 2 cast 1 and station 5 cast 3.

Preliminary results

The profiles from station 2 and station 5 in the Black Sea, show low surface DFe concentrations with intermediate high DFe values and decreasing DFe concentrations with depth. This corresponds well with the increase of the sulphite concentration. However the highest iron concentrations just below the beginning of the anoxic zone, most likely reflects the high remineralisation of organic matter occurring at this depth.

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4.2.A.2. Organic speciation of Fe

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Objectives

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

Our objective is to measure organic speciation of Fe in the Black Sea in the oxic surface layer to study the influence of the Fe solubility here. We measure on-board using competing ligand exchange cathodic stripping voltammetry (CLE-CSV): A commercial Fe binding ligand is added to a series of buffered seawater subsamples with increasing additions of Fe. These subsamples are then electrochemically analysed for the presence of the added ligand complexed with Fe. During the first leg 2,3-dihydroxynaphtalene (DHN) was used as the measuring ligand (van den Berg 2006, Laglera et al., 2013). Normally we use the measuring ligand 2-(2-Thiazolylazo)-p-cresol (TAC) (Croot and Johanssen, 2000), however it was discovered that this chemical contained too much Fe. During leg 1 the chemical DHN proved not as clean as needed either. Between the two legs Gerringa and Slagter (scientist doing these measurements during leg 1) were able to obtain a clean batch of TAC. Therefore now again TAC was used as added ligand. Since voltammetry is sensitive to redox reactions, samples were taken from the oxidised top layer of the Black Sea only (Table 1).

Table 1. Samples taken for the organic complexation of Fe (FeL).

Sample	Stations	Bottles per station
FeL	2,3,4,5,6,11 and 12	24,23,22,21,20,19

Methods and equipment

~900 mL FeL samples were taken from the ultra clean CTD (UCC) and as all other samples filtered over a 0.2 µm filter using N_2 overpressure and measured immediately.

The competing ligand TAC with a final concentration of 10 µM was used and the complex $(TAC)_2$-Fe was measured after equilibration (> 6 h) by cathodic stripping voltammetry (CSV) (Croot and Johansson, 2000). The electrical signal recorded with this method (nA) will be converted into a concentration (nM), then the ligand concentration and the binding strength will be estimated using the non-linear regression of the Langmuir isotherm (Gerringa et al. 1995; Gerringa et al., in press).

CLE-CSV was performed using a 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) (Figures 21 and 22).

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

Figure 21. Equipment setup during 64PE373.

Results

Although the interpretation of the analyses were not finished at the end of the cruise, a pattern could be distinguished from the so far obtained results. In the surface layer (samples taken from bottle 24) the ligands were saturated with Fe. However, samples taken deeper in the water column contained higher concentrations of ligands than dissolved Fe. This means that the excess ligands concentration (the concentration of ligands not bound to Fe) increased from the surface with depth, with a maximum in the chlorophyll max (mostly bottle 22). From the chlorophyll max to the depth where the oxygen decreased, the excess ligand concentration decreased again with depth. In samples from bottle 19, the deepest sampled for this analysis, the ligands were again saturated with Fe.

A preliminary conclusion is that ligands influence/increase Fe solubility in the layer where Fe is needed most by phytoplankton.

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Figure 22. Loes preparing a titration for organic Fe-binding ligands during cruise 64PE373.

4.2.A.3. 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, the concentration of these trace elements in the marine environment can be very low, even at picomolar level. Moreover, the bioavailable fractions of these metals are 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). It 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. On 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 cultures of phytoplankton under unrealistically controlled conditions (Cullen and Sherrell, 1999), which further adds complexity when linking biological processes to iron chemistry.

In the Black Sea, fresh water sources result in a two layer stratification system. As a main source, the Danube itself contributes about 210 km^3 yr^{-1} of water discharge which is more than entire freshwater supply to the North Sea. The Dnieper and Dniester are two additional important sources which deliver about a total of 60 km^3 yr^{-1} of fresh water. Including the numerous smaller fresh water sources around the Black sea basin, the total fresh water input is around 350 km^3 yr^{-1}, as an average which is almost equal to the annual evaporation loss. However, almost an equal volume of direct precipitative input (ca. 300 km^3 yr^{-1}) creates a positive budget which is balanced by a less saline (18 psu) upper layer outflow through the Turkish Strait System (Bosphorus-The Sea of Marmara-Dardanelles) to the Mediterranean Sea (Unluata et al., 1990). With the corresponding inflow of Mediterranean waters into the Black Sea by a saline (36 psu) lower layer a permanent two layer system is formed with a high density gradient and extremely low vertical mixing. The thickness of the upper layer ranges between 120-180 m, while the lower layer reaches down to the bottom (2000 m). In spite of the highly restricted oxygen supply via the inflow from the Mediterranean Sea, the degradation of organic matter originating from the highly productive upper layers and the absence of vertical mixing results in anoxic deep waters with a relative low pH.

During the last 5.000-10.000 years a unique physically and chemically layered basin formed with a total volume of about 547.000 km^3 (Ozsoy and Unluata, 1997). The uniqueness of the system also extends to biogeochemical processes, in particular for those involving organics and metals. Regarding the highly closed geomorphology of its basin, the Black Sea forms a sensitive ecosystem for the impacts of anthropogenic and/or natural (e.g., climate change) driving forces which provides a natural laboratory for understanding the role of key processes under its unique ecological properties.

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 placed 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 constitutes an ion exchange resin of styrene divinylbenzene copolymers containing paired iminodiacetate ions which act as chelating groups. It has a very strong attraction for transition metals, even in a 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, the samples were processed 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 4˚C.

Size fraction filtration

Constitute a separation method based on predefined (pore size) criteria that either can be independent simple filtration or a sequential filtration. 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 (Figure 23). 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

During the period between 13/07/2013-23/07/2013, a total of 78 samples (including replicates) were collected at 4 stations out of 12 stations in the entire survey area, covering the Black sea during Leg 2 (Table 2). Samples for FeDGT and DFeCh were collected from three depth layers, i.e., surface, depths of Chlmax and depths of O2min, also which were the main targets during the Leg 1. Samples for SFFePhyto, as well as for size fraction Chlorophyll, were collected only at the Chl-max for every hyperstation where there were only two in the Black Sea (St 2 and St 5). There were also an additional 21 samples collected from surface (10 m) and Chl_{max} layers for identification of phtyoplankton species.

Results

Onboard processing of samples was partially completed for all three types of samples. For both FeDGT and Chelex samples, this included the deployment of the passive samplers (DGTs) or the addition of the resin in the water sample, and placing them on to the shakers and kept in a temperature controlled container ideally for periods of 72 hrs but no less than 48 hrs. Further processing for both types of samples will involve acidification for extraction of the metals. SFFePhyto samples were frozen and will be processed by acid digestion for metal extraction. Afterwards, all samples will be analyzed by HR-ICP-MS. The phytoplankton samples were fixed with lugol solution and they will be analyzed microscopically under both LM and SEM.

Consequently, considering the sampling effort carried out by DEU-NTNU team in two legs, a total of 480 (391+99) samples were collected for the planned analyses.

Acknowledgements

On the behalf of DEU-NTNU team, I would like to express our appreciations to the Chief Scientists Loes Gerringa and Micha Rijkenberg, for making everything possible and well executed during the cruise. Special thanks also goes to the captain Pieter Kuijt, the technicians and all the crew of the RV Pelagia, all who were impressive with their professionalism in providing assistance and support during the sampling efforts. Finaly, we are grateful to the Dutch GEOTRACERS program and funding institutions.

Figure 23. Can Bizsel size-fractionating the phytoplankton population during cruise 64PE373.

Table 2. Stations and depths sampled for DGT labile iron (FeDGT), dissolved Chelex labile (DFeCh), particulate iron content within the plankton community (FeSFPhyto), and phytoplankton.

Stations Planned	Stations Executed	Depths (m)	Layer	DFeCh	FeDGT	FeSFPhyto	Phytoplankton
1	**12**	10	Surface				**x**
		25	Chl_{max}				**x**
		45	Transition				**x**
		50	Medwater				**x**
		55	Medwater				**x**
		60	Medwater				**x**
		100	O_{2min}				
2	**11**	10	Surface				**x**
		25	Chl_{max}				**x**
		250	O_{2min}				**x**
3	**1**	10	Surface	**x**	**x**		**x**
		55	Chl_{max}	**x**	**x**		**x**
		100	O_{2min}	**x**	**x**		
4	**2**	10	Surface	**x**	**x**	**x**	**x**
HYPERSTATION		50	Chl_{max}	**x**	**x**	**x**	**x**
		100	O_{2min}	**x**	**x**	**x**	
5	**10**	10	Surface				**x**
			Chl_{max}				**x**
		100	O_{2min}				
6	**3**	10	Surface				
			Chl_{max}				
		100	O_{2min}				
7	**9**	10	Surface	**x**	**x**		**x**
			Chl_{max}	**x**	**x**		**x**
		100	O_{2min}	**x**	**x**		
8	**4**	10	Surface				
			Chl_{max}				
		100	O_{2min}				
9	**8**	10	Surface				
			Chl_{max}				
		100	O_{2min}				
10	**5**	10	Surface	**x**	**x**	**x**	**x**
HYPERSTATION		45	Chl_{max}	**x**	**x**	**x**	**x**
		100	O_{2min}	**x**	**x**	**x**	
11	**7**	10	Surface				**x**
		40	Chl_{max}				**x**
		100	O_{2min}				
12	**6**	10	Surface				**x**
		40	Chl_{max}				**x**
		100	O_{2min}				

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4.2.A.4. The biogeochemical cycles of cobalt, and copper in the Black Sea

Marie Boyé

On the behalf of the research group :
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Summary

Our research group at Brest proposes to constrain sources and biogeochemical cycling of key bioessential trace metals (copper and cobalt) in the Black Sea along the GEOTRACES-A04N section, using novel approaches, combining concentration and speciation measurements. In addition, we aim to calibrate proxies for past change, as recorded in coccoliths. Samples have been collected during the LEG2 in the Black Sea, in the water-column (in the dissolved, particulate and soluble fractions).

Objectives

Many trace elements are critical for marine life and as a consequence influence the functioning of ocean ecosystems. Some trace elements are essential like cobalt (Co) and copper (Cu), others are toxic pollutants like Cu at high concentrations, while some 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. Hence our main objectives are *to elucidate important biogeochemical processes, sources and sinks that determine the distribution of the bio-essential trace elements Co and Cu in the Black Sea, and to calibrate new proxies of environmental conditions sensitive to the climate change, especially sea-surface temperature SST, and pH.*

The Black Sea is a meromictic sea with a permanent halocline that limits the supply of oxygen to the deep waters, making the Black Sea the world's largest *anoxic basin*. It 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 like Cu and Co and others, and the associated redox cycling of sulfur (S). The complete redox sequence from oxic, to suboxic to anoxic=sulfidic waters can be found in the Black Sea and was sampled with an unique high vertical resolution. This allows sophisticated high-resolution sampling of all redox gradients and their intrinsic major changes of concentrations and speciation. The distribution of trace metals in the oxic surface layer of the Black Sea can depend on the physical factors leading to upward mixing of reduced Co and Cu, and further on other sources of those trace elements, like atmospheric input, rivers e.g. the *Danube* (Guieu et al., 1998), and the Black Sea hydrography. The Black Sea is an ideal environment to investigate internal cycle of these trace elements including microbial redox reactions, benthic input (e.g., like Fe shuttle, Severmann et al., 2008) and precipitation as sulphides. Yet both the distribution and the internal cycle of bio-essential trace elements Co and Cu are still unknow in the Black Sea.

Studying the biogeochemical cycle of those elements includes their *physical* (dissolved, particulate, soluble, small colloids) and *chemical* (organic speciation) *speciation*, which is critical in understanding their bioavailability and geochemical dynamics. Although recognised for important properties like metal complexation or growth stimulation of planktonic species

(Doblin et al., 1999), humic substances (HS), an important fraction of dissolved organic carbon, have been very poorly quantified in marine environments. Here we will examine HS with the aim to describe for the first time their distribution in the seawater and to assess their relation with Cu and Co complexation.

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

Sampling

Samples have been collected in the seawater column with the Titanium-Frame (UCC) (Table 3). Different size-fractions have been collected for analyses of Co and to a later extend of Cu (total, particulate, dissolved, soluble) and those samples were acidified on board for later measurement in the home laboratory. The organic speciation of Co and Cu will be studied in the dissolved and frozen samples. Proxies will be analyzed in settling inorganic material and in the surficial sediment. Additional samples have been collected for taxonomic analyses and particulate carbon measurements.

Furthermore samples for the inter-calibration exercise of Fe-isotopes measurements were collected and will be analyzed by Olivier Rouxel.

Table 3 - Inventory of the samples collected in the Black Sea

St.#	DCo DCu Humics	TCo TCu	Soluble Co	Organic Co	Organic Cu	Particulate trace metals	POC/PIC	Proxies in coccoliths	Taxono-my	Sediment
1								2	2	X
2	24	16		12	10	6	12		4	(Lars/Jeroen)
3	16									
4	17									X
5	24	16	16	14	11	6	12		2	X
6	19									X
7										X
8								3	3	X
10	17									X (Nourredine)
11	13	13								
12	6	6								

Analyses

The analyses will be performed in the home-labs at Brest. The analyses of **Co** will be performed by Flow-Injection-Analyses and Chemiluminescence detection according to the method we developped (Bown et al., 2011; Dulaquais et al., 2013), apart for the **organic speciation of Co** that will be analysed by Voltammetry (Bown et al., 2012).

Particulate trace metals analyses will be performed by HR-ICPMS using Element II (Pôle Spectrométrie Océan, IUEM), following a 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).

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).

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4.2.A.5. Aluminium

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Introduction

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

Work at sea

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

Preliminary results

The aluminium concentration in the surface waters of the Black Sea varied from ~ 5 - 25 nM, with the lowest values measured in the centre, i.e. farthest from land. Concentrations rapidly declined to a minimum of ~ 1-2 nM at ~ 50 meters depth (Figure 24). A gradual rise in the Al concentrations (up to 4-5 nM) was observed at mid-depths (100 – 500 m), and was followed by a gradual decrease to < 2 nM in deep waters. The same overall trend was observed in all deep stations from east to west.

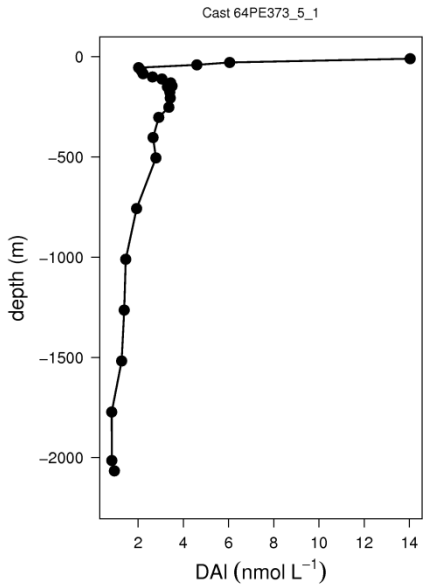

Figure 24) Depth profile of dissolved Aluminium at station 5 cast 1 of cruise 64PE373.

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4.2.A.6. Multi-elements

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Introduction

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

Work at sea

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

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4.2.A.7. GEOTRACES Black Sea Mercury Exploration

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Mercury stable isotopes
Background
Mercury (Hg) isotopes fractionate in nature dependently and independently from their mass (mass dependent fractionation: MDF and mass independent fractionation: MIF). The isotopic signature of Hg can possibly be used to trace its sources and its biogeochemical transformations. It is believed that the main process generating MIF is the photo-degradation of Hg species in the surface ocean and the subsequent separation, via evaporation, of the products from the reactants (Bergquist et al. 2007). This should result in two compartments with essentially different MIF fingerprints: the atmosphere showing negative MIF and the Hg remaining in the oceanic pool should therefore depict positive MIF. Several works have confirmed this hypothesis (Sonke, 2011) using atmospheric (lichens, peat) and oceanic integrators (marine sediments, fish, oceanic top predators). However, those indirect evidences might be afflicted with some bias. For instance, in the oceanic food web top predators essentially accumulate methylated Hg, while the concentration of this Hg species in the surface ocean is as low as some <0.025pM and presents only a minor fraction of the total Hg pool. Only a few and controversial results on direct atmospheric measurements have been published (Gratz et al. 2010; Chen et al. 2012), whereas direct measurements of Hg isotopes in the ocean are still lacking. Dissolved total Hg concentrations in the open ocean are low, from 0.5-2.5pM, making it difficult to determine Hg stable isotopic composition. In the Black Sea dissolved total Hg concentrations are higher, possibly ranging from 2 to 12pM. We have therefore chosen this location to attempt the first marine Hg stable isotope study. There are multiple interests in studying the isotope signatures of dissolved and particulate Hg. The first is to confirm broad observational and modeling projections that marine Hg has a positive MIF signature. The second will be to calibrate the isotope fractionation factor for Hg sorption to particles, if significant at all. Mercury is also the only heavy metal that is present as a gas in the atmosphere and as a dissolved gas in water bodies. One of the key interests in examining the Hg isotope signatures of dissolved gaseous mercury is to contrast them with the signatures of total dissolved Hg. During daytime photoreduction of dissolved Hg produces dissolved gaseous mercury, while during nighttime dark reduction pathways produce dissolved gaseous mercury. The isotope fractionation signs and mechanisms of these two processes have been studied in the lab but not in natural sea water. Finally, the continuously produced dissolved gaseous mercury will outgas to the atmosphere where it mixes with the gaseous elemental mercury pool. Outgassing, a diffusional process, likely favors the lighter Hg isotopes, and we hope to quantify this effect as well.

Sampling
Chen et al. (2010) published a method pre-concentrating Hg from natural freshwater. The resin AG1-X4 (200–400mesh, Bio-rad®) was used for pre-concentration of Hg from dilute aqueous solutions, with Hg concentrations of up to 15600ng.L^{-1}. The greatest challenge in applying this method to sea water is the very low total Hg concentration of about 0.2ng.L^{-1} (1pM) in the global ocean and relatively high blank levels of the used chemicals. We developed a new method pre-concentrating Hg from sea water for Hg isotopic analysis which

involves only a simple acidification step using ultra-clean bi-distilled HCl acid. Further technical details on the method remain disclosed for the moment. We sampled large volumes of sea water using the NIOZ ultra clean rosette system. Inline filtration was performed through a cartridge (Sartorius Sartrobran®300) under a nitrogen pressure in the clean container. Samples of 10-45L where taken into flexible cubitainers for on-bord pre-concentration of approximately 10ng Hg extraction cartridges. Surface water, chlorophyll maximum zone, oxygen minimum zone, anoxic waters and deep waters were sampled at the two hyper-stations. We also sampled gaseous elemental Hg (GEM or $Hg^0(g)$) in the marine boundary layer at 10m height, and dissolved gaseous Hg (DGM, $Hg^0(aq)$) in surface waters provided by the ship's pump system (Figure 25). Both GEM and DGM were sampled at 12h intervals, to observe broad diurnal variability, on extraction cartridges. Recovery of the mercury from each extraction cartridge will yield 10mL of a final solution sufficiently concentrated (~>1000ng.L^{-1}) to perform measurements of the Hg isotopic signature. *In situ* pumps were used to sample particulate Hg at surface water, chlorophyll maximum zone, oxygen minimum zone and anoxic waters.

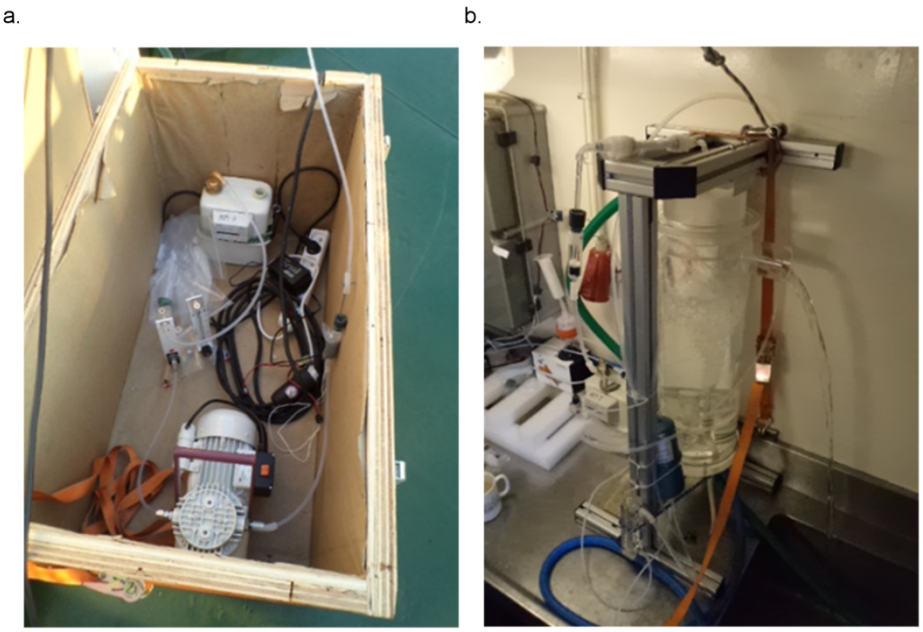

Figure 25. a) Atmospheric gaseous elemental Hg sampling on top of RV Pelagia; visible are the large pump (10 L/min), flow meter and gas volume meter). b) Dissolved gaseous mercury sampler.

High resolution mercury speciation sampling

Background

Inorganic mercury, whether of natural or anthropogenic origin, can be converted into the neurotoxin methylmercury. Presently, we believe this conversion occurs during the bacterial reminerlization of sinking organic matter in the oceanic water column. The Black Sea with its high organic matter inputs and anoxic deep waters is an excellent study site to investigate in more detail the processes yielding methylmercury. To date there is only one vertical profile of mercury speciation near the Western shelf and one vertical profile in the Western Gyre published in the Black Sea (Lamborg et al. 2008).

Sampling
We sampled 250mL filtered seawater at each depth at each station, totaling ~300 samples spread over 12 stations, for the determination of dissolved total and methylated mercury (Figure 26).

Method
Total mercury will be measured according to a standardized protocol (USEPA1632). The two forms of methylated mercury, monomethylmercury and dimethylmercury, will be measured as the sum of both, because the acidification step quantitatively converts dimethylmercury into monomethylmercury. The final measurement will be realized after a derivatization step (propylation) of inorganic and methylmercury present in the seawater sample, extraction into hexane, chromatographic separation via gas chromatography and detection via sector field inductively coupled mass spectrometry. The dataset will cover the whole Black Sea Basin and be the highest resolution Hg speciation transect to date. Mercury concentrations in seawater (~1pM) are amongst the lowest of all trace metals. Methylmercury concentrations are even lower (~0.1pM) and 3 different analytical approaches are used for its determination currently. Those have not been compared yet. We organize a GEOTRACES international intercalibration exercise for *dissolved total methylated mercury* and *dissolved total mercury* in seawater. Over 25 partner laboratories registered.

Expected Outcomes
Mercury isotopes : If successful, this will be the first ever measurements of the isotopic signature of mercury in seawater and a major step forward in understanding the complex biogeochemical cycling of this element.

Mercury speciation : This will be the highest resolution of mercury speciation measurements ever realized and help understanding where and how toxic methylmercury is formed in the ocean.

Intercalibration : This will be the largest incalibration excercise for *dissolved total methylated mercury* and *dissolved total mercury* in seawater.

Acknowledgements
LEH and JES thank Micha Rijkenberg, Loes Gerringa and Hein de Baar for the opportunity for collecting so many precious ultra-clean samples in such a pleasant manner. We enjoyed very much being on Pelagia. We also thank the Captain Pieter Kuijt and his extraordinary crew for their excellent support during the cruise, it was a real pleasure to work in such conditions.

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Figure 26. Jeroen and Lars preparing samples bottles for sampling from the UCC CTD during cruise 4PE373.

4.2.A.8. Transition metals and their isotopes in the Black Sea

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Summary

We aim to constrain the sources and water column cycling of three key bio-essential and/or redox sensitive trace metals and their isotopes (copper, zinc, nickel) in the Black Sea. Using trace metal clean sampling techniques, dissolved water column samples have been collected at the two hyper-stations during Leg 2 of the GEOTRACES-A04N section. The Black Sea is an important analogue for oceanic conditions in the Precambrian, when water column euxinia is thought to have been more widespread. A better understanding of the behaviour of trace metals and their isotopes in modern reducing conditions will thus illuminate their potential use as paleoenvironmental tracers.

Objectives

Transition metals play a key role in regulating biogeochemical processes in the oceans. Some may stimulate biological productivity (e.g. Fe, Zn), whereas others are toxic (e.g. Cu) to phytoplankton. Many are also redox sensitive (e.g. Mo, Cu). To fully understand the oceanic biogeochemical cycling of transition metals, knowledge of their sources, sinks, speciation, and internal recycling (e.g. passive scavenging on particles, active biological uptake) is required (Bruland and Lohan, 2003). Isotopic data can provide valuable constraints both for global mass balance calculations, and in distinguishing local water column processes (e.g. Little et al., in press; Zhao et al., in press). Studying the behavior of transition elements in the modern ocean not only informs about modern biogeochemical cycling, it is also a prerequisite for the use of any of these elements or isotope systems as paleoceanographic or paleoenvironmental tracers. Much of what is known about past ocean conditions has come from analysis of trace element and isotope patterns recorded in marine deposits.

To date, knowledge of the oceanic sources and sinks and internal cycling of the transition metals and their isotopes is limited. These limitations stem from the fundamental problem of sampling ultra-clean seawater containing transition metals at the pico- to nano-mol concentration levels. Furthermore, isotopic measurements of new transition metal stable isotope systems have only been achievable in the last couple of decades (e.g. Maréchal et al., 1999). Improvements in clean sampling protocols and analytical techniques provide an unprecedented ability for high-resolution sampling and measurement of a wide range of trace elements and isotopes. The international community led GEOTRACES program has the specific goal of improving understanding in this field (SCOR Working Group, 2007). The aim of our sampling campaign in the Black Sea was to collect large volume, ultra-trace metal clean seawater samples for the measurement of Cu, Zn and Ni isotopes. This will be the first time such measurements have been attempted in the water column of an anoxic basin.

The Black Sea is an anoxic basin with a chemocline at about ~100 meters depth, separating oxic surface waters from deep anoxic and euxinic waters. As such, the Black Sea differs from the majority of the modern (oxic) open oceans, with associated differences in the biogeochemical cycling of transition metals. One consequence of overlying water column euxinia is strong sedimentary enrichments in a range of trace metals (Calvert and Pederson,

1993; Tribovillard et al., 2006). As a result, reducing environments represent a major output of trace metals from the oceans. Patterns of trace metal enrichments in such settings offer the potential to trace the extent of water column anoxia (and euxinia) in the past, but, as yet, the precise mechanisms of trace metal enrichment are frequently unknown. Combining isotopic measurements in sediments (Little, Vance, Cameron, unpublished data) with those from the overlying water column (this study) offers the chance to unpick these processes of enrichment, and to establish a framework within which to interpret signatures in paleo-sediments from the ancient oceans.

Sampling

Large (1-8 litre), ultra-clean, 0.2 μm filtered seawater samples from the ultra-clean CTD were collected in pre-cleaned (using GEOTRACES protocols) LDPE bottles during the MedBlack GEOTRACES leg 2 cruise in the Black Sea. Samples were acidified on board to pH ~2 using ultrapure SEASTAR HCl acid. Two full seawater profiles at Hyper-Stations 2 and 5 were collected. Our group is also a part of the isotope intercomparison (Cu, Zn, Ni) exercise (see section 4.2.A.8 of this report).

Analyses

Collected samples will be processes under clean laboratory conditions at ETH Zürich, to extract Zn, Cu and Ni for high-precision isotope measurements using already established methods (Bermin et al., 2006; Vance et al., 2008; Cameron and Vance, in press). Analyses will be carried out using a Neptune Plus MC-ICP-MS, also at ETH Zürich.

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4.2.A.9. The isotope intercomparison excercise

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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 unravelling 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 excercise 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

Samples for the stable isotope intercomparison excercise were taken at 2 different stations during 64PE373. The reason that we sampled at 2 stations instead of 1 station is that the 20L containers that we prepared to homogenize samples for the isotope intercomparison excercise could not be used during the MedBlack GEOTRACES cruises. A small metal part on the outside of the tap was badly corroded.

Stable Cd, Cu, Ni, REE, Zn, Ba, Mo isotopes at station 2

At station 2 (15 July) samples were taken during 2 separate casts with the UCC CTD to collect water for the stable isotope systems: Cd, Cu, Ni, REE, Zn, Ba, Mo. In both cases the UCC CTD was, after coming back on deck, immediately transported to the class 100 clean container for filtration and subsampling. Filtration was performed under N_2 pressure using 0.2 µm Sartobran 300 filter cartridges (Sartorius). All seawater for isotope samples 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 (except for Pb). The first large volume sample was taken during cast 4 where bottles 1-12 of the UCC CTD were closed at 100 m depth (suboxic) and bottles13-24 at 30 m depth (oxic). The second large volume sample was taken during cast 6 where bottle 1-24 were closed at 150 m depth (anoxic). Sampled seawater from 30 m depth was collected in 1 x 150 L and 1 x 50L container. Sampled seawater from 100 m depth was collected 1 x 150L and 1 x 50L. Sampled seawater from 150 m depth was collected in 1 x 200 L container.

We acidified and subsampled for the above mentioned stable isotope systems according to the following timeline:

1) 16 July: we acidified the seawater samples with 1 ml/L 12M Baseline grade Seastar HCl
2) 20 July: we sub-sampled for Cd from the anoxic part of the water column at 150m depth from the 200L container, Cd from the suboxic part of the water column at 100m depth from a 150L vessel and Cd from the oxic part of the water column at 30 m from a 150 L vessel.
3) 21 July: Zn, Ba, Mo, Cu, Ni and REE were sub-sampled from the anoxic part of the water column at 150m from a 100L container; Zn, Ba, Mo, Cu, Ni and REE were sub-sampled from the suboxic part of the water column at 100m from a 50L container; Zn, Ba, Mo, Cu, Ni and REE were sub-sampled from the oxic part of the water column at 30m from a 50L container.

Stable Fe, Cr and Tl isotopes at station 10
A second station, station 10 cast 3, was sampled for the stable isotope systems Fe, Cr, Tl and Pb (for sampling of Pb see paragraph below). We collected 100L from the anoxic part of the water column at 150m depth in a 100L container, 100L from the suboxic part of the water column at 100m depth in a 150L container and 100L from the oxic part of the water column at 30m depth in a 150L container. At station 10 the same containers were used for the same depths as at station 2. The containers were first 5 times rinsed with seawater before being filled.

We acidified and subsampled for the Fe, Cr and Tl stable isotope systems according to the following timeline:
1) 24 July: the seawater samples for Fe, Cr and Tl have been acidified with 1 ml/L 12M Baseline grade Seastar HCl
2) 5 August: Tl, Cr and Fe were subsampled from the suboxic part of the water column at 100m depth and the oxic part of the water column at 30m depth, From the oxic part 2 sub-samples were taken to measure DFe. The DFe concentrations were each 0.21 nM. This DFe concentration was lower than we measured on board at station 10 (DFe at 25 m was 0.37 nM).
3) 8 August: Tl, Cr and Fe were sub-sampled from the anoxic part of the water column at 150 m depth.

Stable Pb isotopes at station 10
Samples for stable Pb isotopes were take directly from the UCC CTD sample bottles of cast 3 at station 10. The reason why we took samples directly from the CTD bottles was that we did not have enough large volume containers for the Pb isotopes samples (unfiltered, unacidified). The samples were collected straight from the UCC CTD bottles according to the schedule as shown in Table (4).

Table 4. The sample schedule for the stable Pb isotopes at station 10 cast 3 of cruise 64PE373.

Bottle	Depth (m)	layer	Participants
2	150	anoxic	Galer.Abouchamie, Flierdt.Rehkamper, Abel.Guihoe
12	100	suboxic	Galer.Abouchamie, Flierdt.Rehkamper, Abel.Guihoe
24	30	oxic	Galer.Abouchamie, Flierdt.Rehkamper, Abel.Guihoe
3	150	anoxic	Jason.McAllister, Ed.Boyle, Zurbrick.Flegal
11	100	suboxic	Jason.McAllister, Ed.Boyle, Zurbrick.Flegal
23	30	oxic	Jason.McAllister, Ed.Boyle, Zurbrick.Flegal

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4.2.A.10. In-situ particle sampling in the Black Sea with SAPS

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Overview

Three stand-alone pump (SAP) systems were deployed on 10 occasions during the cruise to sample suspended particulate material in the water column (Figure 27). At each station three depths were sampled simultaneously using Challenger Oceanic SAPs supplied by NMF, NOC, Southampton. Each was fitted with two 293 mm diameter filters prior to every deployment: a Petex nylon mesh pre-filter and a polycarbonate final filter. Samples were photographed, dried and stored frozen for later analysis of trace metal concentration and isotope ratio measurements in Kiel, Germany, and for sub-samples for the stable isotope intercomparison and Hg isotopes.

Method

Deployment

SAPs were pre-programmed to pump for between 1.5 and 2.5 hours following a 0.5 hour initial delay to allow the pumps to be deployed to the intended depths (Table 5). At all stations, pump deployments immediately followed CTD profiles and so the depths were selected according to the local fluorescence, oxygen and particle scattering profiles:

- Depth 1: ca 50-60 m below Depth 2 in anoxic region (85 – 180 m)
- Depth 2: O_2 minimum (85 – 180 m)
- Depth 3: Chl a maximum (35-50 m)

Depth 2 (O_2 minimum) was chosen around the point where oxygen concentrations appeared to have reached zero in the CTD profile. A particle maximum was sometimes observed close to this depth, and where this was the case, Depth 2 was chosen to coincide with this maximum.

Immediately before deployment, the filter assemblies were connected to the systems and filled with ultra-pure water. Flow meter readings were recorded. Once on deck and ready to be deployed, the timers for all three pumps were started simultaneously and the systems were attached to a steel cable. A 100 kg plastic coated weight was attached to the end of the cable to keep it vertical in the water column.

Following recovery of the SAPs, the filter assemblies were immediately removed and placed in a plastic bag. Flow meter readings were taken to determine sample volume. Excess water remaining above the filters was drawn through with a vacuum pump and the assemblies dissassembled in a clean bench. The pump units were rinsed with fresh water and allowed to dry before recharging the batteries.

Filters and filter assemblies

293 mm diameter, 1 μm pore size polycarbonate filters were used as the main filter, supported on a 150 μm nylon (Petex) mesh to prevent tearing. Polycarbonate filters were cleaned before the cruise by soaking in a clean HCl acid bath (Romil SpA grade ca. 1 $mol.L^{-1}$), followed by rinsing thoroughly with ultrapure water (MQ) and transferring to a MQ bath. This process was then repeated with freshly prepared acid and MQ baths (ie. a total of 2 x HCl, 2 x MQ soaks). The filters were then photographed (Figure 28), dried in a laminar flow cabinet before being

packed into zip-lock polyethylene bags.

51 μm (150 μm for Station 1) pore size nylon mesh (Petex) was cut into ca. 293 mm circles and used as pre-filters. The cut nylon circles were cleaned by soaking overnight in detergent solution before rinsing with MQ and transferring to a 1 $mol.L^{-1}$ and soaking overnight. They were then rinsed thoroughly with MQ water prior to use.

Before the first use, filter assemblies were soaked in detergent solution overnight and rinsed thoroughly with MQ water before use. Before subsequent deployments, the assemblies were rinsed thoroughly with ultra-pure water and stored in a plastic bag. Between deployments, the same support mesh - 150 μm Petex, cleaned initially in the same way as the pre-filters - was rinsed with ultra-pure water and re-used.

To minimise the risk of contamination, the handling of filters and pre filters was, where possible, conducted inside a laminar flow bench.

Filter processing

The pre-filters from Station 1 were discarded. For Stations 2 – 5 each pre-filter was folded twice and placed (wet) in a zip-lock bag. For Stations 6-10 a section of ¼ of the filter was cut out using a ceramic knife and a circular template with marked with lines. The material was washed off this filter segment by holding it against the side of an acid-washed (10% HCl) 1 litre plastic beaker using plastic tweezers and rinsing with a wash bottle containing clean, filtered surface seawater. The washed material was then collected on a 25 mm, 1 μm polycarbonate filter (cleaned by soaking overnight in 10% HCl followed by overnight in MQ) using a 25 mm Swinnex filter holder and a 20 mL plastic syringe (without rubber bung), both washed in acid. Due to difficulties associated with blockage of the small filters only ¼ of each pre-filter was rinsed in most cases (see Table 6). Pre-filter segments (washed and unwashed) were folded and stored (wet) in zip-lock plastic bags. The 25 mm polycarbonate filters were allowed to dry in the laminar flow cabinet before packing in plastic zip-lock bags.

To remove salts, the polycarbonate filters were sprayed with a few sprays of MQ from a spray bottle, drawing it through with a vacuum pump. This bottle originally contained window cleaning solution, but it had been rinsed thoroughly before being cleaned in acid (10% HCl). However, at a late point in the cruise it was noted that the odour of the smell remained, so the cleaning had not been sufficient. The spray head of the bottle is apparently very difficult to clean completely. For Stations 8 – 10 no MQ spray was applied. Blank measurements with and without the MQ spray were made (see below).

After removal from the filter housing, the filters were dried in a laminar flow cabinet before being cut into four using a ceramic knife and circular template. Each segment was packed into a zip-lock plastic bag.

Procedural Blanks

After the processing of Station 10, the three filtration housings were rinsed and reloaded with filters as if preparing for another deployment. This time the filter housings were filled completely with MQ water before being pumped off and filters and pre-filters processed exactly as for the other samples. To enable assesment of the possible contamination from the MQ spray described above, for each of the three filters one quarter was sprayed with MQ with the remaining three quarters being left unsprayed.

Storage

All pre-filters and filters have been frozen for shipment to Keele, Germany. Clean, unused filters, have been packed and stored with all the other filters for blank measurements.

Table 5. List of SAPs deployments during MedBlack Leg 2(64PE373).

Cast	Approx. Pos'n (°N)	Approx. Water Depth (m)	Pump start (UTC+3)	Pump dur'n (hr)		Filter 1	Filter 2	Filter 3
1.3	42°15.95' N 30°00.96' E	2073	14/07/13 14:23	1.5	Depth (m)	140	90	50
					Vol (L)	292	368	222
2.5	42°31.28' N 31°24.11' E	2105	15/07/13 14:49	1.5	Depth (m)	150	100	30
					Vol (L)	387	392	267
3.3	43°01.65' N 33°43.84' E	2194	16/07/13 14:18	2.5	Depth (m)	150	85	45
					Vol (L)	321	423	229
4.3	43°08.56' N 36°13.78' E	2232	17/07/13 10:05	2.5	Depth (m)	150	100	45
					Vol (L)	257	573	374
5.3	42°20.94' N 38°41.01' E	2102	18/07/13 08:02	2.5	Depth (m)	150	110	40
					Vol (L)	321	407	362
6.3	41°30.70' N 40°37.18' E	1679	19/07/13 08:18	2.5	Depth (m)	250	180	40
					Vol (L)	327	570	326
7.3	41°56.23' N 39°40.45' E	1977	19/07/13 23:30	2.5	Depth (m)	175	125	35
					Vol (L)	336	460	284
8.4	42°48.67' N 37°34.02' E	2269	20/07/13 22:31	2.5	Depth (m)	150	95	44
					Vol (L)	335	378	232
9.4	43°12.01' N 34°46.22' E	2194	21/07/13 21:31	2.5	Depth (m)	150	100	46
					Vol (L)	345	399	206
10.4	42°44.33' N 32°30.31' E	2180	22/07/13 17:45	2.5	Depth (m)	150	88	46
					Vol (L)	356	515	230

Table 6. Differences in filter processing during MedBlack Leg 2 (64PE373).

Cast	Main filter	MQ spray main filter?	Pre-filter	Pre-filter kept?	Proportion of pre-filter rinsed and filtered		
					Filter 1	Filter 2	Filter 3
1.3	1 µm PC	Yes	150 µm PX	No	none	none	none
2.5	1 µm PC	Yes	51 µm PX	Yes	none	none	none
3.3	1 µm PC	Yes	51 µm PX	Yes	none	none	none
4.3	1 µm PC	Yes	51 µm PX	Yes	none	none	none
5.3	1 µm PC	Yes	51 µm PX	Yes	1	1/4	1/4
6.3	1 µm PC	Yes	51 µm PX	Yes	1/2	1/4	1/4
7.3	1 µm PC	Yes	51 µm PX	Yes	1/4	1/4	1/4
8.4	1 µm PC	No	51 µm PX	Yes	1/4	1/4	1/4
9.4	1 µm PC	No	51 µm PX	Yes	1/4	1/4	1/4
10.4	1 µm PC	No	51 µm PX	Yes	1/4	1/4	1/4

Figure 27. Cor, Matt, Jack and Sjaak handling the SAPS and on the right Matt sub-sampling a 293 mm polycarbonate 1 µm pore size filter.

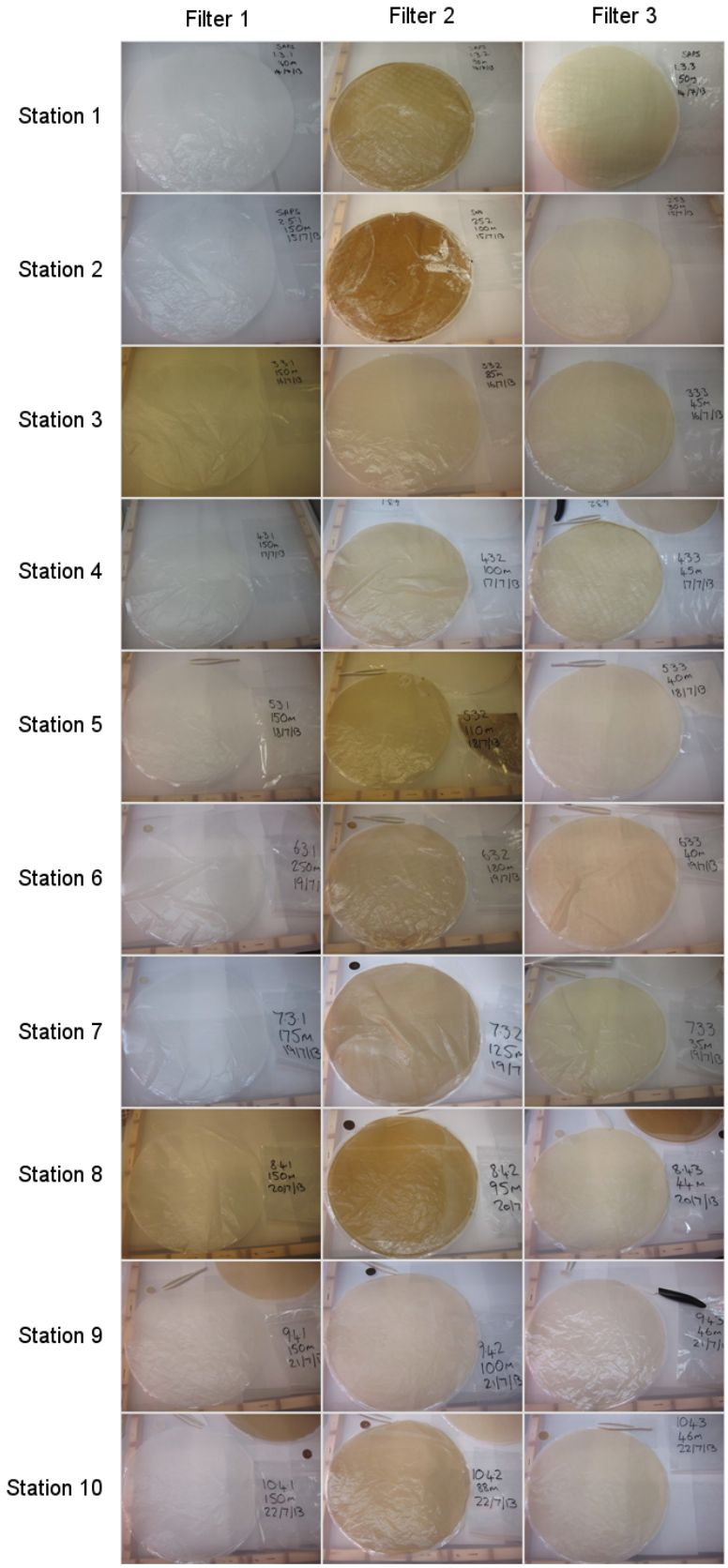

Figure 28) Photographs of the SAPS filters where Filter 1 is from the anoxic part, Filter 2 is of the suboxic part and Filter 3 of the oxic part of the water column during cruise 64PE373.

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, 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 24 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). All samples for A_T, and samples from the surface ~100m for C_T, 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.

Deep anoxic samples were analyzed first to minimize any changes caused by the oxidation of samples. The use of two machines increases our confidence in final results, and allows demonstration and quantification of measurement errors of the machines that would otherwise go unnoticed. No formal analysis and correction of the result have been performed yet.

Dissolved inorganic carbon (C_T)
Dissolved inorganic carbon (C_T) 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. Due to the presence of hydrogen sulphide in the anoxic samples three scrubbers were installed between the stripping chamber and the coulometer cell. The first contained 3g silver nitrate in 100 cm^3 MQ, acidified to a pH of ~3 with sulfuric acid and an addition of 1 cm^3 hydrogen peroxide per 15 ml, as outlined in Dickson et al. (2007). Following this an ORBO scrubber was installed to further remove acidic gases, and finally magnesium perchlorate, to remove water vapour. Due to the large amount of C_T found in the deep samples (~4000 μmol kg^{-1}), the titration time was also elongated from the traditional 16 minutes to 45 minutes, per sample.

Total Alkalinity (A_T)

Determinations of total alkalinity (A_T) 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. Further corrections will also be made to account for the hydrogen sulphide in the sample, which contributes significantly to A_T.

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 C_T and A_T.

References

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Appendix 1. Station list & devices deployment

Station	Cast	Date	Time[1]	Latitude	Longitude	Device name	Action name
1	1	14/07/2013	05:26:51	42.265753	30.015561	Ultra Clean CTD	Begin
1	1	14/07/2013	06:02:48	42.265992	30.015714	Ultra Clean CTD	Bottom
1	1	14/07/2013	07:15:23	42.266162	30.015558	Ultra Clean CTD	End
1	2	14/07/2013	07:45:06	42.266297	30.015687	CTD 25L	Begin
1	2	14/07/2013	08:20:34	42.266095	30.01581	CTD 25L	Bottom
1	2	14/07/2013	09:24:39	42.265868	30.016128	CTD 25L	End
1	3	14/07/2013	10:32:20	42.266055	30.015978	In Situ Pump	Begin
1	3	14/07/2013	11:33:20	42.26586	30.016079	In Situ Pump	Start pump
1	3	14/07/2013	13:26:13	42.266138	30.016407	In Situ Pump	Stop pump
1	3	14/07/2013	13:35:32	42.265862	30.016171	In Situ Pump	End
1	4	14/07/2013	13:50:38	42.265936	30.016302	Ultra Clean CTD	Begin
1	4	14/07/2013	13:58:46	42.265932	30.016569	Ultra Clean CTD	Bottom
1	4	14/07/2013	14:36:32	42.265696	30.016202	Ultra Clean CTD	End
2	1	14/07/2013	21:53:04	42.5215	31.401838	Ultra Clean CTD	Begin
2	1	14/07/2013	22:34:37	42.521454	31.401846	Ultra Clean CTD	Bottom
2	1	14/07/2013	23:45:30	42.521545	31.4019	Ultra Clean CTD	End
2	2	14/07/2013	23:58:24	42.521489	31.40238	CTD 25L	Begin
2	2	15/07/2013	00:49:12	42.521626	31.401985	CTD 25L	Bottom
2	2	15/07/2013	01:36:30	42.521411	31.401885	CTD 25L	End
2	3	15/07/2013	05:52:03	42.52155	31.40189	Ultra Clean CTD	Begin
2	3	15/07/2013	05:57:52	42.521478	31.401818	Ultra Clean CTD	Bottom
2	3	15/07/2013	06:33:55	42.521114	31.402367	Ultra Clean CTD	End
2	4	15/07/2013	10:21:24	42.521145	31.401729	Ultra Clean CTD	Begin
2	4	15/07/2013	10:39:31	42.521279	31.401682	Ultra Clean CTD	Bottom
2	4	15/07/2013	10:41:51	42.521226	31.401634	Ultra Clean CTD	End
2	5	15/07/2013	10:54:20	42.521189	31.401635	In Situ Pump	Begin
2	5	15/07/2013	11:54:06	42.521284	31.402513	In Situ Pump	Start pump
2	5	15/07/2013	13:37:54	42.521153	31.401557	In Situ Pump	Stop pump
2	5	15/07/2013	13:47:13	42.521281	31.40164	In Situ Pump	End
2	6	15/07/2013	14:19:39	42.521336	31.401597	Ultra Clean CTD	Begin
2	6	15/07/2013	14:26:47	42.521389	31.401709	Ultra Clean CTD	Bottom
2	6	15/07/2013	14:35:55	42.5213	31.401879	Ultra Clean CTD	End
2	7	15/07/2013	17:15:22	42.521242	31.401917	Ultra Clean CTD	Begin
2	7	15/07/2013	17:51:48	42.521377	31.401894	Ultra Clean CTD	Bottom
2	7	15/07/2013	18:56:33	42.521397	31.401998	Ultra Clean CTD	End
3	7	16/07/2013	06:14:23	43.0274	33.730783	Ultra Clean CTD	Begin
3	1	16/07/2013	06:52:01	43.027488	33.730773	Ultra Clean CTD	Bottom
3	1	16/07/2013	08:02:01	43.027436	33.730727	Ultra Clean CTD	End
3	2	16/07/2013	08:20:49	43.027326	33.730707	CTD 25L	Begin
3	2	16/07/2013	08:57:58	43.027297	33.73091	CTD 25L	Bottom
3	2	16/07/2013	10:07:58	43.027709	33.730683	CTD 25L	End

3	3	16/07/2013	10:19:59	43.027557	33.73052	In Situ Pump	Begin
3	3	16/07/2013	10:51:21	43.027344	33.73072	In Situ Pump	Start pump
3	3	16/07/2013	13:38:21	43.027337	33.730126	In Situ Pump	Stop pump
3	3	16/07/2013	13:48:39	43.027344	33.730249	In Situ Pump	End
3	4	16/07/2013	13:59:58	43.027408	33.730405	Ultra Clean CTD	Begin
3	4	16/07/2013	14:05:58	43.027546	33.730779	Ultra Clean CTD	Bottom
3	4	16/07/2013	14:40:10	43.027476	33.730472	Ultra Clean CTD	End
4	1	17/07/2013	02:39:35	43.142623	36.229777	Ultra Clean CTD	Begin
4	1	17/07/2013	03:16:36	43.142551	36.229598	Ultra Clean CTD	Bottom
4	1	17/07/2013	04:34:55	43.142569	36.229733	Ultra Clean CTD	End
4	2	17/07/2013	04:48:49	43.142593	36.229652	CTD 25L	Begin
4	2	17/07/2013	05:25:54	43.142415	36.229566	CTD 25L	Bottom
4	2	17/07/2013	06:31:30	43.142505	36.229702	CTD 25L	End
4	3	17/07/2013	06:43:49	43.142513	36.229616	In Situ Pump	Begin
4	3	17/07/2013	07:27:48	43.142504	36.229538	In Situ Pump	Start pump
4	3	17/07/2013	10:03:11	43.142604	36.229753	In Situ Pump	Stop pump
4	3	17/07/2013	10:05:37	43.142469	36.229752	In Situ Pump	End
4	4	17/07/2013	10:24:43	43.142521	36.229417	Ultra Clean CTD	Begin
4	4	17/07/2013	10:30:27	43.14253	36.229482	Ultra Clean CTD	Bottom
4	4	17/07/2013	11:03:02	43.142261	36.229471	Ultra Clean CTD	End
5	1	17/07/2013	23:54:44	42.348688	38.683961	Ultra Clean CTD	Begin
5	1	18/07/2013	00:34:17	42.348893	38.683862	Ultra Clean CTD	Bottom
5	1	18/07/2013	02:03:17	42.348808	38.683736	Ultra Clean CTD	End
5	2	18/07/2013	02:38:47	42.348962	38.683745	CTD 25L	Begin
5	2	18/07/2013	03:20:14	42.349068	38.683616	CTD 25L	Bottom
5	2	18/07/2013	04:25:33	42.349031	38.683646	CTD 25L	End
5	3	18/07/2013	04:37:16	42.348936	38.683492	In Situ Pump	Begin
5	3	18/07/2013	05:06:01	42.348934	38.683267	In Situ Pump	Start pump
5	3	18/07/2013	07:50:43	42.349237	38.684051	In Situ Pump	Stop pump
5	3	18/07/2013	08:01:17	42.348903	38.684103	In Situ Pump	End
5	4	18/07/2013	08:20:42	42.348885	38.68346	Ultra Clean CTD	Begin
5	4	18/07/2013	08:24:37	42.349002	38.683523	Ultra Clean CTD	Bottom
5	4	18/07/2013	09:01:38	42.348873	38.683683	Ultra Clean CTD	End
5	5	18/07/2013	12:04:45	42.348764	38.683437	Ultra Clean CTD	Begin
5	5	18/07/2013	12:42:02	42.34906	38.683132	Ultra Clean CTD	Bottom
5	5	18/07/2013	13:49:35	42.348985	38.683608	Ultra Clean CTD	End
6	1	19/07/2013	01:07:39	41.511533	40.619865	Ultra Clean CTD	Begin
6	1	19/07/2013	01:39:08	41.511727	40.619717	Ultra Clean CTD	Bottom
6	1	19/07/2013	02:42:56	41.51168	40.619718	Ultra Clean CTD	End
6	2	19/07/2013	02:59:54	41.511468	40.619868	CTD 25L	Begin
6	2	19/07/2013	03:30:21	41.511621	40.619714	CTD 25L	Bottom
6	2	19/07/2013	04:28:23	41.511572	40.619666	CTD 25L	End
6	3	19/07/2013	04:37:51	41.511765	40.619675	In Situ Pump	Begin
6	3	19/07/2013	05:30:34	41.511642	40.619922	In Situ Pump	Start pump

6	3	19/07/2013	06:46:41	41.511936	40.619769	In Situ Pump	Stop pump
6	3	19/07/2013	08:12:41	41.511971	40.61961	In Situ Pump	Stop pump
6	3	19/07/2013	08:20:51	41.512139	40.619871	In Situ Pump	End
6	4	19/07/2013	08:38:37	41.511768	40.6198	Ultra Clean CTD	Begin
6	4	19/07/2013	08:45:14	41.511772	40.619697	Ultra Clean CTD	Bottom
6	4	19/07/2013	09:29:24	41.511482	40.619759	Ultra Clean CTD	End
7	1	19/07/2013	15:42:24	41.937126	39.674238	Ultra Clean CTD	Begin
7	1	19/07/2013	16:16:12	41.937204	39.674224	Ultra Clean CTD	Bottom
7	1	19/07/2013	17:40:01	41.936985	39.674208	Ultra Clean CTD	End
7	2	19/07/2013	18:00:58	41.937035	39.674174	CTD 25L	Begin
7	2	19/07/2013	18:47:14	41.93699	39.675362	CTD 25L	Bottom
7	2	19/07/2013	19:52:45	41.937209	39.674173	CTD 25L	End
7	3	19/07/2013	20:09:18	41.937249	39.674288	In Situ Pump	Begin
7	3	19/07/2013	20:34:15	41.936965	39.674425	In Situ Pump	Start pump
7	3	19/07/2013	23:09:39	41.937228	39.674239	In Situ Pump	Stop pump
7	3	19/07/2013	23:15:11	41.93716	39.674054	In Situ Pump	End
7	4	19/07/2013	23:39:00	41.937068	39.674098	Ultra Clean CTD	Begin
7	4	19/07/2013	23:49:05	41.936939	39.674148	Ultra Clean CTD	Bottom
7	4	20/07/2013	00:29:30	41.937135	39.673899	Ultra Clean CTD	End
8	1	20/07/2013	13:22:08	42.811288	37.567068	Ultra Clean CTD	Begin
8	1	20/07/2013	13:59:18	42.811211	37.567162	Ultra Clean CTD	Bottom
8	1	20/07/2013	15:10:33	42.811178	37.567119	Ultra Clean CTD	End
8	2	20/07/2013	15:24:59	42.811176	37.567242	CTD 25L	Begin
8	2	20/07/2013	16:01:07	42.811206	37.567023	CTD 25L	Bottom
8	2	20/07/2013	17:15:52	42.811226	37.56711	CTD 25L	End
8	3	20/07/2013	18:13:46	42.811143	37.567439	Ultra Clean CTD	Begin
8	3	20/07/2013	18:18:08	42.811088	37.567314	Ultra Clean CTD	Bottom
8	3	20/07/2013	18:52:51	42.811199	37.56703	Ultra Clean CTD	End
8	4	20/07/2013	19:14:29	42.811107	37.566717	In Situ Pump	Begin
8	4	20/07/2013	19:31:00	42.811244	37.567215	In Situ Pump	Start pump
8	4	20/07/2013	22:08:51	42.811048	37.566913	In Situ Pump	Stop pump
8	4	20/07/2013	22:19:33	42.811029	37.566687	In Situ Pump	End
9	1	21/07/2013	12:38:39	43.200122	34.770031	Ultra Clean CTD	Begin
9	1	21/07/2013	13:16:18	43.200127	34.770412	Ultra Clean CTD	Bottom
9	1	21/07/2013	14:31:00	43.200111	34.770239	Ultra Clean CTD	End
9	2	21/07/2013	14:48:35	43.200111	34.77024	CTD 25L	Begin
9	2	21/07/2013	15:25:50	43.200099	34.770194	CTD 25L	Bottom
9	2	21/07/2013	16:33:44	43.200072	34.770393	CTD 25L	End
9	3	21/07/2013	17:05:13	43.200123	34.770447	Ultra Clean CTD	Begin
9	3	21/07/2013	17:10:18	43.200124	34.770392	Ultra Clean CTD	Bottom
9	3	21/07/2013	17:49:57	43.199982	34.770343	Ultra Clean CTD	End
9	4	21/07/2013	18:02:36	43.20002	34.770452	In Situ Pump	Begin
9	4	21/07/2013	18:35:06	43.200294	34.770573	In Situ Pump	Start pump
9	4	21/07/2013	21:09:17	43.200384	34.769848	In Situ Pump	Stop pump

9	4	21/07/2013	21:21:21	43.200701	34.769863	In Situ Pump	End
10	1	22/07/2013	09:25:53	42.738897	32.505335	Ultra Clean CTD	Begin
10	1	22/07/2013	10:04:12	42.738819	32.505161	Ultra Clean CTD	Bottom
10	1	22/07/2013	11:19:37	42.738796	32.505207	Ultra Clean CTD	End
10	2	22/07/2013	11:30:59	42.738612	32.505146	CTD 25L	Begin
10	2	22/07/2013	12:07:11	42.738803	32.50484	CTD 25L	Bottom
10	2	22/07/2013	13:29:24	42.738816	32.505273	CTD 25L	End
10	3	22/07/2013	13:52:45	42.738766	32.505285	Ultra Clean CTD	Begin
10	3	22/07/2013	14:05:58	42.738796	32.505213	Ultra Clean CTD	Bottom
10	3	22/07/2013	14:07:04	42.738857	32.505163	Ultra Clean CTD	End
10	4	22/07/2013	14:20:27	42.738761	32.505193	In Situ Pump	Begin
10	4	22/07/2013	14:49:26	42.738849	32.505361	In Situ Pump	Start pump
10	4	22/07/2013	17:31:34	42.73875	32.505261	In Situ Pump	Stop pump
10	4	22/07/2013	17:38:43	42.738696	32.504967	In Situ Pump	End
10	5	22/07/2013	17:48:37	42.738701	32.505324	Ultra Clean CTD	Begin
10	5	22/07/2013	17:51:53	42.73883	32.505083	Ultra Clean CTD	Bottom
10	5	22/07/2013	18:27:10	42.738712	32.505305	Ultra Clean CTD	End
11	1	23/07/2013	12:08:49	41.570397	29.139294	Ultra Clean CTD	Begin
11	1	23/07/2013	12:20:00	41.570494	29.1391	Ultra Clean CTD	Bottom
11	1	23/07/2013	12:34:07	41.570456	29.139208	Ultra Clean CTD	End
11	2	23/07/2013	12:53:36	41.571728	29.146616	Ultra Clean CTD	Begin
11	2	23/07/2013	13:07:06	41.571819	29.146642	Ultra Clean CTD	Bottom
11	2	23/07/2013	14:03:31	41.571692	29.146504	Ultra Clean CTD	End
11	3	23/07/2013	14:18:41	41.571777	29.146607	CTD 25L	Begin
11	3	23/07/2013	14:30:53	41.571709	29.146505	CTD 25L	Bottom
11	3	23/07/2013	15:10:09	41.571857	29.146591	CTD 25L	End
12	1	23/07/2013	17:54:27	41.223915	29.125782	Ultra Clean CTD	Begin
12	1	23/07/2013	17:56:04	41.223923	29.125759	Ultra Clean CTD	Bottom
12	1	23/07/2013	18:08:50	41.224006	29.125621	Ultra Clean CTD	End

[1] Time in UTC

Appendix 2.

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