Cruise report 64 PE 319 on RV Pelagia

Geotraces West Atlantic leg 1

Scrabster 28-04-2010 to Bermuda 25-05-2010

Loes J.A. Gerringa

Royal NIOZ

With contributions of participants

Acknowledgements

On behalf of all participants I want to thank captain John Ellen for his help advice and hospitality on his ship Pelagia. The crew of Pelagia consisting of Joep van Haaren, Jaap Seepma, David Verheyen, Marcel de Kleine, Wout Pronk, Sjaak Maas, Cor Stevens, Jose Vitoria, Hans van de Linde and Alexander Popov helped whenever and wherever necessary. They made our stay on Pelagia a very pleasant time.
We acknowledge ZKO (project number 839.08.410) for funding of this work.

Wout Pronk and Cor Stevens ready to lower the UC CTD into the water

Front page: the new ultraclean CTD frame with 24 27L PVDF samplers

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Summary

The cruise Geotraces West Atlantic leg 1; 64 PE 319 on RV Pelagia started 28 April 2010 from Scrabster (Scotland) and arrived in Bermuda 25 May 2010 with Loes Gerringa (Royal NIOZ) as chief scientist. The cruise was originally planned to start from Reykjavik, Iceland. However, air traffic was extremely difficult to plan due to the ash plume from the volcano under the Eyjafjallajoekull. During the transit Texel-Reykjavik it was decided that the port stop for exchanging scientists and fuelling was changed into Scrabster harbour in northernmost Scotland (fig 1). Travel to and from the ship by nine and five scientists, respectively, was diverted accordingly.
Because leaving from Scrabster instead of Reykjavik meant two more days of steaming two days were lost from the program. These lost days were among others the reason not to spend too much time on sampling surface waters for volcanic ash influences during the transit to the first station location west of Iceland. This was a rather difficult decision since the feeling of "once in a life time chance of being there where the action was", was hard to resist. However, we were financed and equipped to do the extensive GEOTRACES West Atlantic cruise leg 1, and as soon as possible we steamed to the first station location. It was possible to deploy the fish without reducing speed and so we did sample the surface waters when passing south of Iceland (at a considerable distance..).
We used two CTD systems, both with large volume samplers. One the ultraclean all-titanium frame, the so called UC CTD (UCC in the cruise summary file) collecting 24 samples of 27 Litres with novel butterfly-valve type ultraclean samplers made from clean PVDF plastic. Closed bottles were lowered into the water and were opened at a depth of 30 m. preventing any contamination. After recovery the frame was placed on a trolley and wheeled into a clean container for sampling. The other CTD system consists of 24 new Niskin-type samplers of large 25 L volume that were mounted on a new stainless steel rosette sampler (ROS in the cruise summary file). In Situ Pumps (7 in total) were used in 6 stations. Underway sampling was executed by deploying a fish, dust samples were taken by two dust samplers on the top deck of Pelagia. For more details see section 2.2 for the list of parameters, and the appendices Station list and Devices list.
Both CTD's performed perfectly, except for a little problem with a leak in a cable of the 25L CTD at station 8. The UC CTD has a high centre of gravity, therefore when on deck a danger exists in rough weather that the frame topples sideways. A solution will certainly be found for this problem.
17 stations were successfully sampled.

Patrick Laan as chief ultra clean CTD (UC CTD) asked for a station, before reaching the actual planned cruise track to rinse and clean the PVDF water samplers; this became our station 1. One rinse is sufficient to make these samplers Fe-clean. We thus started with station number 2 as being the first real station (fig 1). This station was immediately an important one since west of Iceland we intended to sample the Denmark Strait Overflow Water (DSOW). It was therefore to become the first so-called hyperstation, which means more than one cast of each of the CTD frames to enable sampling of many parameters, also those that needed large volumes and the deployment of the in situ pumps from AWI. It is not easy to find the DSOW, we had no time to search for it and we were very lucky to immediately strike gold. Due to a misunderstanding, ^{227}Ac was unfortunately not sampled in DSOW while ^{228}Ra and anthropogenic radionuclides were not sampled according to schedule at this station (see 3.2.A.7).
A hyperstation was in fact an extended superstation, where in situ pumps were deployed and Pa/Th was sampled. We had 6 superstations with ISP and Pa/Th being 2, 6, 8, 11, 13 and 15

of which 2, 11 and 15 were hyperstations. Station 17 was also sampled for Pa/Th (fig 1).

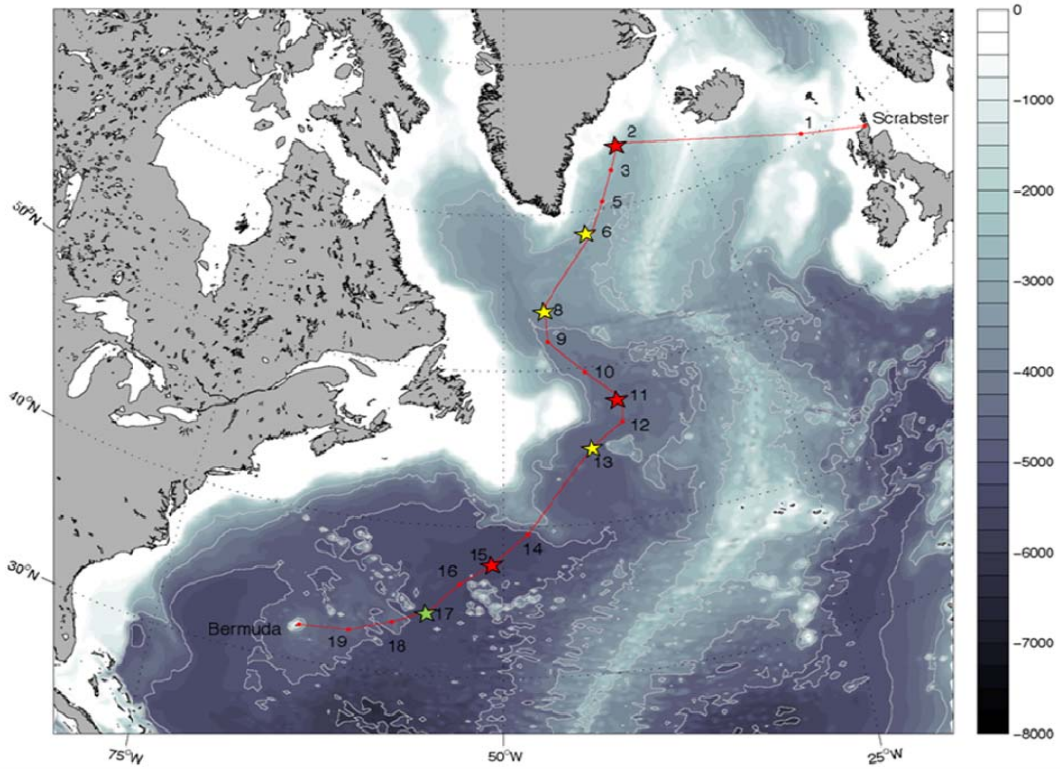

Figure 1: the cruise track with the stations, stations with a red star are hyperstations, with a yellow star superstations and the green star from station 17 indicates that also Pa/Th was sampled there.

Since we were the first cruise after the transect on a new Pelagia, we had little experience with working with the upgraded ABC with Casino+ a voyage logbook. This system is easy to handle, but still beginners-errors were made. We have no station number 4, since the third fish deployment was named station 4, whereas fish deployments are called (strangely enough) profiles and have their own numbering sequence.
During the cruise we had several times bad weather conditions and the first storm happened where we planned and started to execute station 7, the CTD operator Martin Laan already reserved the number 7 for the first deployment when it was decided that the weather forecast was really too bad; this station is therefore missing and the first gap in the transect created. Station 8 was planned to become a hyperstation, but due to problems with the CTD the samplers of the second cast of the 25 L CTD could not be closed. By using the UC CTD as a fourth cast and deploying the ISP, this station could be turned still into a superstation, but it was not possible to do all the work and reach the hyperstation status. East of Newfoundland the second storm lasted 4 days making work impossible. The only reason that the gap between stations 13 and 14 in the transect is not enormous is due to the very strong winds reducing the speed of Pelagia to 2 knots. We planned the cruise track along the deepest parts of the west side of the Atlantic Ocean but we had to cross the extension of the Grand Banks of Newfoundland between stations 13 and 14 in order to spare time. Luckily we then had some nice days in which we tried to catch up as best as we could. The last station planned was to be the hyperstation BATS, but a last storm prevented us from doing so. This station is not lost, it will be sampled during the second leg of GEOTRACES West Atlantic.

1 General introduction of GEOTRACES the project

The GEOTRACES project wants to re-visit in 2010-2011 the West Atlantic GEOSECS-1972 cruise to produce complete ocean sections of (A) novel trace elements and several isotopes, (B) transient tracers of global change, (C) microbial biodiversity and metabolism, and (D) interpretation by ocean modelling where the ocean observations A-C serve for verification of the models.
Many of these 'tracers in the sea' are the first-ever ocean sections (sub-projects A, (B), C), while others (sub-project B) will allow unravelling of transient global changes over the past ~35 years by comparison with data of 1972-1973 GEOSECS and later cruises (notably 1981-1983 TTO, WOCE 1990's; CLIVAR).
A) The first-ever high resolution Atlantic deep section of trace metals Fe, Al, Zn, Mn, Cd, Cu, Co, Ni, Ag were sampled, in conjunction with lower resolution sampling for Rare Earths, natural isotopes 234Th, 230Th, 231Pa, 223Ra, 224Ra, 226Ra, 228Ra, 227Ac and anthropogenic isotopes 129I, 99Tc, 137Cs, 239,240Pu, 238Pu.
B) Water masses, circulation and mixing are defined by classical S, T, p combined with datasets of dissolved nutrients and O_2, as well as transient tracers DIC, CFCs, novel SF6, 3H/3He and $13CO_2$, $14CO_2$ also to derive 'ages' of a water mass. The invasion of transients is mostly in the North Atlantic Ocean and partly overlaps with warming of upper ocean waters, and with the increase of CO_2 inventory, hence ocean acidification.
C) Biodiversity, abundance and metabolic rates of microbes (eukaryotes, prokaryotes and viruses) were determined in the meso- and bathypelagic ocean. Particularly, the role of chemoautotrophy in the deep ocean is investigated as it might represent a thus far unrecognized source of dark ocean ‘primary productivity’.
D) The above datasets A,B,C are in mutual support and moreover combine to serve for Ocean Biogeochemical Climate Modelling towards more rigorous, integrated understanding of processes including the role of the Atlantic Ocean in global change.

Overall aim and hypothesis
Major objective is the re-visiting of West Atlantic GEOSECS-1972 to produce complete ocean sections of (A) novel trace elements and several isotopes, (B) 2009-2010 status of transient tracers of global change, (C) novel microbial diversity and metabolism, and (D) interpretation by ocean modelling.

Below the different subjects of GEOTRACES are discussed in more detail with the exception of D) the modelling part of GEOTRACES, since this is not part of the cruise, but will be done afterwards when al data is available.

A) Trace elements and isotopes of the international GEOTRACES program

More than thirty years after GEOSECS the techniques for ultraclean sampling in a time efficient manner (De Baar et al., 2008) and final analyses have improved enormously. Nowadays it is feasible to determine for the first time ever the oceanic distributions of key trace metals, other trace elements, and various isotopes, along ocean sections throughout the

full 4-6 km depth of the oceans. In the GEOTRACES Science Plan (www.geotraces.org) we have defined 6 key trace metals Fe, Al, Zn, Mn, Cd, Cu, which, together with additional metals Co, Ni, Ag is investigated with high priority in the GEOTRACES West Atlantic Ocean sections. The distribution and biological availability of Fe is strongly controlled by its physical-chemical speciation within seawater, where colloids and Fe-organic complexes are dominant actors. For phytoplankton growth, Cu at the cell wall acts in reductive dissociation of Fe-organic complexes, hence facilitates Fe uptake. This may partly explain the nutrient-type distribution of Cu in the oceans. The external sources of Fe into the oceans are either from above (dust) and below (sediments) and will be constrained by Al and Mn for aeolian dust input and sedimentary redox cycling sources, respectively. Iron enhances phytoplankton growth, which in turn controls the biological pump for uptake of CO_2 from the atmosphere. Due to fossil fuel burning the CO_2 also increases in ocean waters and this may affect phytoplankton ecophysiology, with key links of metals Fe and Zn in overall photosynthesis and in carbonic anhydrase, respectively, where Cd and Co may substitute for Zn in the latter carbonic anhydrase.

B) Global change of anthropogenic CO_2 invasion and other transient anthropogenic tracers

Aim is the determination of anthropogenic CO_2 inventory by measurements of DIC, Alkalinity and transient radiocarbon, and interpretation relying also on other transients (CFC's; SF6; 3H/3He; other noble gases) measured by international partners

The overarching hypothesis is the very obvious statement:

The best possible estimate of the inventory of anthropogenic CO_2 in the Atlantic Ocean can be achieved by optimizing between a suite of transient tracers and approaches, for optimal concordance between them.

This being stated one is aware of the ambition of trying to reach such concordance. Nevertheless without high ambition or targets one may as well stay home.

First major objective is to quantify the inventory of anthropogenic CO_2 along the transect in the West Atlantic Ocean by a suite of different approaches, as follows:

(i) simple (or simplistic) comparison of DIC inventories over the period between 1981-1983 and 2009-2010, as to derive an inventory increase over this circa three decades time interval;

(ii) instantaneous back calculations using DIC, nutrients, O_2, by several methods like delta C*, TROCA, eMLR;

(iii) combinations of DIC data and one or more transient tracers.

Each one of these approaches requires insight and skill, but is in itself quite feasible to pursue. Next these various findings will be evaluated, and the most promising approaches will be applied for an expansion both in time and in space, by developing a time history of increasing anthropogenic CO_2 inventory in the complete North Atlantic Ocean basin, also relying on preceding data in the CARINA database. This expansion towards a basin wide estimate will be in conjunction with the sub-project D. global ocean modelling.

C) Microbial oceanography: biodiversity and turnover rates of prokaryotes, eukaryotes and viruses

Aims and objective and the relevance for the ocean theme

The main objective of the proposed study is to mechanistically understand the dynamics in diversity and function of the meso- and bathypelagic food web in relation to hydrodynamic conditions in distinct deep-water masses of the North Atlantic and at water-mass boundaries

where diversity hotspots are expected to occur as predicted by the ecotone concept. The main objective translates into the following **specific objectives**:
i) To link phylogenetic prokaryotic diversity to selected prokaryotic functions relevant for the dark ocean's biogeochemical fluxes (remineralisation of organic matter, organic matter production, ectoenzymatic activity, etc.) using a combination of approaches.
ii) To differentiate between the distribution of abundant and rare prokaryotic taxa and to determine the significance of rare taxa for the functioning of the community.
iii) To determine the extent of the recently discovered archaeal chemoautotrophy in the meso- and bathypelagic realm.
iv) To relate dynamics in abundance and activity of the dark ocean biota to changes in the quantity and quality of the organic matter, water mass age and remineralisation activity.
v) To determine the expression of selected functional genes for Archaea and Bacteria indicative of major metabolic pathways using targeted Q-PCR analyses in specific deep-water masses.
vi) To assess the role of viruses as compared to protists as consumers of prokaryotes.

Hypothesis
The overarching hypothesis is that the seemingly homogenous water column of the dark ocean is highly structured due to the hydrodynamics of the different water masses. Each water mass carries its specific biogeochemical characteristics and allows the expression of distinct diversity and function patterns of the dark ocean biota. At the interface and mixing zones of deepwater masses, persistent deep-sea ecotones exist, representing 'hotspots' in diversity and activity of microbes with significant influence on the overall biogeochemical cycles of the dark ocean.

2. Participants and parameters

2.1 List of participants

1	**Loes Gerringa PI**	NIOZ; BIO-Chemical Oceanography
2	**Martin Laan**	NIOZ; MTE
3	**Lorendz Boom**	NIOZ; MTM
4	**Jan van Ooijen**	NIOZ
5	**Steven van Heuven**	Ocean Ecosystems, Univ.Groningen (RuG)
6	**Lesley Salt**	NIOZ; BIO-Chemical Oceanography
7	**Patrick Schmidt**	University Bremen (UB)
8	**Patrick Laan**	NIOZ; BIO-Chemical Oceanography
9	**Micha Rijkenberg**	NIOZ; BIO-Chemical Oceanography
10	**Rob Middag**	NIOZ; BIO-Chemical Oceanography
11	**Jeroen de Jong**	Université Libre, Bruxelles (ULB)
12	**Michiel RvdLoeff**	AWI
13	**Sven Kretschmer**	AWI
14	**Viena Puigcorbe**	Universitat Autònoma de Barcelona
15	**Merce Bermejo**	Universitat Autònoma de Barcelona
16	**Thomas Reinthaler**	University of Viena
17	**Taichi Yokokawa**	NIOZ; BIO-Chemical Oceanography
18	**Daniele De Corte**	NIOZ/RuG
19	**Santiago Gonzalez**	NIOZ; BIO-Chemical Oceanography

For complete addresses and email see Appendix 1

2 .2. List of parameters

sample equipment and parameter	collected by	responsible for analysis and data
UC CTD (UCC)		
Library metals totals	Patrick Laan	P. Laan, H de Baar
Library metals dissolved	Patrick Laan	P. Laan, H de Baar
Nutrients	Jan van Ooijen	Jan van Ooijen
Unfiltered Fe	Patrick Laan	P. Laan, L Gerringa
Fe	Patrick Laan	P. Laan, M. Rijkenberg
Mn	Rob Middag	Rob Middag
Al	Rob Middag	Rob Middag
Fe ultra filtration	Micha Rijkenberg	P. Laan, M. Rijkenberg
Fe Speciation	Micha Rijkenberg	Loes Gerringa
Ag	Patrick Laan	Eric Achterberg
Pt	Patrick Laan	Antonio Cobelo
Co, Zn, Cd	Patrick Laan	Marie Boye
Co-speciation	Patrick Laan	Marie Boye
Cd Isotopes	J. de Jong, P.Laan	Wafa Abouchami
Nd	J. de Jong, P.Laan	Tina van de Flierdt
234 Th	Viena Puigcorbe	V. Puigcorbe, M. van der Loeff
210Pb and 210Po	V Puigcorbe, M Bermejo	Pere Masque
DOM	Michiel Rutgers van der Loeff	Oliver Lechtenfeld
Si-isotopes	Patrick Laan	Gregory de Souza
T Fe isotopes	Jeroen de Jong	J. de Jong, V. Schoemann
DFe isotopes	Jeroen de Jong	J. de Jong, V. Schoemann
Fe, Cu, Zn isotopes	Jeroen de Jong	J. de Jong, V. Schoemann
14C/13C	S. van Heuven, L. Salt	Harro Meijer

sample equipment and parameter	collected by	responsible for analysis and data
25 L CTD (ROS)		
CFC	Patrick Schmidt	Reiner Steinfeldt
O_2	S. van Heuven, L. Salt	S. van Heuven, L. Salt
DIC-ALK	S. van Heuven, L. Salt	S. van Heuven, L. Salt
DOC / DON / FDOM	Santiago Gonzalez	
Nutrients	Jan van Ooijen	Jan van Ooijen
nitrate isotopes	Jan van Ooijen	Daniel Sigman
BA / Vir/ Abundance	Daniele De Corte	Daniele De Corte
3H-Leu / Bacterial production	Thomas Reinthaler	Thomas Reinthaler
14C-DIC / Archaeal Production	Santiago Gonzalez	Thomas Reinthaler
3H-FISH	Thomas Reinthaler	Thomas Reinthaler
14C-FISH	Thomas Reinthaler	Thomas Reinthaler
FISH	Taichi Yokokawa	Taichi Yokokawa
DNA	Thomas Reinthaler	Thomas Reinthaler
POC	Thomas Reinthaler	Thomas Reinthaler
13C/15 Nanosims	Thomas Reinthaler	Thomas Reinthaler
Nitrification/NH3	Taichi Yokokawa	Taichi Yokokawa
Burst Size	Daniele De Corte	Daniele De Corte
Viral production/Decay	Daniele De Corte	Daniele De Corte
qPCR	Thomas Reinthaler	Paul Berube
230Th and 231Pa	Sven Kirchner	Michiel Rutgers van der Loeff
226 Ra	Michiel Rutgers van der Loeff	Michiel Rutgers van der Loeff

Ac Ra, Cs (large-volume analysis)	V Puigcorbe, M Bermejo	Ac	P. Masque, M. Rutgers vd Loeff, W. Geibert
		Ra	Pere Masque, M. Rutgers vd Loeff
		Cs	Pere Masque
Pu, Cs, Np (20L)	V Puigcorbe, M Bermejo		Tim Kenna
I-129 and Tc	V Puigcorbe, M Bermejo		Pere Masque

In Situ Pumps

230Th and 231Pa, particulate	S. Kirchner ,M. Rutgers v.d. Loeff	231Pa 230Th	Michiel Rutgers van der Loeff
we try to save a fraction for Nd		eps Nd	Tina vd Fliert
		biogenic opal	Michiel Rutgers van der Loeff
		carbonate	Michiel Rutgers van der Loeff

Dust collectors

Dust	P Schmidt, R Middag	Alex Baker

FISH

Pt	M Rijkenberg	Antonio Cobelo
Pb-isotopes	M Rijkenberg	Wafa Abouchami

3 Analyses and measurements,

3.1 Data management and general parameters

3.1.1 Data Management

Steven van Heuven

A MATLAB script was written that allowed straightforward concatenation of CTD bottle files (SeaBird's standard .btl format) and user-provided datasets (listing either measurement results or notifications of which samples were collected). The fully automatic nature of the script, together with the very simple requirements of the data suppliers facilitated regular updating of the shipboard 'merged dataset' as new data came in. Output consisted of a single large data file and of section plots of all submitted parameters, which allowed for convenient monitoring of data quality. Profiles of selected parameters were made that allowed for comparison of the two CTD frames. Many of the figures provided in this cruise report are unaltered output of this script.

3.1.2 CTD systems
Martin Laan

Two CTD frames were used; the UC CTD consists of a titanium frame with 24 NIOZ made, PVDF water samplers of 27 L volume with special butterfly lids. This frame was tested on the 64PE318 cruise and worked perfectly. The butterfly-type valves in top and bottom of the samplers, accumulator and modified Multivalve worked perfectly. The samplers passed the air/water-interface with closed valves, the valves opened automatically at about 25 meters depth. After the cast the frame was rolled into the clean container the bottles were pressurized with nitrogen to enable filtration during sampling.
Beside the UCC-system a so called CTD 25 L was used. In this enlarged rosette CTD-frame 24 25-liter-Niskins were mounted.
Both CTD-systems were equipped with a Seabird SBE-9+ underwater-unit, a SBE 3+ thermometer, a SBE4-conductivity-sensor, a SBE 5T under-water pump, a Chelsea Aquatracka fluorometer and a Wetlabs CStar- transmissiometer. For bottom-detection a bottom-switch was mounted and as "early-warning" system a Benthos PSA-916 altimeter was applied.
Both CTD-system were lowered through the water column using the big Kley-France winch with the new and very long (about 9500 m) super-aramide-cable.

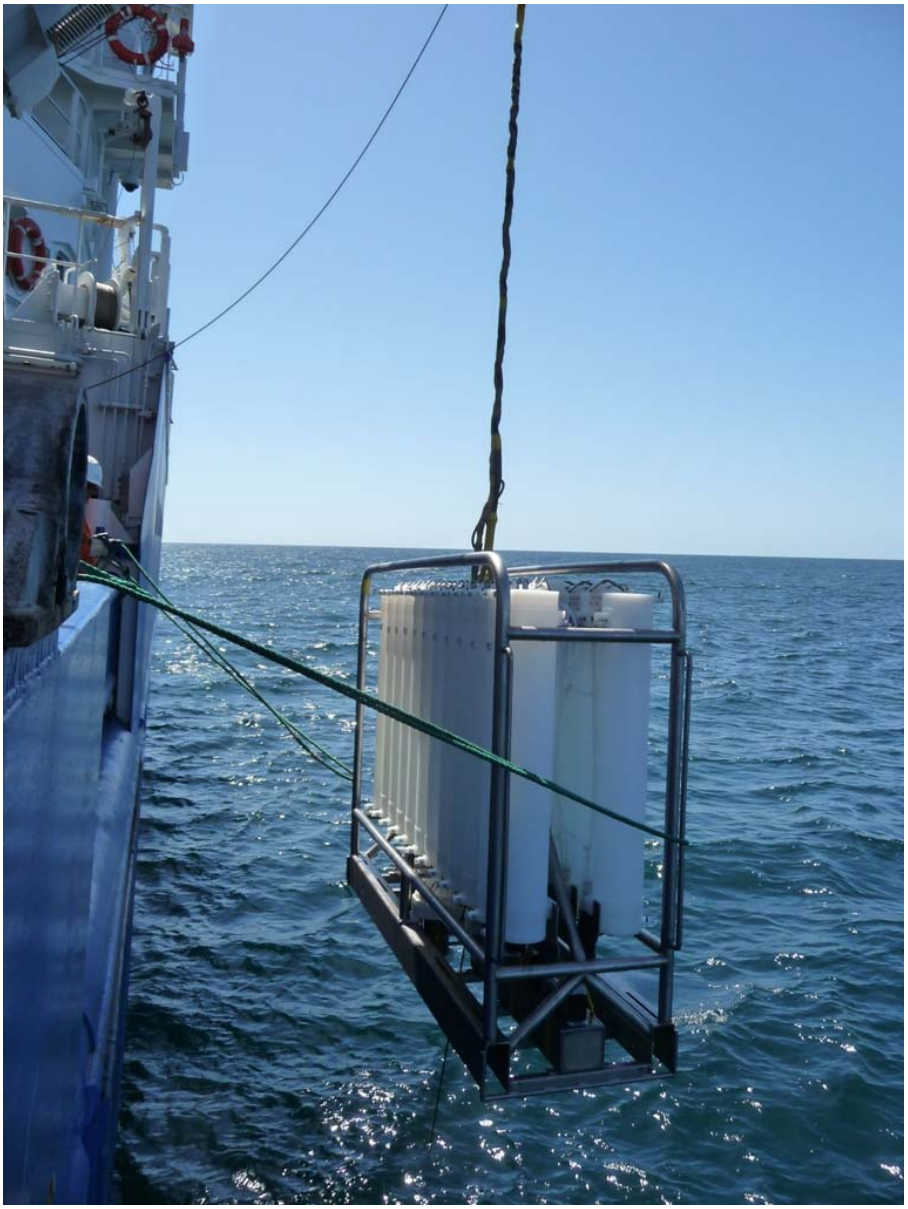

Figure 2: the Ultra Clean CTD hanging next to the starboard side of Pelagia.

Performance

The UC CTD needed only one rinse to be metal clean, which is a great advantage. Once we had a problem with the pigtail cable; a leak was observed so that seawater could enter; this was quickly solved.

The bottles closed perfectly. Jan van Ooijen confirmed this with his nutrient data from both CTD's.

Figure 3: Underway repair of the CTD by Lorendz Boom (inside the frame) and Martin Laan, searching for the problem, which in the end proved to be a leaking cable.

Only when in the clean container pressurised for sampling it can happen (10%) that lids are somewhat askew and then leak air, a manual adjustment is necessary to stop the air leaking and then sampling can continue. Therefore new air release valves will be mounted in Bermuda by Martin Laan (manufactured by Edwin Keijzer, brought by Jan-Dirk de Visser). These new valves have a little more tolerance in closing capabilities. They have a conical form instead of cylindrical and if they are askew when pressurized they still close airtight.

The UC CTD has one disadvantage; it cannot be safely used above wind force 5 on board Pelagia. The centre of gravity is high and therefore when on deck with a moving ship it can

topple sideways. This is extremely dangerous when the CTD is brought to the container pushed by persons at the side. This problem will be solved back when Pelagia arrives back home on Texel.

With the CTD 25 L we had a problem that bottles could not be closed at depth, the CTD probe functioned normally. During the search to solve this problem the CTD probe and the step motor were exchanged. These proved not to be the cause of the problem. After a lot of searching the problem was located. The cable between CTD and the sea cable had a hole in the covering material, where sea water could enter, this disturbed the signal. Once the cable was replaced the problem was solved.
Since station 15 the altimeter of the CTD 25 L was not functioning properly, a reflection is seen at 5 meters, either it is broken or some material near the altimeter is causing this reflection.

3.1.3 Nutrient Measurements

Jan van Ooijen, Laboratory for Nutrient Analysis,
Royal N.I.O.Z.
Summary

On this cruise samples were analysed on Phosphate, Silicate, Nitrate and Nitrite.

During the cruise there were about 3000 analysis (750 samples) accomplished on a Seal Analytical QuAAtro Autoanalyser connected to an autosampler. The different nutrients were determined colorimetrical as described by Grashoff (1983).

Methods

Samples were obtained from both CTD's, the large volume CTD rosette sampler with 24 bottles of 25 Litre each and the ultra clean CTD with 24 bottles of 27 Litre. All samples were obtained in a polypropylene vial and were unfiltered. The samples were subsampled in a 5 ml polyethylene vial. These vials were all stored dark at 4 °C. All samples were analysed within 24 hours on a QuAAtro autonalyser. As a light source the QuAAtro uses a LED instead of a lamp to avoid the noise effect of the movements of the ship on the light source and therefore on the baseline.

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

In every run a mixed nutrient standard containing silicate, phosphate and nitrate in a constant and well known concentration, a so called cocktail, was measured in duplicate. There was also a duplicate Reference Nutrient Sample (RMNS) containing a known concentration of silicate,

phosphate, nitrate and nitrite analysed in every run. This cocktail and this RMNS were used as a guide to check the performance of the analysis. The RMNS was also used to make a correction at the end of a transect obtaining the final data.

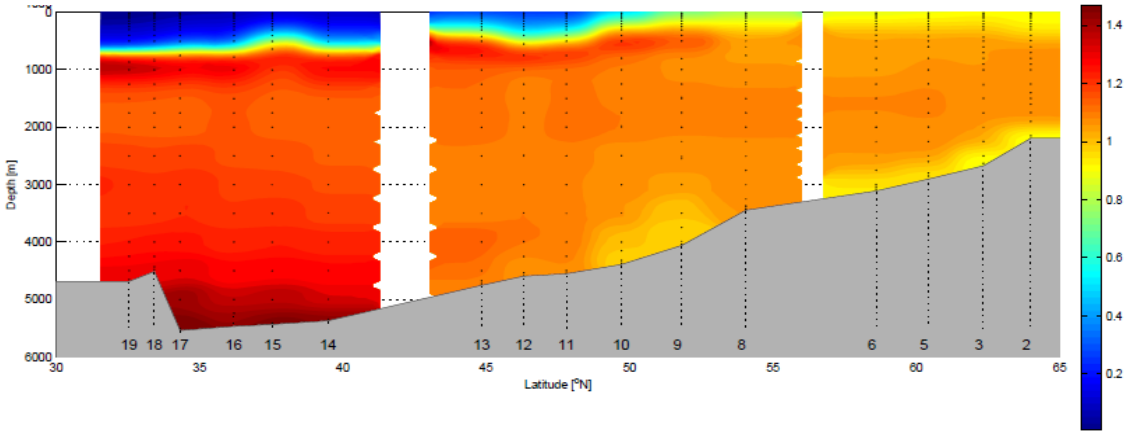

Fig 4: PO_4 in µmol/kg along the transect, stations are indicated

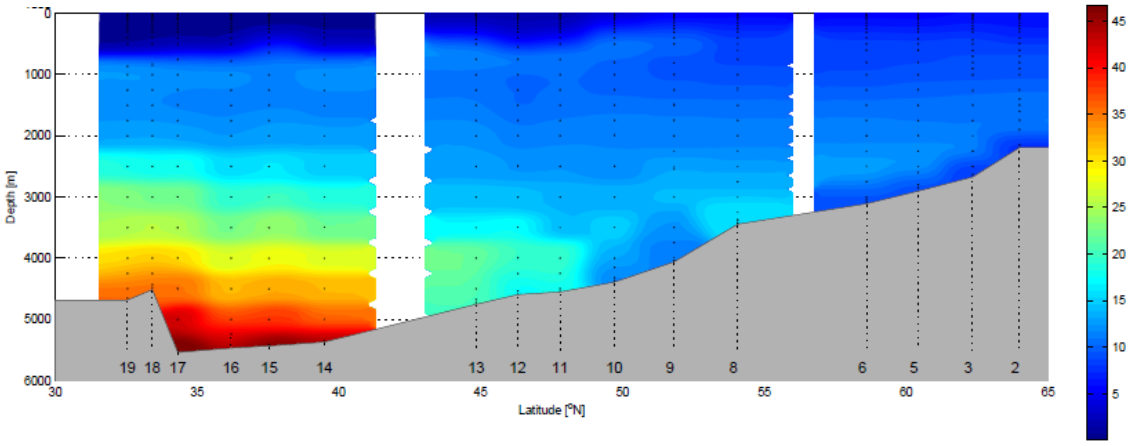

Fig 5: Si in µmol/kg along the transect, stations are indicated

Chemistry:

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

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

Nitrate plus nitrite (NOx) was mixed with a buffer imidazol at pH 7.5 and reduced by a copperized cadmium column to nitrite. This was diazotated with sulphanylamide and naphtylethylenediamine to a pink coloured complex and measured at 550nm.

After subtracting the nitrite value of the nitrite channel the nitrate value was achieved.

Nitrite was diazotated with sulphanylamide and naphtylethylenediamine to a pink coloured complex and measured at 550nm.

Statistics of the analysis of this cruise:

The standard deviation of the analysis of 24 bottles taken from the Ultra Clean CTD analysed in one run:

PO4:	0.006 µM	0.16% of full scale value
Si :	0.084 µM	0.06% of full scale value
NOx:	0.063 µM	0.13% of full scale value
NO2:	0.001 µM	0.05% of full scale value

The standard deviation of reference material between different runs:

PO4:	0.010 µM	0.41% of full scale value
Si :	0.30 µM	0.43% of full scale value
NOx:	0.066 µM	0.22% of full scale value
NO2:	0.0075 µM	0.38% of full scale value

The standard deviation of the samples after correction with RMNS:

PO4:	0.0050 µM	0.20% of full scale value
Si :	0.18 µM	0.26% of full scale value
NOx:	0.085 µM	0.27% of full scale value
NO2:	0.0097 µM	0.48% of full scale value

3.1.4. Dissolved Oxygen

Lesley Salt, Steven van Heuven

Water samples were taken from the large volume 25 L CTD at every station for the determination of concentrations of dissolved oxygen in order to calibrate the CTD sensor of that CTD frame. It is deemed feasible to subsequently calibrate UCC frame against the bottle-calibrated sensor on the 25 L rosette frame. Samples were drawn into volume-calibrated ~120ml Pyrex glass bottles using Tygon tubing, flushing the bottle with at least 3 times its volume. Addition of chemicals was performed immediately afterward, after which glass stoppers were secured in place with an elastic band. The samples were stored underwater and in the dark at 24-25ºC. Analysis of series of circa 35 samples at a time took place at the same temperature.

The determination of the volumetric dissolved oxygen concentration of water samples was performed colourimetrically by measuring the absorbance of iodine at 460nm on a Hitachi U-

1100 Spectrophotometer (see Su-Chen Pai *et al*., Marine Chemistry 41 (1993), 343-351). The spectrophotometer was calibrated using standards of seawater spiked with known amounts of KIO_3 (a stock solution of KIO_3 of concentration 73.344M was used). The R^2 value of the calibration line was never less than 0.99, with an average standard deviation of the residuals between the calibration line and the calibration standards of ±0.7 μmol l^{-1}. The absorbance and the voltage of the photo-cell were recorded manually and oxygen values calculated later, expressed in μmol l^{-1}, for later conversion to μmol kg^{-1} when calibrated salinity values become available.

At each station at least one sample was taken in duplicate. The standard deviation (1 S.D.) of circa 30 replicates was approximately 0.8 µmol l^{-1}, after discarding 5 samples with unacceptable replicate differences of >2 µmol l^{-1}. An improvement in replicate analysis is clearly observed over the course of the cruise, reflecting increasing experience with the slightly temperamental spectrophotometer, as well as more standardized sampling methodology between personnel.

No reference standard exists for the measurement of dissolved oxygen and it is thus difficult to ascertain the accuracy of the analyses, despite the care taken in the preparation of the stock solution of KIO_3. To alleviate this shortcoming, subsamples of a 20-L sample of deep-ocean water, brought to equilibrium with the atmosphere, were analyzed during the subsequent leg of this cruise (i.e., 64PE321). Due to the strongly fluctuating air pressure this exercise could not be performed during 64PE319. Results of this analysis will be available in time for the definitive version of this cruise report.

Subsequent utilization of the bottle oxygen measurements for the calibration of the CTD frames' oxygen sensors will be performed back at NIOZ by Hendrik van Aken.

3.1.5 Dissolved Organic Carbon (DOC) and Fluorescent Organic Matter (FDOM) Sampling

S.R. Gonzalez
NIOZ The Netherlands

Duplicates samples for DOC and FDOM were taken directly from de CTD in each station. For DOC from 10-125 m depth filtered samples were taken (0.7 µm Whatman GF/F filters), whereas unfiltered 20 ml samples were taken from 400 m to the bottom. For FDOM unfiltered 20 ml samples were taken.

After sealing samples were stored at -20 ^{o}C.

3.2 Analyses and Measurements of key parameters

A Metals and isotopes

3.2.A.1 Dissolved Fe

Patrick Laan

Work at sea

Dissolved iron (DFe) concentrations of 17 stations with 24 depths each, were measured directly on board by an automated Flow Injection Analysis (FIA) after a modified method of De Jong et al. 1998. For some selected stations also Fe filtered into three different size fractions were measured directly on board (for details see below section 3.2.A.2). In addition, unfiltered samples from 8 stations were acidified and stored to determine the total Fe concentrations in the NIOZ laboratory after 6-12 months of dissolution.

Filtered (0.2μm) 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 on the NBP0901 cruise ranged from 33 pM in the oligotrophic surface waters up to 1.5 nM nM in the deep water. The standard deviation varied between 0% and 20% (the latter being exceptional), but was on average 2.7% and generally < 5% in samples with DFe concentrations higher than 0.1nM. Since samples containing less than 0.06nM DFe values are near the detection limit of the system; the standard deviation of these measurements were higher than the average value.
The average blank was determined at 0.012nM±0.090nM and was defined as a sample loaded for 5 seconds and measured daily. The average limit of detection,0.009nM±0.008nM and was defined as 3*standard deviation of the mean blank and measured daily. To better understand the day to day variation duplicate sample bottles were measured at least 24h later as a so called profile check. The differences between these measurements were rather large, in the order of 5-20%, 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 was measured daily. All data will be corrected for the mean average of this value after the cruise and all data presented so far are 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. The drift was observed to be less than 7% per run and no corrections have been made for this drift. A certified SAFe standard (Johnson et al. 2007) for the long term consistency and absolute accuracy was measured at a regular basis.

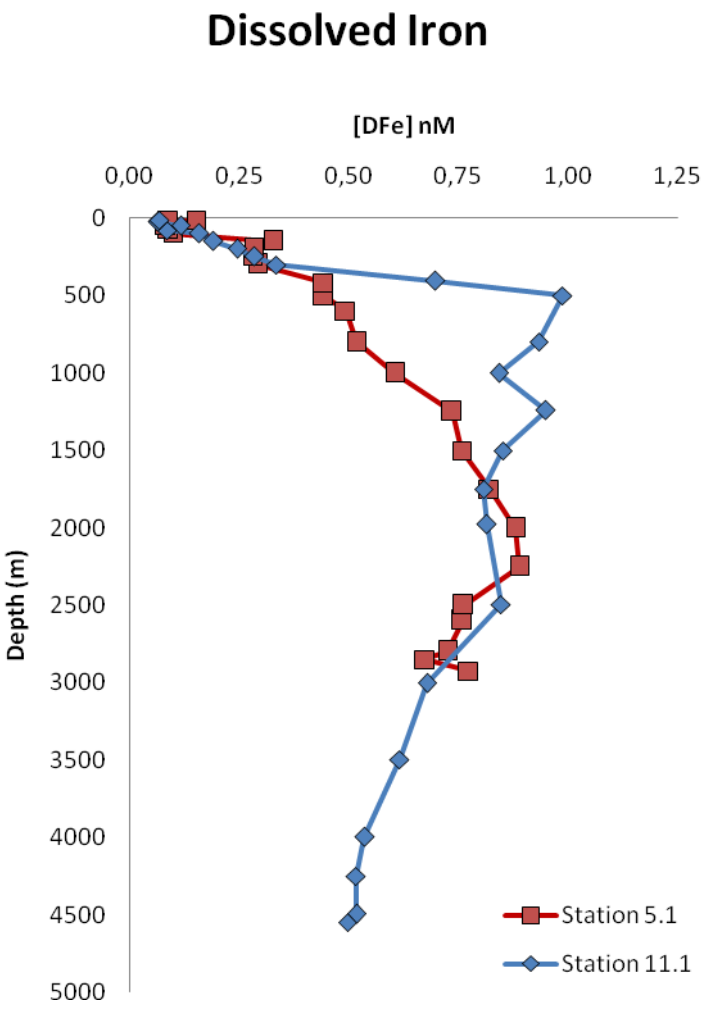

Figure 6: depth profiles of dissolved iron versus depth.

Preliminary results

The profile from station 5.1 in the northern part of the cruise, shows a nutrient type of iron profile. Low surface values and increasing values with depth. Station 11.1 shows a clear subsurface maximum in the profile. This subsurface maximum correspond with the oxygen minimum zone which is clearly seen during the southern part of the transect but is absent in the northern part.

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3.2.A.2 Size fractionation of iron

Micha J.A. Rijkenberg, Loes J.A. Gerringa, Patrick Laan

Introduction.

Iron (Fe) is a critical nutrient for the primary productivity in the ocean. It's an important element in many proteins, enzymes and pigments. Due to its low solubility, Fe limits phytoplankton growth in large parts of the ocean (Martin and Fitzwater, 1988; de Baar et al. 1990). Notwithstanding its low solubility concentrations of dissolved Fe (DFe, < 0.2 μm) are higher than predicted by its solubility product only and vary widely over the water column and across the surface ocean. This variation in DFe concentrations can be explained by i) the chemistry of Fe in the dissolved phase, ii) the proximity of Fe sources, and iii) biological processes (e.g. high DFe at the oxygen minimum).

DFe consists of several distinguishable and measurable fractions such as a truly soluble Fe fraction (Fe(III) and Fe(II)), a truly soluble organically complexed Fe fraction and a colloidal Fe fraction. These different size fractions are often defined by the pore size of the filters and may vary with study.

We used size fractionation (filters with 0.2 μm, 0.1 μm, 0.02 μm and 1000 kDa pore size) to investigate the distribution of the different size fractions of Fe over the water column, the interplay between these fractions, and the relation between relative differences in Fe concentration of the size fractions and environmental parameters such as the excess organic Fe-binding ligand concentration, oxygen etc.

Materials and methods.

Filtered seawater (0.2 μm, Sartobran 300 cartridges) samples of different depths, representing the entire water column, were sampled from the ultraclean titanium CTD (de Baar et al. 2008). Two types of filters were used for further size fractionation, namely 0.02 and 0.1 μm Anotop alumina syringe filters and 1000 kDa hollow fiber filters (Mitsubishi). Using a pump speed of 1 ml/min, the 0.02 and 0.1 μm Anotop alumina syringe filters were cleaned with 30

ml 0.1% HCl (Merck, Suprapur), 60 ml MQ (de-ionized ultrapure water; < 18.2 MΩ) and 60 ml of sample before sample collection (Ussher et al. 2010). The 1000 kDa hollow fibre filters were pre-cleaned in the home laboratory with 10 ml quartz-distilled HCl (5 ml/min), 10 ml MQ water (5 ml/min), 60 ml HCl (Merck, suprapur) (20 ml/day), 210 ml MQ water (7 ml/min) followed by storage in 0.025% HCl (Merck, suprapur) until use. Before use the 1000 kDa hollow fibre filters were cleaned with 210 ml 0.05% HCl (Merck, suprapur) (7 ml/min), 210 ml MQ water (7 ml/min) and 210 ml sample (7 ml/min) before sample collection. Samples filtered with the 0.02 and 0.1 Anotop alumina syringe filters were only measured for DFe (see cruise report of Patrick Laan) while samples filtered with 1000 kDa hollow fibre filters were measured for DFe and organic Fe-binding ligand concentration (FeL).

Samples for ultra filtration

Samples for ultra filtration were taken during a transect south of Iceland (Table 1) and at hyperstations (Table 2).

Table 1) Surface samples taken from the fish during a transect south of Iceland

Operation ID[1]	Code	date	time (UTC)	filter	sampled for
319_FISH1	ICE1	30/04/2010	16:00	0.02 & 0.01 µm	DFe
319_FISH1	ICE1	30/04/2010	16:00	1000 kDa	DFe & FeL
319_FISH1	ICE7	01/05/2010	10:00	0.02 & 0.01 µm	DFe
319_FISH1	ICE7	01/05/2010	10:00	1000 kDa	DFe & FeL
319_FISH1	ICE9	01/05/2010	16:00	0.02 & 0.01 µm	DFe
319_FISH1	ICE9	01/05/2010	16:00	1000 kDa	DFe & FeL

[1] Operation ID of the station book

Table 2) Water column samples taken from the ultraclean titanium CTD Rosette at hyperstations

station	cast	Bottles	filter	sampled for
2	1	1, 2, 4, 6, 8, 9, 11, 14, 16, 20, 22, 24	0.02 & 0.01 μm	DFe
2	1	1, 2, 4, 6, 8, 9, 11, 14, 16, 20, 22, 24	1000 kDa	DFe & FeL
8	1	1, 2, 4, 6, 8, 10, 12, 13, 14, 16, 18, 20, 22, 24	0.02 & 0.01 μm	DFe
8	1	1, 2, 4, 6, 8, 10, 12, 13, 14, 16, 18, 20, 22, 24	1000 kDa	DFe & FeL
11	1	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24[1]	0.02 & 0.01 μm	DFe
11	1	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24	1000 kDa	DFe & FeL
15	2	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24[1]	0.02 & 0.01 μm	DFe
15	2	2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, 24	1000 kDa	DFe & FeL

[1] due to a lack of filters 1 or 2 samples were not size fractionated using 0.1 μm Anotop syringe filters

Results

Results are not yet available.

Acknowledgements.

We want to thank Charles-Edouard Thuróczy, Maarten Klunder and Rob Middag for all their help in the preparations for the cruise.

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3.2.A.3 Organic speciation of Fe

Loes Gerringa, Micha Rijkenberg and Patrick Laan

Objectives

The distribution and biological availability of Fe is strongly controlled by its physical-chemical speciation within seawater, where colloids and Fe-organic complexes are dominant factors. In order to study the distribution chemical species of Fe over the whole water depth the chemical speciation is determined in two different size fractions, the filtered <0.2 μm and the <1000kDa fractions. Special attention was given that distinct water masses present were sampled as well.

Samples were collected by the UC CTD in stations 2, 5, 8, 11, 14 and 15 and during the transit Scrabster –station 2 by the fish in three profiles ICE 2, ICE 7 and ICE 9 (see also: 3.2.A.2: Size fractionation of iron) .

Method

The analysis is so time consuming that not all analyses could be executed within the time limits of the cruise. The fraction <0.2 μm was analysed on board, the fraction <1000kDa was frozen after ultra filtration and will be analyzed in the NIOZ home laboratory. It was chosen to analyse the largest fraction, since in the finest fraction the chances that freezing disturbs and breaks colloidal particles or bacteria is smallest.

The natural ligand characteristics were determined by doing a complexing ligand titration with addition of iron (between 0 and 8 nM of Fe added) in buffered seawater (mixed NH_3/NH_4OH borate buffer, 5 mM). The competing ligand 'TAC' (2-(2-Thiazolylazo)-p-cresol) 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) was converted as a

concentration (nM), then the ligand concentration and the binding strength were estimated using the non-linear regression of the Langmuir isotherm (Gerringa and al., 1995).

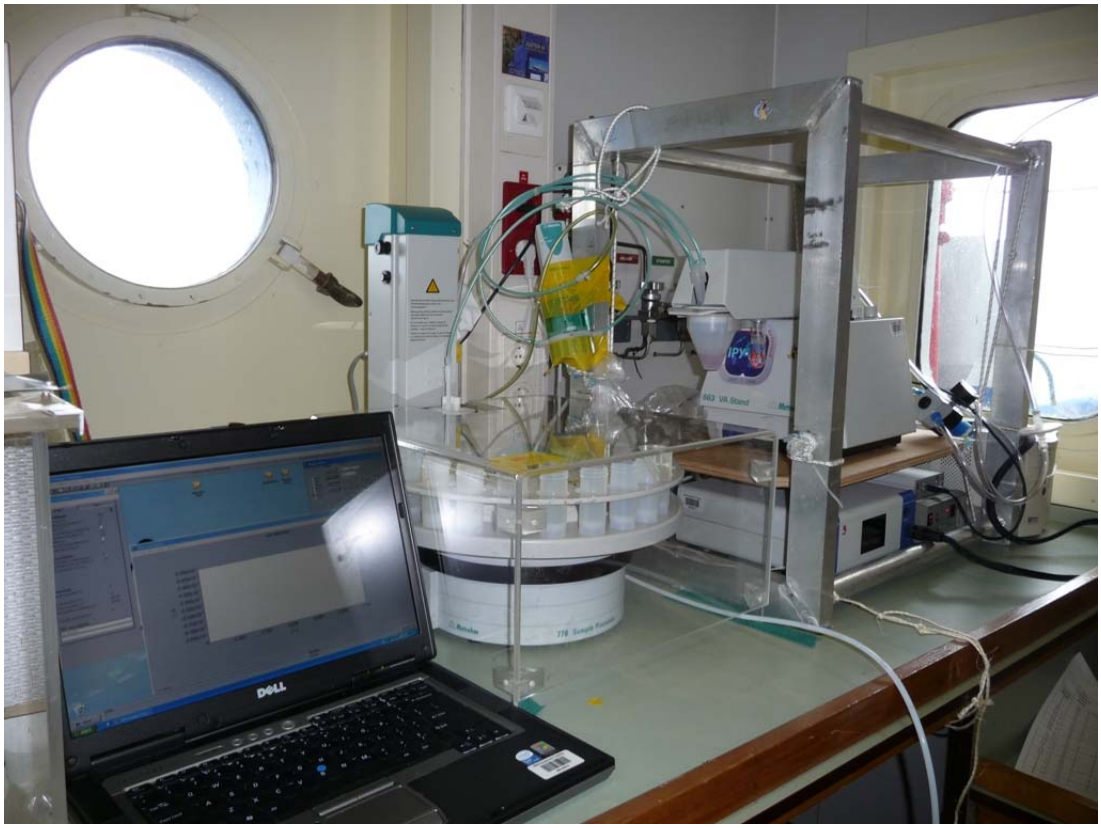

Figure 7: The voltammetric equipment with in front the sample changer. The electrode stand is mounted in a NIOZ home-made aluminium frame on a wooden board that is hanging in elastic bands, preventing scans to be disturbed by motions of the ship.

The voltammetric equipment consisted of a µAutolab potentiostat (Type II and III, Ecochemie, The Netherlands), a mercury drop electrode (model VA 663 from Metrohm) and a brand new sample changer . All equipment was protected against electrical noise by a current filter (Fortress 750, Best Power).

Results

All samples <0.2 µm were analysed (see figure 8), but not yet calculated into the proper parameters : the ligand concentration and the conditional binding constant.

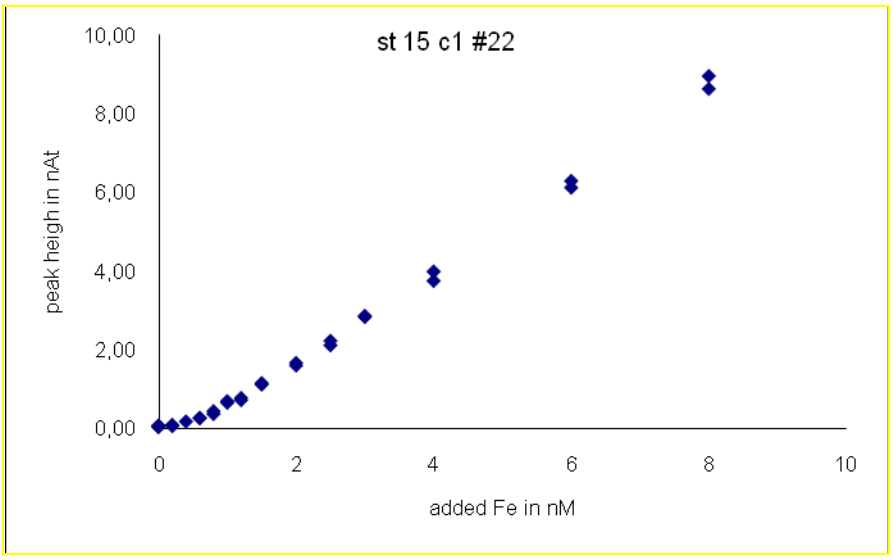

Figure 8: An example of a titration, on the horizontal axis the added Fe concentration, on the vertical axis the peak height in nA.

References:

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3.2.A.4 Dissolved Al and Mn

Rob Middag

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 build 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., in press a).

Dissolved Mn is a trace metal with a scavenged-type distribution due the formation of insoluble oxides in oxygenated sea water and the distribution of Mn is strongly influenced by external inputs. Dissolved Mn can be a tracer of hydrothermal sources and of reducing sediment input. Like dissolved Al, the distribution of dissolved Mn can potentially provide insight into Fe inputs as Mn and Fe can come from the same sources. Dissolved Mn is a trace nutrient that has been suggested to become quite important for phytoplankton (especially diatoms) under low Fe conditions (Peers and Price, 2004; Middag et al., in press b).

Work at sea

Dissolved Al and dissolved Mn were measured directly 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 and 8.5 for Al and Mn, respectively. The metals are concentrated on a column which contains the column 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.

The Al is determined using lumogallion after Brown and Bruland (2008). Lumogallion is a fluorometric agent and reacts with aluminium. 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 25 litre tank that was filled 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, SAFe and GEOTRACES seawater samples were analysed daily and the values are consistent with those found previously.

The Mn is detected using the chemo luminescence method of Doi et al. 2004. The oxidation of luminol by hydrogen peroxide produces a blue light. This oxidation reaction is catalyzed by manganese and the increase in the production of blue light is detected by a photon counter and used as a measure for the dissolved Mn concentration.

Also for Mn similar consistency checks as for Al have been performed with samples from the 25 litre tank and duplicate samples. Also SAFe and GEOTRACES seawater was analysed

which was consistent with the values found previously. The daily consistency of the system was verified using a so-called drift standard.

Preliminary results

Concentrations of Al were low in the northern surface waters (~ 1 nM) and increased in the southward direction to values up to ~18 nM. With increasing depth the concentrations of Al increased above 30 nM (see Figure 8). In the southern part the deep Al concentrations were lower (~25 nM). A subsurface maximum was observed in the southern part of the transect between 200 and 500 meter depth.

Concentrations of Mn were also lower in the northern surface water compare to the southern part of the transect, but the increase from 0.5 nM to around 0.7 nM Mn was only minor compared to Al. With depth the concentrations of Mn decreased to low concentrations in the deep basin (see Figure 8). In the northern part the concentrations were with ~0.3 nM higher than the concentrations of ~0.1 nM observed in the southern part of the transect.

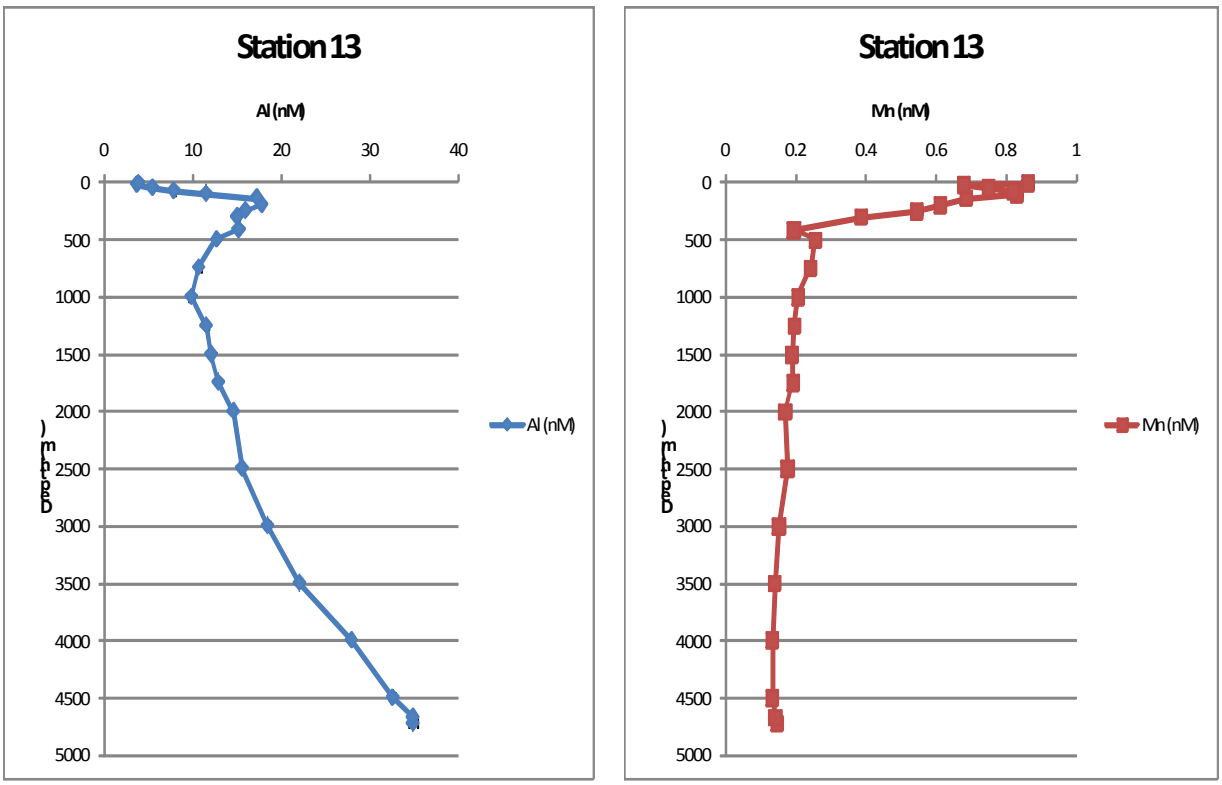

Figure 8: Dissolved Al (nM) (left) and dissolved Mn (nM) (right) versus depth (m) at station 13. Error bars (hardly visible) represent standard deviation of triplicate measurement.

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3.2.A.5 Trace Metal and major Ion Input by Aerosols

Rob Middag

The input of air blown dust particles (aerosols) into surface waters will be assessed by collection of marine aerosols in combination with a settling model and estimation of partial dissolution of aerosol components into surface seawater. Shipboard collection of the aerosols was done by Patrick Schmidt and Rob Middag. This project is in collaboration with Dr. Alex Baker (University of East Anglia), relying on his expertise and equipment and he'll analyse the aerosols for trace metals in his laboratory. There is a close link with the distributions of Al in surface waters as they are determined as independent tracer for aerosol input.

Work at sea

Every 24 hours a new filter was placed in the aerosol collector. Unfortunately some sampling days were lost due adverse weather conditions and the breaking down of one engine of the aerosol collector which had to be replaced. In total 21 trace metal and 23 major ion filters were collected.

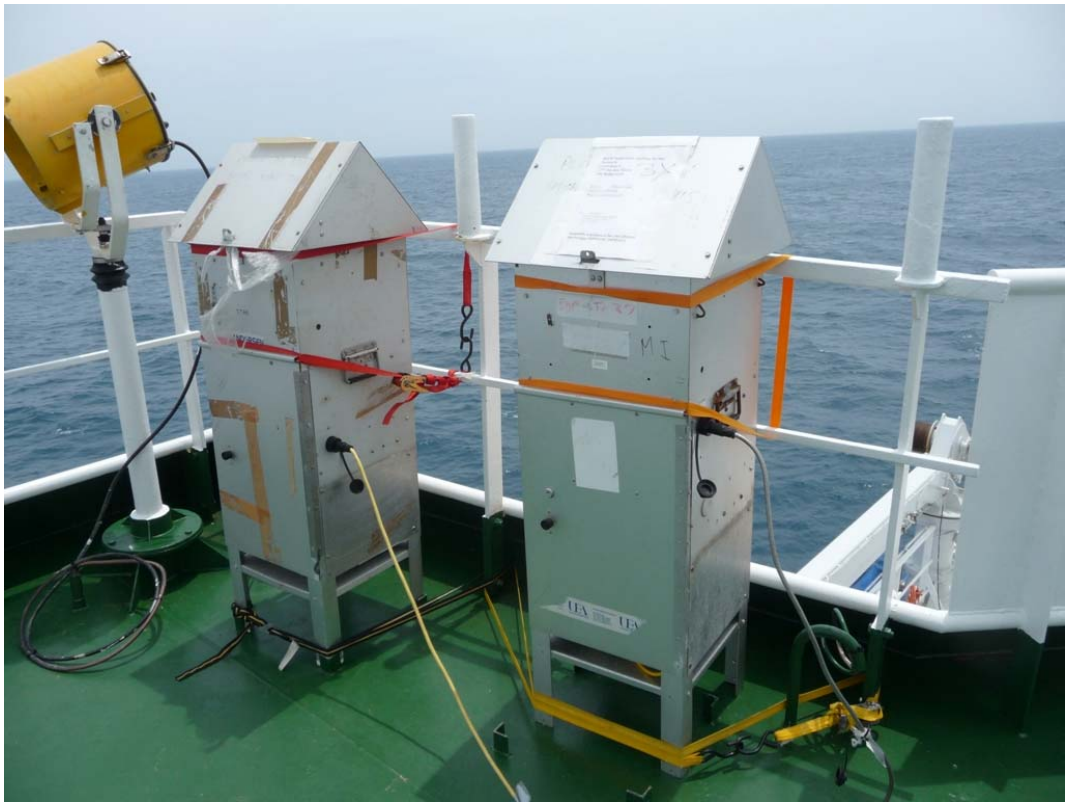

Figure 9: The aerosol collectors on top of the bridge of Pelagia

Preliminary results

Results will not be available till the filters have been transported to the University of East Anglia and analysed over there. The filters will stay on Pelagia till Texel in a -20 ° freezer.

3.2.A.6 Iron (Fe), zinc (Zn) and their stable isotopes in seawater of the western North Atlantic.

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Introduction

The availability of bio-active trace metals such as Fe, Zn, Co, Cu and Mn may limit primary productivity and the associated uptake of carbon over large areas of the ocean. They play hence an important role in the carbon cycle, and changes in its supply to the surface ocean may have had a significant effect on atmospheric carbon dioxide concentrations over glacial–interglacial cycles (Martin, 1990).

Since recent years a continuing scientific effort was initiated by the development of sensitive multicollector ICP-MS and TIMS techniques to expand isotope geochemistry research into the oceanic realm. Apart from the traditional isotopic systems (e.g. Pb, Nd, Sr and Hf) also the so-called non-traditional isotopes receive increased attention, in particular Li, B, Mg, Si, Ca, Fe, Cu, Zn, Mo and Cd. The idea is that biogeochemical processes in the ocean interior leave distinct isotopic signatures, which may provide a means of tracking these processes. The first ocean profiles for Fe (Lacan et al. 2008), Cu and Zn (Bermin et al. 2006) were recently published.

During the GEOTRACES Western Atlantic cruise leg 1 (64PE319) with RV *Pelagia*, samples were taken to study the evolution in the distribution and behaviour of iron, zinc and their isotopes in seawater along a transect in the western North Atlantic. On a north-south transect crossing the Denmark Strait, Irminger Sea, Labrador Sea and the western Atlantic basin, four full water column profiles were sampled for iron, copper and zinc concentration measurement to provide new data for this ocean region for which only very few data exist. By measuring iron and zinc isotopic compositions at six selected depths of each of these four stations, we hope to shed some light on isotopic signatures of biological processes e.g. autotrophic/heterotrophic uptake and remineralization; or a-biologic processes such as physico-chemically driven dissolution/precipitation processes associated with atmospheric input, organic complexation, oxygen minimum, sediment release. This sampling was coordinated with that for Cd isotopes by Wafa Abouchami (University of Mainz). Our sampling effort will be continued on leg 2 from Bermuda to Fortaleza (Brazil), cruise 64PE321.

Sampling for total metal concentration measurement.

Prior to our arrival at the first station in the Denmark Strait we carried out underway surface sampling for total dissolvable (unfiltered) and dissolved (filtered) Fe, Cu and Zn concentrations on a latitudinal transect south of Iceland by means of a towed ‘fish’, connected with braided PVC tubing to a PTFE bellows pump and a Sartorius Sartobran 300 filter cartridge of 0.2 µm pore size. We hope to find an atmospheric input signal from the recently erupted and at the time of writing still active volcano under the Eyjafjallajökull glacier on Iceland.

Water column samples were collected at four stations (2, 8,11 and 15) with the NIOZ ‘Titan’ ultraclean CTD (‘UCC’) (De Baar et al. 2008), equipped with a Seabird CTD package,

oxygen sensor, fluorimeter and transmissiometer. Samplers were 24 PVDF tubes of 27L of a completely new design with piston controlled externally closable end caps.

Inside a class 100 clean air van, 250 mL sub-samples for total dissolvable (unfiltered) and dissolved (filtered) iron, copper and zinc concentrations were collected from each UCC sampler. The filtration was carried out with Sartorius Sartobran P filtration cartridges of 0.2 µm pore size.

All samples were acidified to pH = 1.9 (1mL acid per litre of sample) with sub boiling (Analab) double-distilled ultrapure 14M nitric acid (HNO_3).

Sampling for iron isotopic ratio measurement

Seawater samples were directly filtered from the UCC samplers through 0.2 mm pore size 142mm diameter polycarbonate membrane filter in polycarbonate filtration units (GeoTech) in 20L Nalgene low density polyethylene carboys using about 0.5-1 bar N_2 overpressure. The filtrate was acidified to pH 1.9 and the filters stored at -20 °C.

Analytical methods

Total metal concentrations. Fe, Cu and Zn concentrations will be measured in the home laboratory at ULB by multi-spike isotope dilution multi-collector inductively coupled mass spectrometry (MC-ICP-MS) using a Nu Plasma mass spectrometer. To this end, samples are amended with pure Fe-54, Cu-65 and Zn-67 spikes prior to simultaneous pre-concentration/separation on a resin with the NTA functional group (Lohan et al. 2005, de Jong et al. 2008).

Fe and Zn isotopic ratio measurement. Using the same Nu Plasma mass spectrometer, iron and zinc isotopic compositions of the dissolved phase will be measured after a newly developed lanthanum hydroxide co-precipitation technique (de Jong et al. in prep.), followed by purification of the sample by ion exchange chromatography with the BioRad AG-MP1 anion exchange resin. For the determination of the Fe and Zn isotopic compositions of particulate matter, the filters will be acid-digested in a nitric acid/hydrofluoric acid/hydrogen peroxide digestion, and purified with the aforementioned resin as well. (de Jong et al. 2007).

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3.2.A.7 Natural and anthropogenic radionuclides.

Viena Puigcorbe, Merce Bermejo, Sven Kretschmer, Michiel Rutgers van der Loeff

Objectives:

The geochemistry group collected samples for analysis of a suite of natural and anthropogenic radionuclides.

Natural radionuclides:

The nuclide pairs $^{234}Th/^{238}U$ and $^{210}Po/^{210}Pb$ provide information on export production. In a closed system, a radioactive isotope should be in secular equilibrium with its progeny, but if the parent is soluble and its decay products are particle-reactive, then they can be removed by uptake by particles and the reactive daughter nuclide will be deficient in seawater relative to the concentration of its parent. Disequilibria among the activities of these tracer pairs indicate exportation to deeper waters and these disequilibria can be used to derive the flux of particles that are removed from the surface layer on time scales of weeks (half life of ^{234}Th: 24 days) to months (half life ^{210}Po: 138 days).

Figure 9: Sampling of the radionuclides was quite a job, here some of the different sample bottles at the foot of Merce Bermejo (including the big blue ones, yes!)

^{231}Pa and ^{230}Th are produced at a fixed activity ratio throughout the water column. As a result of a difference in particle reactivity, ^{231}Pa is carried further by ocean currents before it is removed by scavenging than ^{230}Th. It is therefore hoped that ^{231}Pa/^{230}Th ratios in sediments can be used to reconstruct deep water ventilation but this application is presently intensively debated because of the possible influence of other factors like particle rain rate and particle composition. The deep water formation area we visit in this cruise is the area where we have most chance that the effect of deep water ventilation can be distinguished. We therefore determined the distribution of the isotopes in the water column (sampled with the regular Rosette) and in suspended particles (sampled with the in situ pumps). Moreover we collected subsamples from the suspended matter (punched from the filters) for the determination of carbonate and biogenic silica. After digestion of the filters and during the isotope separation by ion exchange we envisage to collect a fraction containing Nd for isotope determination by the group of Tina van de Flierdt.

^{228}Ra is a tracer that is produced in sediments and is released into the ocean both in shallow shelf sediments and in the deep sea. ^{227}Ac is also released by sediments, but primarily from the deep sea while the shelf source is small. ^{227}Ac is therefore a tracer for deep upwelling and diapycnal mixing in deep waters. Worldwide the amount of profiles where this isotope has been measured is very low. At three stations we have collected samples for the analysis of ^{228}Ra and ^{227}Ac by passing 60-120L of water through MnO_2 coated acrylic fibre. Moreover

we have equipped the in situ pumps with a MnO_2-coated cartridge in order to collect radium isotopes. This technique is not quantitative but is used here to determine the $^{228}Ra/^{226}Ra$ ratio.

Anthropogenic radionuclide's: Pu, Cs, Np and I.

Viena Puigcorbe, Merce Bermejo, Pere Masque, Tim Kenna

The anthropogenic radionuclide's ^{137}Cs, ^{239}Pu, ^{240}Pu, ^{237}Np and ^{139}I have been introduced to the oceans primarily as a result of atmospheric and surface testing of nuclear weapons in the late 1950's and early 1960's and also through the discharge of nuclear wastes into the sea or by nuclear accidents. The isotopes of interest, in addition to being transient tracers, exhibit a range of Kd values (sediment water distribution coefficients, Pu>Np, Cs), and geochemical behaviours as well as provide a means to resolve different sources of radioactive contamination. This will allow us to address processes such as advection (new water mass tracers), determine sources and sinks (characteristic isotopic signatures), as well as study processes related to scavenging and particle dynamics across a range of contrasting regions.

By comparing radionuclide distributions, isotopic composition, inventories, and inventory ratios of particle reactive (Pu) to conservative (Cs and Np) elements, we will learn first order information about rates of scavenging and transport of these nuclides that is complementary to that gained through the study of other trace elements and their isotopes.

Work at Sea:

Unfortunately, a misunderstanding caused the sampling at Denmark Strait for ^{227}Ac, ^{228}Ra and anthropogenic radionuclides to be different from the schedule. During the fourth Rosette cast three bottles were designed to be closed on the same depth to obtain large volume samples for these isotopes. Instead, bottles were closed on this fourth cast according to the normal schedule with one bottle per depth. As a result, ^{227}Ac, Cs, Pu and ^{228}Ra were sampled as mixed (depth) samples. The important sampling of the Denmark Street Overflow Water (DSOW) was therefore not done as scheduled. For ^{228}Ra we have a backup because we can use the $^{228}Ra/^{226}Ra$ ratios to be obtained from the cartridges mounted in the in situ pumps. For Cs and Pu there is also a backup because duplicate samples have been taken for Tim Kenna. This duplication was meant for a comparison of Cs results between Barcelona (Pere Masque) and Lamont (Tim Kenna) and is now based on the other hyperstations. Sampling of ^{227}Ac in DSOW is not done and although not a priority parameter, this is regretted.

$^{234}Th/^{238}U$ and $^{210}Po/^{210}Pb$:

Viena Puigcorbe, Merce Bermejo, Michiel Rutgers van der Loeff

Total ^{234}Th

The water samples were analysed following the procedures of Buesseler et al. (2001) as adapted by Cai et al., (2006) but omitting the heating step.

From ten depths along the profile, 4L samples were collected and acidified with 5mL of nitric acid (65%). A ^{230}Th spike was added and after that we waited 12h for the equilibration before we raised the pH to 8.5 adding ammonia and produced a MnO_2 precipitate through the addition of $KMnO_4$ and $MnCl_2$.

We used QMA filters to retain the precipitate. At the beginning of the cruise the vacuum system was not working properly so the filtrations took more than a day to complete. When the problem was fixed the filtration per sample took on the average 3h.

The filters were dried and prepared for beta counting putting a piece of plastic foil in contact with the sample and above that a piece of Al foil to block the lower energetic beta radiation. Having done that, their beta activity was measured in a RISØ beta counter.

At station 10 we collected 5 deep samples (1750m) in order to be able to do the calibration. At this depth ^{234}Th and ^{238}U should be in secular equilibrium, that means that both isotopes have the same activity. The expected ^{234}Th activity is then given by the known activity of its parent ^{238}U.

<u>POC/^{234}Th ratios</u>.

For the determination of the POC/^{234}Th ratio on sinking particles we collected >50 µm particles at the export depth of 100 m on all deployments of the in situ pumps (see section on ISP). The amount of particles collected was highly variable. At station 2 it was not visible with the naked eye, at station 6 there was a thick green algae cover, whereas at station 11 the material looked much more like greyish detritus. At this latter station, sampled at night, we had seen abundant life at the surface with medusae, fish, squids, birds.

The material was washed off the screen with filtered seawater and an aliquot was filtered over a 1.2 µm silver filter. Moreover, at selected stations we filtered 4-8L samples from the 25L Niskin Rosette (25L CTD) from 100-150m depth over combusted QMA or silver filters for the determination of POC/^{234}Th on the total suspended material. Filters were beta counted on board for ^{234}Th. POC will be determined later in the home laboratory.

<u>Total ^{210}Po/^{210}Pb</u>

Recent studies like Stewart *et al.* (2007) and Verdeny *et al.* (2008) combine the use of ^{234}Th/^{238}U with these two tracers to study the POC export. The combined use of both tracer pairs can give us a more robust approach to study the particle settling along the water column.

We collected 6 profiles of 6 depths each. The depths were the same as used for the analysis of ^{234}Th in order to be able to compare both results. Each sample was collected in 3 bottles of 3L (9L is the total volume per sample) and, after tapping the water, each subsample was acidified with 6mL of hydrochloric acid (32%).

The samples were stored until the arrival to Bermuda where they were transferred to 10L cubitainers. Later processing steps will be realized at BIOS during the two weeks before the second leg (cruise number 64PE321) and Tom Church, from the University of Delaware, will measure them by alpha spectrometry.

^{231}Pa and ^{230}Th

Sven Kretschmer, Merce Bermejo, Michiel Rutgers van der Loeff

Dissolved ^{231}Pa and ^{230}Th

Samples for dissolved ^{231}Pa and ^{230}Th were collected at 7 stations from the 25L CTD. At each station we sampled 7-10 water depths, 20L each. Samples were filtered through supor filters (142 mm, 0.45 µm). Before using the supor filters we have cleaned them by soaking in hydrochloric acid (10 %, double distilled quality) for 24 h and rinsing them 6 times with Milli-Q water. The filtrate was collected in an acid cleaned canister. Samples were acidified to pH 2 by addition of 20 mL nitric acid (65 %, double distilled quality). Samples were packed in plastic bags and cardboard boxes and stored in the container on deck of RV Pelagia until arrival at home. At the home lab samples will be spiked with internal standards ^{233}Pa and ^{229}Th, and extraction of Pa and Th from the dissolved phase will be done by iron co-precipitation. Chemical separation and purification of Pa and Th will be done by column chromatography. Pa and Th isotopes will be analysed on a ICP-mass spectrometer.

Particulate ^{231}Pa and ^{230}Th : In -situ pumps

For the collection of particulate matter we have deployed in situ pumps at 6 stations. 6 pumps were equipped with 142 mm 0.8 µm supor filters and distributed over the entire water column. The deepest pump was deployed in the nepheloid layer, approx. 50 m above the seafloor. At all stations this sample contained visibly more particles and a higher ^{234}Th activity (see preliminary results).
A 7th pump was equipped with a 293 mm diameter 50 µm screen and deployed at 100m. This sample was used only for the determination of the POC/^{234}Th ratio of large sinking particles (see section on ^{234}Th).
The electronics of the pumps turned out to be very sensitive to moisture in the pump container positioned on deck. Original malfunctions were corrected by installing a 1.5 kW heater in the container and by cleaning and repair of corroded spots on the timer board prints by Martin Laan.
At the beginning of the cruise leg, the supor filters (142 mm, 0.8 µm) were cleaned by soaking them in an acid bath (10 % HCl, double distilled quality) for 24 h and rinsing them 6 times with Milli-Q water. Each in-situ pump is equipped with one filter head containing one 0.8 µm supor filter. The programmed pumping duration was 2.5 h. The volume of water that L (with 0.8 µm filter) and about 1900 L (with 50 µm screen). Out of 42 deployments, four failed due to corroded spots on the timer board, and one due to a broken supor filter and a leaking tube connection. After deployment and recovery on deck the filter heads were disassembled from the in-situ pumps and taken to the lab. Before opening the filter head, the remaining water on the supor filter was sucked off with a water jet pump. Then the supor filter was taken out from the filter head. Four subsamples were taken from each filter. To

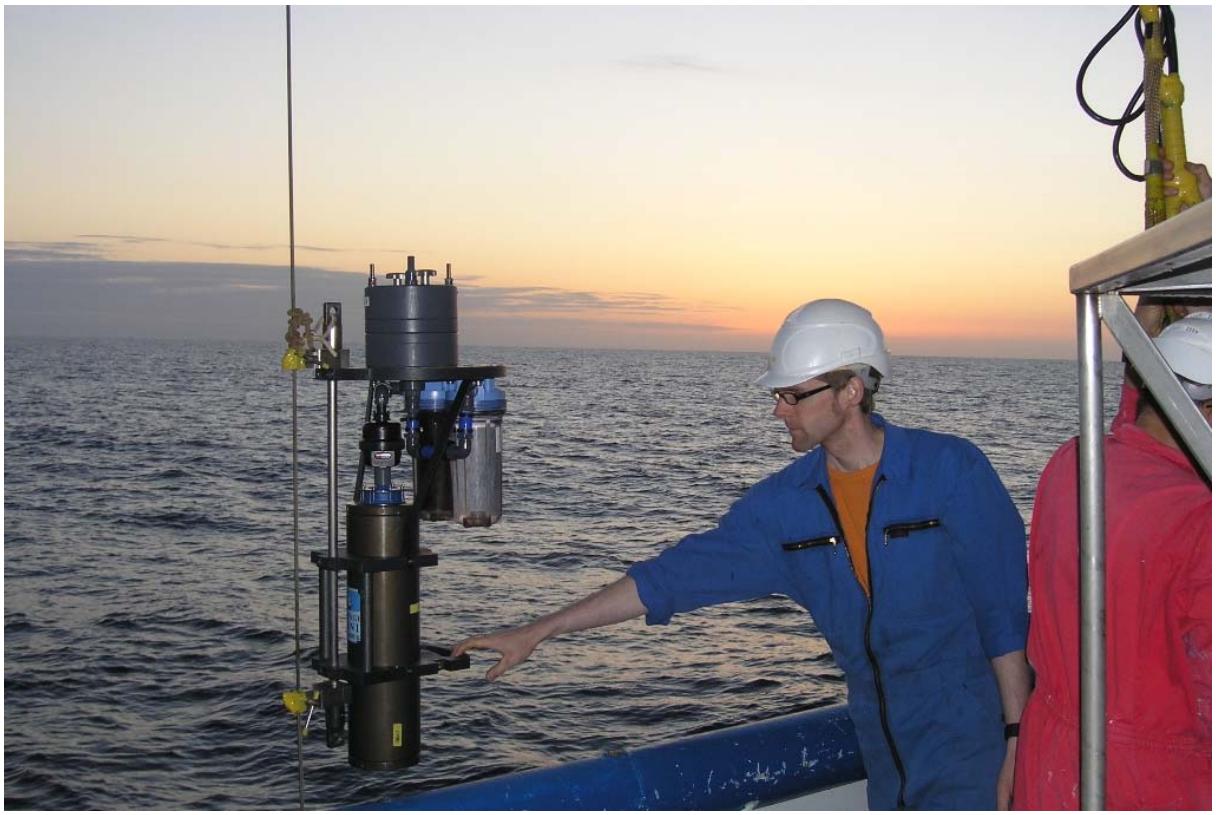

Figure 11: In situ pump is lowered into the ocean with a helping hand of Sven Kreschmer.

avoid contamination the sub sampling work was done under a laminar flow bench. A triangle-shaped section (1/6th of the filter size) was cut out; then three subsamples (each 22 mm or 23 mm diameter) were punched out from this filter triangle. The three small subsamples are meant for analysis of opal and carbonate concentrations (analysis at home lab) and for ^{234}Th activity (analysis on board by counting the beta decay). The remaining 5/6th of the filter is for analysis of particulate ^{231}Pa, ^{230}Th and Nd isotopes. They are stored at 5°C. At the home lab the filters will be acid digested and ^{231}Pa and ^{230}Th will be analysed by isotope dilution as described in the previous section for dissolved samples.

^{228}Ra and ^{227}Ac:

Viena Puigcorbe, Merce Bermejo, Michiel Rutgers van der Loeff

At all deployments of the in situ pumps, we have used one MnO_2-coated cartridge in each pump for the determination of the ^{228}Ra/^{226}Ra ratio. For ^{226}Ra analysis by $BaSO_4$-coprecipitation a profile of 6 20-L samples was sampled at station 16. At 3 “hyper”stations (2,11,15) we have collected large volume samples, varying from 75L at great depths to 125L at shallow depths with the Niskin Rosette. Due to a misunderstanding the large-volume sampling at station 2 (Denmark Strait) was effectively made as mixed sampling over 3-5

depths. In addition, we collected at these stations a 120L surface water sample from the ship's seawater supply. The water was passed over MnO_2 coated acrylic fibre to adsorb radium and actinium. These samples will be analysed for Ra isotopes and Ac by delayed coincidence counting and alpha and gamma spectroscopy in the home laboratories. The effluent of the fibre was used for analysis of anthropogenic radionuclides.

Anthropogenic radionuclide's:

Viena Puigcorbe, Merce Bermejo

^{239,240}Pu, ^{137}Cs and ^{237}Np

We collected 20L of unfiltered seawater samples for the analysis of these radionuclide's at 4 stations (2, 9, 15 and 18), 10 depths per profile. The depths were distributed over the water column.

The samples were acidified with 60mL of ultrapure hydrochloric acid 6M and stored until the arrival to Bermuda where they will be sent to Columbia University where Tim Kenna is going to analyse them.

^{129}I

In order to analyse this anthropogenic radionuclide, 3L of water were collected at 10 depths over the water column at 4 stations (2, 9, 15 and 18). The samples were stored without acidifying them.

^{137}Cs

The water used for the analysis of ^{137}Cs at UAB (Barcelona) was the effluent of the fibre used to retain Ra and Ac isotopes (explained above). These samples were collected at 3 "hyper" stations (2, 11 and 15). The volume of the three sallower samples was 100L whereas 60L was used for the 4 deeper ones. We had to deploy 2 CTD 25L casts in order to have enough water to do a 6 depths profile. As mentioned above, we also collected surface water (120L) from the ship's seawater supply.

The samples were acidified using 10mL of nitric acid (65%) per L of sample and a spike of stable Cs was added. After 12h to let the sample equilibrate, we added ~30g of AMP (ammonium molybdophosphate) and stirred well with a Teflon rod. The Cs- AMP complex precipitated (~24h) and when the water was clear, we removed it, keeping the yellow precipitate and transferring it to smaller bottles until the sample fitted the wished volume (<500mL).

The 500mL bottles with the precipitate were stored until they can be analysed in the home laboratory.

Preliminary results:

^{234}Th activity on in situ pump filters

The oven dry subsamples from the in situ pump supor filters have been analysed for ^{234}Th activity by beta counting. ^{234}Th is produced in seawater at a constant rate from the decay of dissolved ^{238}U. Soon after its production, ^{234}Th adsorbs to particles which are suspended in seawater, because Thorium is nearly insoluble in seawater and very particle reactive. We did not determine directly (by weighing the filters) the concentration of suspended particles in the water column. Instead, we could use the particulate ^{234}Th activity as a tracer for the relative particle concentrations. Higher ^{234}Th activity indicates a higher concentration of suspended particles and vice versa. These results will be compared with the results of the transmissometer.

Figure 12 displays the particulate ^{234}Th activities in the water column of all 6 ISP stations. At all profiles, we found maximum activities at those in situ pumps that had been deployed closest to the bottom (about 50 m above the seafloor). Here, activities are three to five times higher than in the overlying water column. This indicates that we successfully collected particles from the benthic nepheloid layer on our filters. ^{231}Pa/^{230}Th will be determined on the same filter samples at the home lab. Data on particulate ^{231}Pa/^{230}Th from the benthic nepheloid layer will provide valuable information about the ^{231}Pa/^{230}Th signal that is going to be recorded within the sediment.

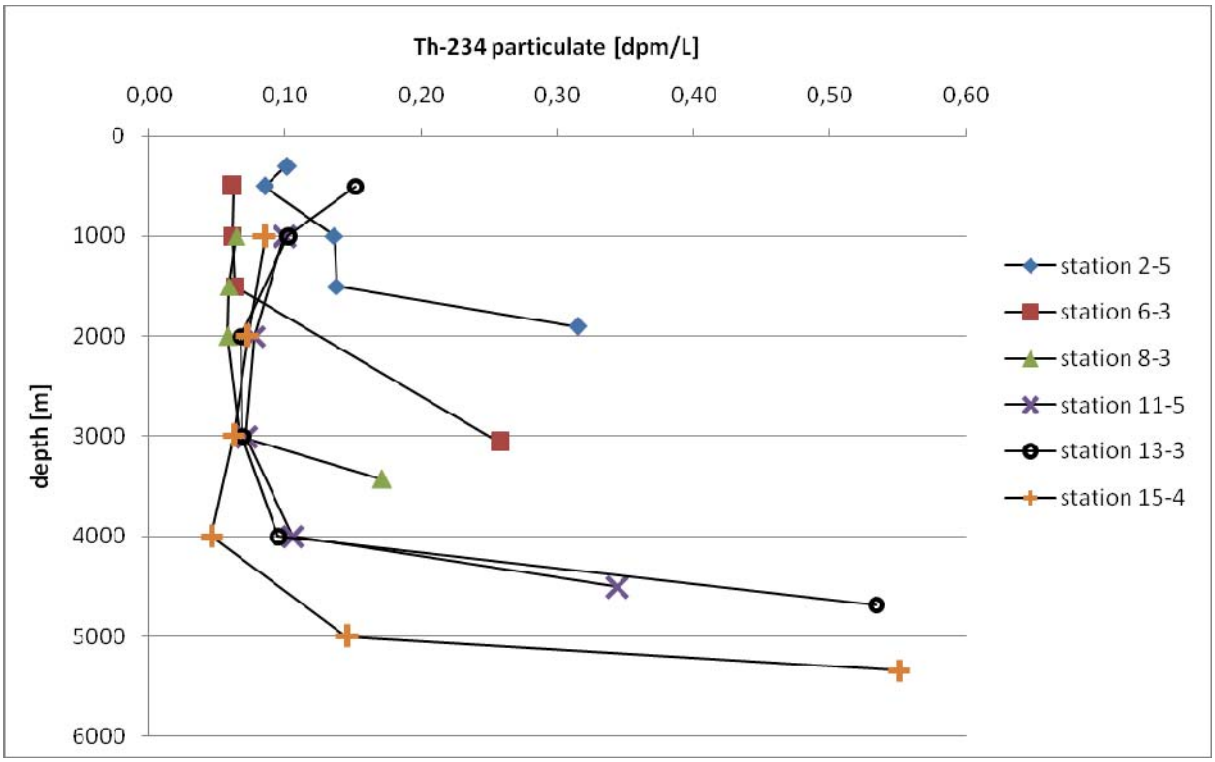

Figure 12: Particulate ^{234}Th activities determined on in situ pump filters. Maximum activities at the largest depths, approximately 50m above the seafloor, show the intensity of the benthic nepheloid layer.

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3.2.A.8 DOM
Dissolved Organic Matter

Oliver Lechtenfeld, Michiel Rutgers van der Loeff.

Objectives:

Most of marine DOC (90-95%) is present in the deep-sea and represents a refractory background with low concentrations of 35-45 µM DOC (HANSELL, 2002) and average residence times of several thousand years (WILLIAMS and DRUFFEL, 1987). It is initially formed by primary producers (land plants, plankton) from atmospheric CO_2 and transported by rivers into the oceans or released either directly by plankton organisms or is formed during their decomposition. As a consequence of the persistent nature of degraded DOM a large amount of carbon which initially was derived from the atmosphere gets stored in the ocean, circulates within the ocean currents and serves as a buffer in the organic carbon cycle. Most refractory organic compounds are then distributed over the world oceans via the global ocean conveyor belt and are trapped from active cycles for many thousands of years. Semi-labile compounds, on the other hand, can be mineralized to CO_2 by photo- or microbial degradation in the deep ocean. Hundreds of years later the mineralization products are eventually released as CO_2 into the atmosphere in upwelling regions where deep water masses again equilibrate with the atmosphere.

Recent progress in ultrahigh-resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) promises major advances in the chemical characterisation of DOM and the development of new molecular tracers (e.g. KOCH et al., 2005; STENSON et al.,

2003) and DOM response to photo- and microbial degradation and modification (KUJAWINSKI et al., 2004).

Additionally, coupling reversed-phase chromatography (RP-HPLC) with trace-metal selective plasma mass spectrometry (ICP-MS) will provide extensive insights in the complexation of trace metals by organic ligands. This method aims at the detection of stable metal-DOM complexes which could inhibit (or force) microbial degradation of certain DOM fractions. Studying the behaviour of these complexes with the formation and pathway of NADW is therefore a major task. Finally, structural and stability information for both parts (inorganic, biogeochemical relevant trace metals as well as biologically reworked, refractory organic matter) can be derived from these techniques.

Work at Sea:

At 10 stations the Titan team collected for us 0.2-mu filtered samples from the Ultra Clean Frame (CTD UC) at 6 depths: 25m, 50m or fluorescence maximum, 250m, 1250m, 2000m and bottom. One 0.5-L sample was collected in LDPE bottles and frozen immediately for the RP-HPLC study of complexation of trace metals by organic ligands at AWI. A second sample was acidified to pH2 and passed over a column to extract DOM. These columns were stored frozen for their later analysis with FT-ICR-MS for the characterization of DOM. Sampling for DOM was generally coordinated with the sampling for DOC by the microbiology group.

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B CO2 and other transient anthropogenic tracers

3.2.B.1 Dissolved Inorganic Carbon, Total Alkalinity

Steven van Heuven, Lesley Salt

Sampling and analysis for carbonate system parameters broadly followed the standard operating procedures outlined by Dickson *et al.*, 2007.

Specifically, water samples of 0.6l were collected from the large volume 25 L CTD at one cast of every station, at all of 24 depths, into borosilicate sample bottles with plastic caps, using silicone tubing. In each profile, three duplicate samples were collected, generally at shallow, intermediate and deep parts of the profile. Samples analysis commenced immediately after collection. Analysis of profiles was in all cases completed within 16 hours after sampling. All analyses were performed on each of two VINDTA 3C's (Versatile INstrument for the Determination of Total Alkalinity, designed and built by Dr. L. Mintrop, Marine Analytics and Data, Kiel, Germany), referred to as A and B (VINDTA #15 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 meter 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 25ºC (±0.1ºC), irrespective of the samples' initial temperature.

Surface samples were analysed first, as were the duplicate samples. After analysis of the first ~10 samples (i.e., the shallow most ~500m), the remainder of the profile was measured deep-to-shallow. This assured that any 'start-up drift' in the coulometric cells does not affect the deep samples, nor are they impacted by potential problems that coulometric cells sometimes experience at the end of a long run (~35 samples in total).

The use of two machines increases our confidence in final results, and allows demonstration and quantification of measurement errors of the machines that would otherwise go unnoticed. No formal analysis and correction of the result have been performed yet. Such a more formal treatment of the carbon data will in due time be available as a separate report.

Dissolved inorganic carbon (DIC)

DIC was determined by coulometric titration. An automated extraction line takes a 20ml subsample which is subsequently purged of CO_2 in a stripping chamber containing ~1ml 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

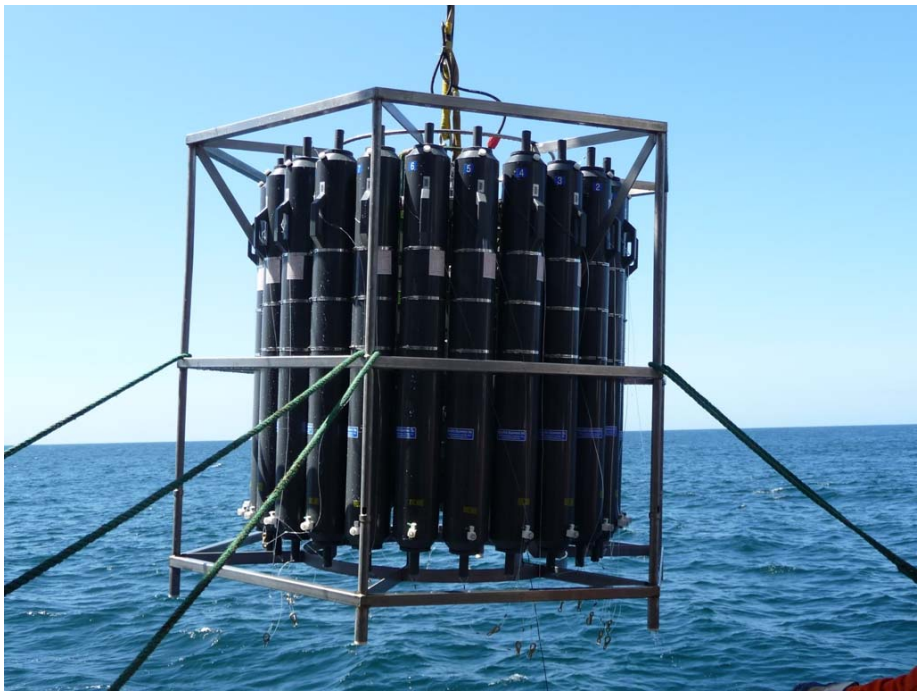

Figure 13: Large volume 25 L CTD

integrated over the duration of the titration to obtain the total amount of carbon titrated. Calibration of the coulometers was done using a gas-loop calibration system (GLCS) that feeds known quantities of pure CO_2 to the coulometer. Additionally, certified reference material (CRM, Batch #100) obtained from dr. Andrew Dickson at Scripps Institute of Oceanography (San Diego, California) was used for quality control. An initial look (before application of the GLCS-obtained calibration factors for the coulometers) at the results of analyses of CRM suggest an overall accuracy and precision of instrument A of +1.1±1.4 µmol kg^{-1}, exhibiting no noticeable drift over time. For instrument B these numbers are a more sobering -7±8.0 µmol kg^{-1}. However, measurements by this instrument exhibit two periods of clear drift, which will likely to large extent be compensated for by the application of the GLCS results.

Total Alkalinity (TA)

Determinations of TA were performed by acid titration that combines aspects from both the commonly used ‘closed cell' method and the ‘open cell’ method, following the VINDTAs standard settings. A single 20L batch of acid of ~0.1M and salinity 35 was prepared to be used by both VINDTAs. Potential drift in acid strength due to HCl-gas loss to acid vessel headspace is not accounted for. Samples were collected for post-cruise determination of acid strength.

Initially, new electrodes from Metrohm were used for both the reference and the measurement electrode. After the Metrohm measurement electrodes were found to be slow (in the sense that they take long to reach a stable EMF), one of those was replaced with a Thermo Orion. No formal assessment was made of electrode quality (E0, Nernst response), although a brief test

using buffers of TRIS and AMP confirmed that the chosen electrodes had acceptable Nernst response (i.e., >97% of theoretical).

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3.2.B.2 pH

Lesley Salt, Steven van Heuven

pH measurements were made spectrophotometrically, using a SAMI-underway pH instrument (Sunburst Sensors), modified for discrete sample analysis. A subsample of a few ml was drawn from the same bottle as DIC and TA just before VINDTA analysis. This subsample is transported through a coil in the SAMI housing, with a through flow of water from a 25ºC water bath. The temperature in the housing is monitored with each measurement and it is assumed to be equal to the sample temperature by the time the sample reaches the measurement cell.

The indicator meta-cresol purple is added to the flowing sample and the absorbance's of the mixture at 730, 578 and 434nm are determined, following the SAMI's default protocol. pH is then calculated using the following equation:

$$pH = pK_2 + \log10[(A_1/A_2 - \varepsilon_1(HI^-)/\varepsilon_2(HI^-)) /$$

$$\varepsilon_1(I_2^-)/\varepsilon_1(HI^-)-(A_1/A_2)\ \varepsilon_2(I_2^-)/\varepsilon_2(HI^-)]$$

Where ε represents the extinction coefficient ratios for m-cresol purple, A the measured absorbance's, and I is the indicator dye. Drift was monitored by occasionally measuring TRIS-buffer, made up to 0.8M according to Dickson *et al.*, 2007. The CRM's used for TA and DIC quality control were also analysed on the SAMI as an extra control, again just before VINDTA analysis.

3.2.B.3 $^{12}C/^{13}C$, $^{12}C/^{14}C$

Steven van Heuven, Lesley Salt

Samples were collected for shore based determination of carbon isotope ratios at the Centre for Isotope Research (CIO) at the University of Groningen. At each station, duplicate samples were collected from all bottles of the Ultra Clean CTD, i.e., 2x24 samples per station.

Significant risk of contamination of the samples was present during this cruise because ^{14}C-spiking experiments were performed for analysis of microbial production. The initial spiking of microbial cultures was followed after 72 hours by acidification and filtration of acidified samples. During both activities, but especially the latter, large amounts of $^{14}CO_2$ are evolved, that were evacuated from the isotope container and vented onto deck. From there the $^{14}CO_2$ is expected to have reached the hold of the ship in some concentration, although most likely most $^{14}CO_2$ was blown away by the wind (the isotope container was on the back deck, wind was generally from SW, while course was S/SW). However, significant care was taken to avoid any work on the natural-^{14}C samples in the ~20 hours after spiking activities.

Preparation, sampling and storage:

Sample bottles were prepared as short as possible before sampling. Empty sample bottles (200ml brown glass 'medicine' bottles, not treated in any way before the cruise) were stored in their original shrink-wrapping (in batches of 14), while screw caps and bottle neck inserts were repackaged from bulk into Ziploc'ed batches of 50, before leaving port. Shortly (<3h) before UC-CTD came on deck, bottles were removed from shrink-wrapping and insert and caps were placed, using gloves.

Bottles were rinsed, gently filled using silicone tubing, over flown ~1-2 times their volume and capped with a ~3% headspace. After collecting, samples and sampling trays were rinsed off with about 2 litres of distilled water to remove salt water. Within 60 minutes, all samples were poisoned using 0.1ml of 50% $HgCl_2$, which required the samples to be reopened briefly (<10s). Care was taken to avoid contact between samples and the pipette tip. New pipette tips were used for each station. Bottle neck and screw caps were “parafilmed” and stored in batches of ~85 per crate. Crates are stored in thick trash bags and stored at ~25ºC.

All material for sampling and poisoning was kept in Ziploc bags between use from station 12 onwards. A selection of these materials was already stored in such bags since earlier in the cruise: gloves and pipette tips since S1, pipette since S10, poison bottle, parafilm and sampling tubes since S12.

Preliminary results

A preliminary analysis (between cruises 64PE319 and 64PE321) of a full-depth subset of samples of station 17 shows no obvious contamination, with $^{14}C/^{12}C$ ratios between 91% and 106% of "modern" ratios. These numbers will be converted into $\Delta C14$ for comparison with historical datasets. The particular analysis series appears to have been jeopardized by insufficient compaction of the graphite targets, resulting in a low carbon yield, but this problem is expected to be solved before analysis of the full set of samples.

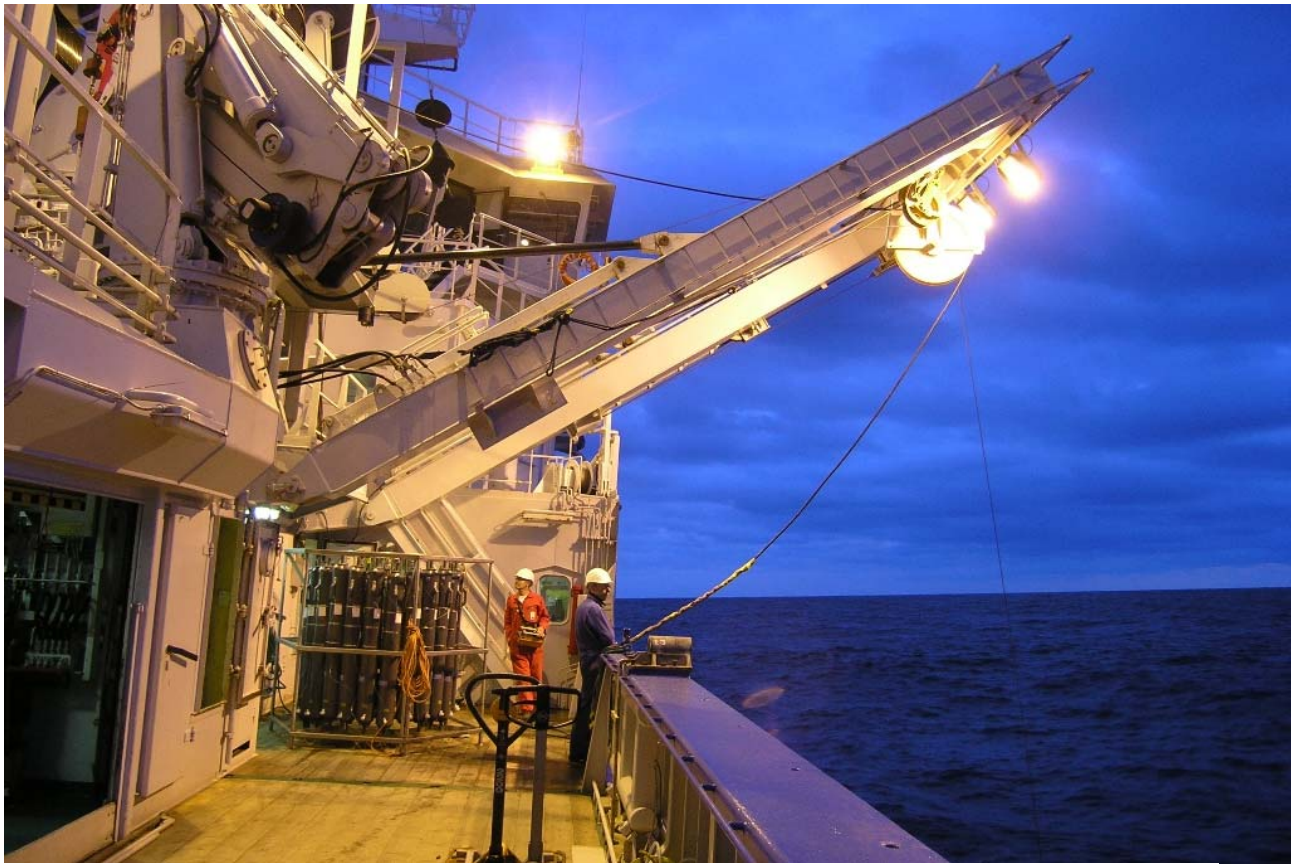

Figure 14: Work continued during night time (Picture: Sven Kreschmer)

3.2.B.3 CFC's

Patrick Schmidt

Introduction

Chlorofluorocarbons (CFCs) are anthropogenic trace gases that enter the ocean by gas exchange with the atmosphere. The evolution of these transient tracers in the ocean interior is determined by their temporal increase in the atmosphere since the middle of the last century and the formation, advection and mixing processes of intermediate, deep and bottom water. Hence, these transient tracers enable to determine transit times, i.e. the time elapsed since the water has left the surface mixed layer.

Work at sea, water sampling, and analyzes in the IUP Bremen laboratories

In total 280 samples for chlorofluorocarbons (CFC-11 and CFC-12) distributed on 14 deep profiles along the entire section were taken. Water samples from the 25 L CTD system were collected into 100 ml glass ampoules and sealed off after a CFC free headspace of pure nitrogen had been applied. The CFC samples are shipped home for analysis in the CFC-laboratory at the IUP Bremen. The determination of CFC concentration will be accomplished

by purge and trap sample pre-treatment followed by gas chromatographic (GC) separation on a capillary column and electron capture detection (ECD). The amount of CFC degassing into the headspace will be accounted for during the measurement procedure in the lab. The system will be calibrated by analyzing several different volumes of a known standard gas. Additionally the blank of the system will be analyzed regularly. Due to limited measurement capacity and high number of samples analyzed in the laboratory, measurement will be probably finished in 2011.

Expected results

Chlorofluorocarbons (CFCs) are gaseous, anthropogenic tracers that enter the ocean by gas exchange with the atmosphere. The evolution of these transient tracers in the ocean interior is determined by their temporal increase in the atmospheric and by the formation and mixing processes of the deep water. The total inventories of CFCs in the deep water reflect the accumulation of CFCs carried by its surface near source water masses. Together with the known atmospheric CFC evolution, CFC inventories allow, thus, estimating the renewal or formation rates of recently formed deep water.

Other methods using CFCs as age tracers include transit time distributions (TTDs, or age spectra). By applying a "mean age", a "width of the age", and, if appropriate, a tracer free (i.e. "old") component, this dating method accounts for advection and mixing, other than the "CFC-ratio age" approach, which accounts – as a first approach – for advection and tracer free dilution only. This improves the estimates of ventilation time scales, mixing parameters, and ventilation or formation rates significantly. To constrain the parameters of the TTD well, it is valuable to use transient tracers from different observation times (e.g. CFC time series). Furthermore, the derived TTDs can be used to estimate the input, internal transfer, and storage of anthropogenic CO_2.

C Microbial oceanography: biodiversity and turnover rates of prokaryotes, eukaryotes and viruses

3.2.C.1 Prokaryotic Activity in the major water masses of the northern North Atlantic

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Introduction

About 75% of the ocean is deeper than 200 m, however, most concepts on the interaction between the physical and chemical environment and the biota are derived from the relatively thin ocean surface layer. Moreover the link between prokaryotic activity and biogeochemistry

in the dark ocean is not firmly established despite recent studies that highlight the role of Bacteria and Archaea in the cycling of organic and inorganic matter in the dark ocean (Baltar et al., 2009a; Herndl et al., 2005b; Reinthaler et al., 2006). Among others, the observation that the most important source of substrate for prokaryotes, i.e. DOC, is not depleted (Barber, 1986) led to the longstanding view that microbes in the deep are dormant or even dead (Jannasch and Wirsen, 1973). This paradigm is challenged, however, by recent evidence suggesting that prokaryotes in the dark ocean are as active (or even more active) as compared to the sunlit surface (Kirchman et al., 2007; Reinthaler et al., 2006; Varela et al., 2008)(see Figure 15).

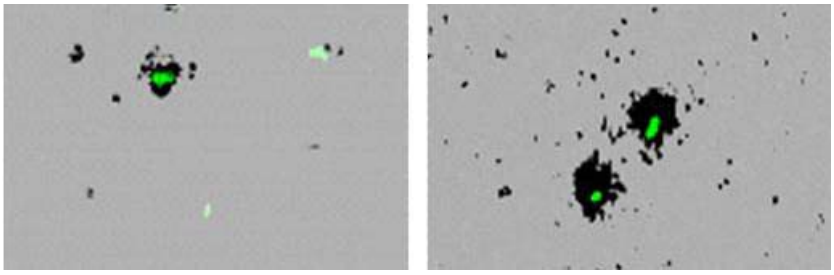

Figure 15: Illustration of the MICRO-CARD-FISH analysis from prokaryotes of the North Atlantic sampled at 3000 m depth during an earlier cruise in 2002. The silver grain halo around the cells indicates the activity of cells taking up 3H-Leucine as substrate.

Despite the major insights gained from studies on microbial activity in the surface ocean, knowledge on the microbial processing of organic matter and nutrients in the dark ocean is still in its infancy due to the lack of data. For this reason the IPCC called attention to the fact that it is not possible to parameterize prokaryotic activity for an enhanced understanding of the global ocean carbon cycle (Intergovernmental Panel on Climate Change, 2001) and an interdisciplinary workshop of experts on integrating biogeochemistry and ecosystems in a changing ocean emphasized to study the interactions of the physics, chemistry and biology on an interdisciplinary basis (IMBER IMBIZO http://www.imber.info/IMBIZO1.html). In this respect Geotraces provides a unique opportunity to compare trace metal concentrations and biogeochemical measurements conducted during the cruise with the prokaryotic activity found in the pelagic ocean.

Objectives

1. To assess the abundance of prokaryotes and viruses in the water column of the North Atlantic.
2. To study the heterotrophic production and chemoautotrophic production of prokaryotes in the major deep water masses of the North Atlantic.
3. To assess the community composition of prokaryotes in the major deep water masses

Methods

Generally, samples were taken at every occupied station (total of 14) and at 7 depth layers. The depth layers were chosen to cover the bottom waters, the Denmark Strait Overflow Water (DSOW), the North Atlantic Deep Water (NADW), the Labrador Sea Water (LSW).

Additionally the oxygen minimum zone, the base of the euphotic zone (~250m) and the subsurface at 50m were sampled. Samples were transferred from the 25 L Niskin bottles into acid rinsed polycarbonate bottles. Filtration and/or fixing of samples was done within 15 min after sampling the 25L CTD rosette.

Particulate organic carbon

Samples of seawater were taken for each water mass studied and filtered onto pre-combusted (450°C, 12 hours) 25 mm Whatman GF/F filters. The volumes taken were 4 L for the shallower depths (50 and 100 m) and 10 L for the rest. The filters were wrapped in pre-combusted aluminium foil and frozen at –20°C until processed. In the laboratory the filters will be thawed and dried overnight at 65°C and packed in pre-combusted nickel sleeves. The carbon analyses will be performed on a Perkin Elmer-2400 CHN elemental analyzer, according to the JGOFS protocol (UNESCO, 1994).

Prokaryotic abundance

To evaluate the dynamic of the microbial food web samples for prokaryotic and viral abundance were collected in every station and depth from the surface to the bottom layers. 1.5 ml of samples were fixed with glutaraldehyde (final concentration 0.5%), frozen in liquid nitrogen and stored at -80°C. The abundance of prokaryotes and viruses will be measured by flow cytometry (Beckton Dickinson) after nucleic acid staining with SyBR-Green I. The abundance will be estimated using an internal standard of fluorescent beads, and will be corrected by calculating the flow rate.

Prokaryotic heterotrophic production using the filter method

Immediately after the recovery of the CTD rosette, samples for microbial heterotrophic production and DIC fixation measurements were collected from the Niskin bottles. Samples were taken at 50 m, 250 m, 400 or 500 m, 1250 m, 2000 m, 3000 m, 4000 m depth. Processing of the samples, from collecting water from the Niskin bottles to incubating the samples with the radiolabeled tracers in temperature-controlled incubators, took less than 15 min.

Microbial heterotrophic production was measured by incubating 5-40 ml of seawater (depending on the depth) in triplicate with 5 nM [^{3}H]-leucine (final concentration, specific activity 120 Ci mmol^{-1}, American Radiolabeled Chemicals) in the dark at in situ temperature (±1°C) for 1 to 24 h. Duplicate formaldehyde-killed blanks were treated in the same way as the samples. Incubations were terminated by adding formaldehyde (2% final concentration) to the samples. Samples and blanks were filtered through 0.2-µm polycarbonate filters (Whatman Nuclepore, 25 mm filter diameter) supported by cellulose acetate filters (Millipore, HA, 0.45-µm pore size). Subsequently, the filters were rinsed twice with 5% ice-cold trichloroacetic acid, twice with Milli-Q and with 80% Ethanol. Subsequently filters were dried, 8 ml of scintillation cocktail (FilterCount, Canberra-Packard) added, and after about 18 h counted on board in a liquid scintillation counter (Perkin Elmer Tricarb). The instrument was calibrated with internal and external standards. The blank-corrected leucine incorporation

rates were converted into microbial carbon production using the theoretical conversion of 1.55 kg mol^{-1} leucine incorporated (Kirchman, 1993; Simon and Azam, 1989).

DIC fixation was measured via the incorporation of [^{14}C]-bicarbonate (3.7 x 106 Bq, Amersham) in 50 ml seawater samples. Triplicate samples and formaldehyde-fixed blanks were incubated in the dark at in situ temperature for 72 h. Incubations were terminated by adding glutaraldehyde (2% final concentration) to the samples, filtered onto 0.2-µm polycarbonate filters and rinsed with 10 ml 0.2 µm filtered seawater. Subsequently, the filters were fumed with concentrated HCl for 12 h. The filters were then processed as described above and counted in the scintillation counter for 10 min. The resulting mean disintegrations per minute (DPM) of the samples were corrected for the mean DPM of the blanks and converted into organic carbon fixed over time and corrected for the natural DIC.

Prokaryotic heterotrophic production using the micro centrifuge method

^{3}H-leucine incorporation rate was determined as a proxy for prokaryotic production (Kirchman 2001, Methods in microbiology, vol. 30). Triplicate subsamples (1.5 mL) dispensed into screw-capped centrifuge tubes amended with 10 nmol L^{-1} (final concentration) of [^{3}H]-leucine (Cat#: ART0840, American Radiolabeled Chemicals, Inc.) and incubated at in situ temperature (± 2ºC) in the dark. One trichloroacetic acid (TCA) killed blank was prepared for each sample. Incubation periods were 1 hour and 24 hours for the upper (0 – 250 m) and deeper (300 – bottom) water layers, respectively. After the incubation, proteins were TCA (final conc. 5%) extracted twice by centrifugation (14000 rpm, 10 min), followed by the extraction with ice-cold 80% ethanol. The samples were radio assayed with a liquid scintillation counter (Tri-Carb 3100TR, PerkinElmer) using Ultima-GOLD (Packard) as scintillation cocktail. Quenching was corrected by External standard channel ratio. The disintegrations per minute (DPM) of the TCA-killed blank was subtracted from the average DPM of the samples, and the resulting DPM was converted into leucine incorporation rates.

MICRO-CARD-FISH

The relative abundance and activity of the major prokaryotic groups will be determined by MICRO-CARD-FISH analysis. Fifty millilitres were incubated with ^{3}H-Leucine of high specific activity (10nM final concentration). After the incubations, the life samples were fixed by adding paraformaldehyde (2% final concentration) and, subsequently, stored at 4ºC in the dark for 18 h. Thereafter the samples were filtered onto 0.2-µm polycarbonate filters and stored at -80ºC.

The analysis of MICRO-CARD-FISH samples in the lab will be done as described elsewhere (Teira et al. 2004; see also http://www.microbial-oceanography.eu/methods.htotal metal concentration). To evaluate the relative abundance and activity of Bacteria we will use a probe mix of EUB338-II-III (EUB338: 5'-GCT GCC TCC CGT AGG AGT-3', EUB338-II: 5'-GCA GCC ACC CGT AGG TGT-3', EUB338-III: 5'-GCT GCC ACC CGT AGG TGT-3', see Daims et al., 1999). To target Crenarchaea we will use a probe mix of CREN537 and GI554 (CREN537: 5'-TGA CCA CTT GAG GTG CTG-3', Teira et al., 2004; GI554: 5'-TTA GGC CCA ATA ATC MTC CT-3', Massana et al., 1997). To cover Euryarchaea we will use the probe EURY806 (5'-CAC AGC GTT TAC ACC TAG-3'; Teira et al., 2004). To evaluate unspecific hybridization of probes and background fluorescence we will use antisense probes.

Microautoradiography will be performed on previously hybridized filter sections and processed as described in Teira et al. (2004). The slides will be examined under an epifluorescence microscope equipped with a 100-W mercury lamp and appropriate filter sets for DAPI and Alexa488. The presence of silver grains surrounding cells will be recorded by using the transmission mode of the microscope. The data will be expressed as percent of DAPI-stained cells.

Prokaryotic community composition

The prokaryotic community composition of Bacteria and Archaea will be determined by T-RFLP analysis as described in Moeseneder et al. (2001). Seawater samples 10 L were collected onto 0.22-µm Sterivex filter units (Millipore). The filter units were stored at -80ºC for later analysis in the lab. The total RNA will be extracted from the filter units using a bead beating protocol and the RNeasy Mini Kit (Quiagen). The DNA will be removed by DNAse and a subsequent PCR amplification on the treated samples will be used to check for remaining DNA contamination. The quality of the RNA will be checked by the Experion microfluidics automated electrophoresis system (BioRad). The total RNA will be reverse transcribed into cDNA. Subsequently, the reverse transcribed 16S rRNA gene fragments of Bacteria and Archaea will be amplified by PCR using fluorescently 5'-end labelled forward and reverse primer pairs. Bacteria will be amplified using the primer pair 27F-1492R (27F: 5'-AGA GTT TGA TCC TGG CTC AG-3'; 1492R: 5'-GGT TAC CTT GTT ACG ACT T-3'; Lane, 1991) and archaeal 16S rRNA gene fragments will be amplified using the primer pair 21F-958R (21F: 5'-TTC CGG TTG ATC CYG CCG GA-3'; 958R: 5'-YCC GGC GTT GAM TCC AAT T-3'; DeLong, 1992). The PCR fragments will be cut using the restriction enzyme HhaI and then analyzed using the GeneScan mode of a capillary sequencer (ABI 3130XL). The resulting peaks in the electropherogram of the Genescan software represent the predominating phylotypes in the sample. The data will be converted to presence/absence matrixes and similarities between communities will be analyzed using the Primer software (Primer-E).

Viral Production

The main task was to evaluate the viral production and the viral decay through different depths and water masses. 5 L water samples were collected at Station 6, 10, 15, three depths at each station, varying from 50 to 4500 m.

The samples were filtered through 0.22 µm tangential flow ultra filtration Vivaflow filters to separate the bacteria from the viruses; we obtained two fractions: the bacterial fraction (viruses free) > 0.22 µm and the viruses < 0.22 µm.

The bacterial fraction was used for the viral production experiments. Six 300 mL subsamples of the bacterial fraction were collected in polycarbonate bottles and two treatments were carried on in triplicate to distinguish the lysogenic and the lytic cycles: with and without addition of Mitomycin C (final concentration 1 µg ml^{-1}) respectively. The samples were incubated at *in situ* temperature for 48 hours. 1.5 ml subsamples were collected from each bottle every 4-6 hours, fixed with glutaraldehyde (final concentration 0.5%), frozen in liquid nitrogen and stored at -80°C. The abundance of prokaryotes and viruses abundance will be estimated by flow cytometry after Sybr-Green I staining. The viral production rate (viruses $mL^{-1}h^{-1}$) will be estimated from the increase in viral abundance over a period of time.

Viral decay

To study the viral decay rates, the water samples were filtered through 0.2 µm by tangential flow ultra filtration. Samples for viral enumeration were taken and fixed with glutaraldehyde (final concentration 0.5%) every 12 h during 144 h. Viral abundance will be estimated by flow cytometry after Sybr-Green I staining.

Results

POC analysis will be done in the labs of the NIOZ. The biological parameters will be analyzed at the Department of Marine Biology in Vienna. Preliminary data of prokaryotic heterotrophic production that was measured on board suggests a transition from high productivity in the northern North Atlantic probably due to the fresher water masses there (Figure 16).

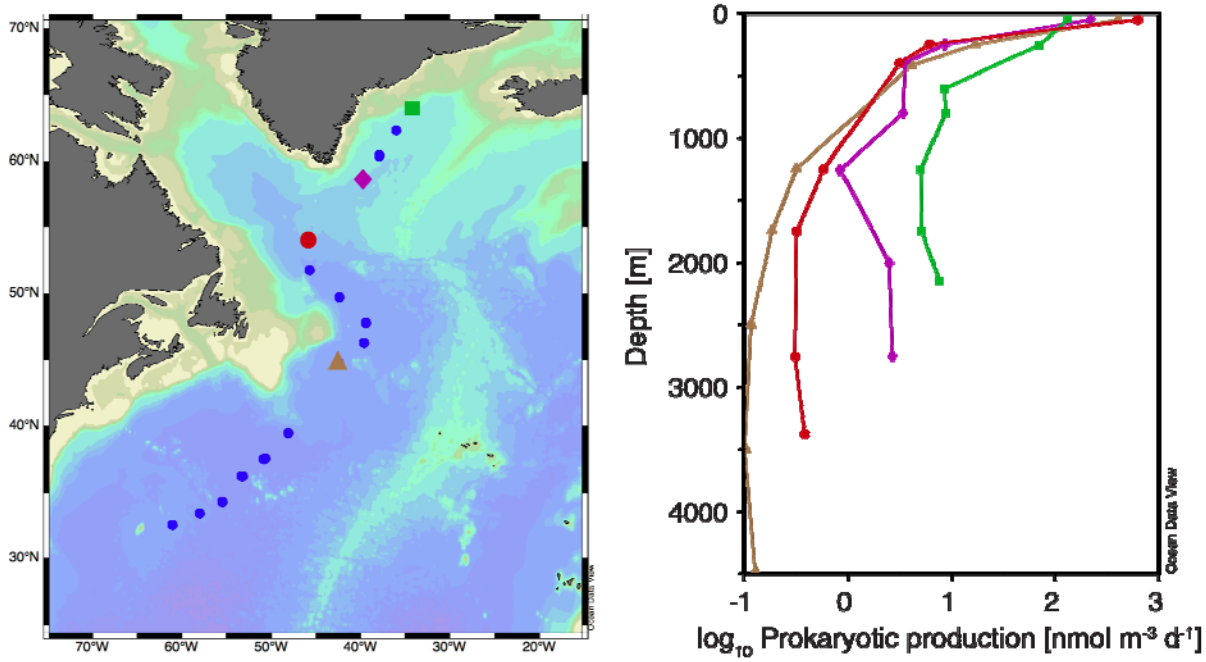

Figure 16: Selected stations of prokaryotic heterotrophic production showing the decrease in productivity along the transect from the northern North Atlantic toward the south.

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3.2.C.2 Prochlorococcus and Synechococcus in relation to trace metals

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The Chisholm Lab at MIT will be focused on evaluating the relationship between pico-cyanobacteria and trace metal abundance and speciation. The cyanobacteria Prochlorococcus and Synechococcus form the base of the food web in most marine systems and represent a significant fraction of global productivity. Although some targeted studies have examined the effect of some trace metals on the abundance, distribution, and activity of these important marine organisms, GEOTRACES offers an unprecedented opportunity to study their ecology with respect to nearly all bioactive trace metals across many marine basins.

For the Chisholm Lab DNA and cell samples were collected from the euphotic zone, being approximately the upper 200 meters of the water column. Pending future funding for sample processing, the DNA will be used to determine the distribution and abundance of several types of Prochlorococcus with different physiological characteristics. In addition, targeted metagenomics studies will allow us to formulate hypotheses on how trace metal speciation influences the genetic repertoire of the ecosystem. Cell samples will be used to determine the total numbers of Prochlorococcus and Synechococcus across the transect and genomes of single cells (both phototrophs and heterotrophs) will allow us to examine the diversity of bacteria that are not amenable to culturing in the laboratory. The availability of an extensive trace metal dataset will allow us to target our work to build a greater understanding of how trace metal speciation influences marine ecology.

Appendix 1

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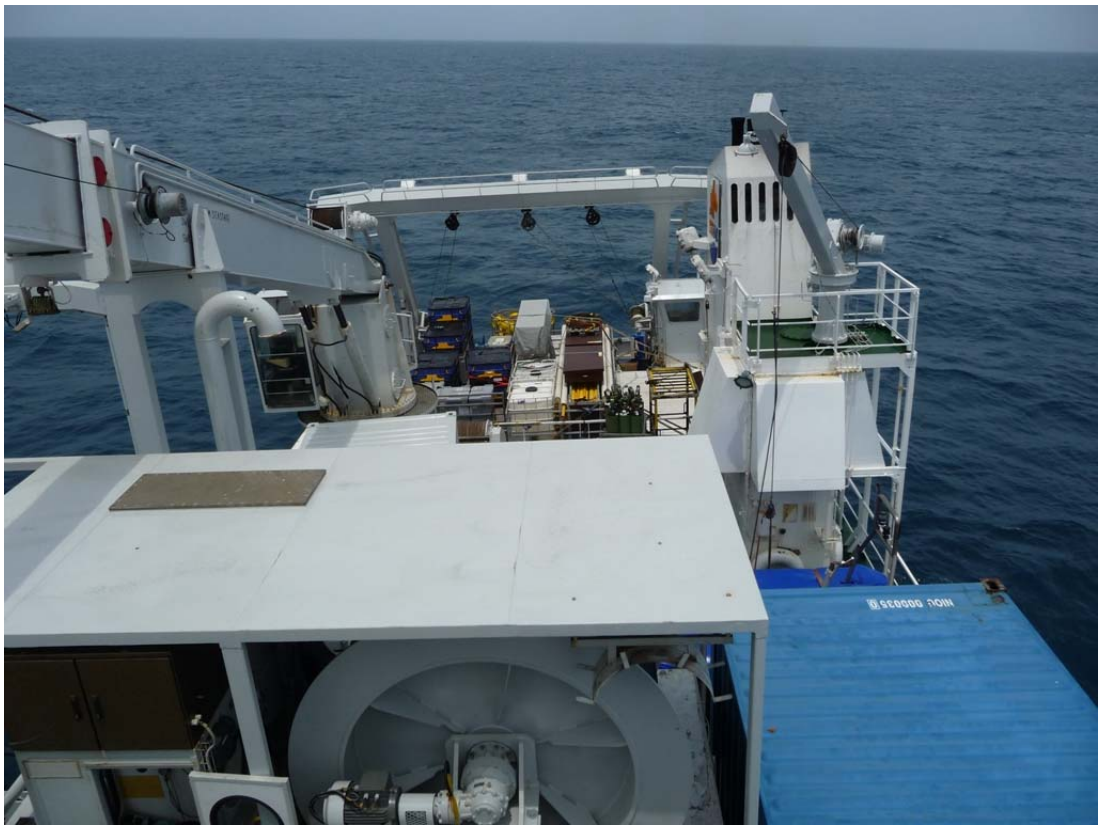

Appendix 2 station list

stn	cst	latitude	longitude	Year	month	day	bottom depth	CTD id*	no of samples
1	1	6.040.532	-1.098.705	2010	4	29	760.0	1	24
2	1	6.400.026	-3.425.107	2010	5	2	2192.0	1	24
2	2	6.399.990	-3.425.054	2010	5	2	2189.0	2	24
2	3	6.400.028	-3.425.025	2010	5	2	2197.0	1	24
2	3	6.400.028	-3.425.025	2010	5	2	2197.0	1	24
2	4	6.400.012	-3.425.132	2010	5	2	2197.0	2	24
2	6	6.399.996	-3.424.996	2010	5	3	2189.0	2	8
3	1	6.234.470	-3.599.736	2010	5	3	2673.0	1	24
3	2	6.234.488	-3.599.816	2010	5	3	2673.0	2	24
5	1	6.042.817	-3.790.794	2010	5	4	2903.0	1	24
5	2	6.042.584	-3.791.074	2010	5	4	2903.0	2	24
6	1	5.860.299	-3.970.618	2010	5	5	3109.0	1	24
6	2	5.860.312	-3.970.568	2010	5	5	3109.0	2	24
8	1	5.406.338	-4.583.447	2010	5	7	3444.0	1	24
8	4	5.406.390	-4.583.399	2010	5	8	3438.0	1	24
9	1	5.182.022	-4.573.246	2010	5	9	4058.0	1	24
9	2	5.182.088	-4.572.958	2010	5	9	4059.0	2	24
10	1	4.972.166	-4.244.770	2010	5	10	4389.0	1	24
10	2	4.972.556	-4.244.578	2010	5	10	3491.0	2	24
11	1	4.780.054	-3.939.930	2010	5	11	4552.0	1	24
11	2	4.780.048	-3.939.915	2010	5	11	4551.0	2	24
11	3	4.779.958	-3.940.010	2010	5	11	4553.0	1	24
11	4	4.779.994	-3.940.002	2010	5	11	4550.0	2	24

12	1	4.631.220	-3.965.919	2010	5	12	4593.0	1	24
12	2	4.631.727	-3.965.632	2010	5	12	4592.0	2	24
13	1	4.484.410	-4.252.596	2010	5	13	4754.0	1	24
13	2	4.484.436	-4.254.362	2010	5	13	4756.0	2	24
14	1	3.949.661	-4.808.546	2010	5	17	5371.0	1	24
15	1	3.755.396	-5.071.190	2010	5	18	5433.0	2	24
15	2	3.753.188	-5.073.650	2010	5	18	5455.0	1	24
15	3	3.751.204	-5.076.944	2010	5	19	5449.0	2	24
15	5	3.751.710	-5.087.106	2010	5	19	5449.0	2	24
15	6	3.751.630	-5.089.086	2010	5	19	5451.0	1	24
16	1	3.620.780	-5.329.238	2010	5	20	5467.0	1	24
16	2	3.621.148	-5.325.462	2010	5	20	5467.0	2	24
17	1	3.432.626	-5.542.994	2010	5	21	5539.0	1	24
17	2	3.431.840	-5.543.708	2010	5	21	5535.0	2	24
18	1	3.343.344	-5.804.974	2010	5	22	4513.0	1	24
18	2	3.343.338	-5.805.002	2010	5	22	4507.0	2	24
19	1	3.255.144	-6.109.858	2010	5	23	4683.0	1	24
19	2	3.255.424	-6.109.672	2010	5	23	4684.0	2	24

*CTD id
CTD 1=UC CTD
CTD 2= 25 L CTD

Picture taken by Sven Kreschmer

Appendix 3: Devices deployment

Device	Action	Date/time	Phase
64pe319			
64pe319-CTD 25L CTD25L Rosette Sampler			
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L1	Begin BEGIN	02-05-10 16:58	STATION2
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L1	End END	02-05-10 18:39	STATION2
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L2	Begin BEGIN	02-05-10 21:11	STATION2
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L2	End END	03-05-10 00:02	STATION2
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L3	Begin BEGIN	03-05-10 07:10	STATION2
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L3	End END	03-05-10 07:24	STATION2
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L4	Begin BEGIN	03-05-10 22:34	STATION3
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L4	End END	04-05-10 00:31	STATION3
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L5	Begin BEGIN	04-05-10 16:47	STATION5
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L5	End END	04-05-10 19:33	STATION5
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L6	Begin BEGIN	05-05-10 11:58	STATION6
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L6	End END	05-05-10 14:39	STATION6
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L7	Begin BEGIN	07-05-10 14:34	STATION8
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L7	End END	07-05-10 16:02	STATION8
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L9	Begin BEGIN	09-05-10 10:10	STATION9
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L9	End END	09-05-10 12:58	STATION9
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L10	Begin BEGIN	10-05-10 12:13	STATION10
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L10	End END	10-05-10 15:07	STATION10
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L11	Begin BEGIN	11-05-10 13:26	STATION11
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L11	End END	11-05-10 16:26	STATION11
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L12	Begin BEGIN	11-05-10 19:42	STATION11
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L12	End END	11-05-10 22:18	STATION11
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L13	Begin BEGIN	12-05-10 20:39	STATION12
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L13	End END	12-05-10 23:31	STATION12
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L14	Begin BEGIN	13-05-10 21:42	STATION13
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L14	End END	14-05-10 00:37	STATION13
64pe319-CTD 25L CTD25L-Begin/End			

64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L15	Begin BEGIN	18-05-10 13:22	STATION15
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L16	End END	18-05-10 17:04	STATION15
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L17	Begin BEGIN	18-05-10 22:32	STATION15
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L17	End END	19-05-10 01:32	STATION15
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L18	Begin BEGIN	19-05-10 09:18	STATION15
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L18	End END	19-05-10 09:45	STATION15
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L19	Begin BEGIN	20-05-10 13:30	STATION16
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L19	End END	20-05-10 16:34	STATION16
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L20	Begin BEGIN	21-05-10 13:30	STATION17
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L21	End END	21-05-10 16:46	STATION17
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L22	Begin BEGIN	22-05-10 13:07	STATION18
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L22	End END	22-05-10 15:45	STATION18
64pe319-CTD 25L CTD25L-Begin/End			
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L23	Begin BEGIN	23-05-10 14:00	STATION19
64pe319-CTD 25L CTD25L-Begin/End-319_CTD25L23	End END	23-05-10 16:51	STATION19
64pe319-Ultra Clean CTD UCCTD			
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD1	Begin BEGIN	29-04-10 14:19	STATION1
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD1	End END	29-04-10 14:56	STATION1
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD2	Begin BEGIN	02-05-10 15:04	STATION2
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD2	End END	02-05-10 16:39	STATION2
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD3	Begin BEGIN	02-05-10 20:24	STATION2
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD3	End END	02-05-10 22:00	STATION2
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD4	Begin BEGIN	03-05-10 20:26	STATION3
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD4	End END	03-05-10 22:20	STATION3
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD5	Begin BEGIN	04-05-10 14:33	STATION5
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD5	End END	04-05-10 16:38	STATION5
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD6	Begin BEGIN	05-05-10 09:25	STATION6
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD6	End END	05-05-10 11:46	STATION6
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD7	Begin BEGIN	07-05-10 11:49	STATION8
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD7	End END	07-05-10 14:22	STATION8
64pe319-Ultra Clean CTD UCCTD-Begin/End			
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD8	Begin BEGIN	08-05-10 04:44	STATION8
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD8	End END	08-05-10 07:30	STATION8

64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD9 Begin BEGIN 09-05-10 07:07 STATION9
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD9 End END 09-05-10 09:53 STATION9
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD10 Begin BEGIN 10-05-10 09:08 STATION10
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD10 End END 10-05-10 11:59 STATION10
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD11 Begin BEGIN 11-05-10 10:15 STATION11
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD11 End END 11-05-10 13:09 STATION11
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD12 Begin BEGIN 11-05-10 16:43 STATION11
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD12 End END 11-05-10 19:30 STATION11
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD13 Begin BEGIN 12-05-10 17:15 STATION12
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD13 End END 12-05-10 20:24 STATION12
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD14 Begin BEGIN 13-05-10 18:29 STATION13
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD14 End END 13-05-10 21:28 STATION13
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD15 Begin BEGIN 17-05-10 10:30 STATION14
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD15 End END 17-05-10 14:02 STATION14
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD16 Begin BEGIN 18-05-10 19:12 STATION15
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD16 End END 18-05-10 22:19 STATION15
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD17 Begin BEGIN 19-05-10 10:16 STATION15
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD17 End END 19-05-10 13:27 STATION15
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD18 Begin BEGIN 20-05-10 10:07 STATION16
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD18 End END 20-05-10 13:18 STATION16
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD19 Begin BEGIN 21-05-10 10:06 STATION17
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD19 End END 21-05-10 13:19 STATION17
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD20 Begin BEGIN 22-05-10 10:12 STATION18
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD20 End END 22-05-10 12:58 STATION18
64pe319-Ultra Clean CTD UCCTD-Begin/End
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD21 Begin BEGIN 23-05-10 11:08 STATION19
64pe319-Ultra Clean CTD UCCTD-Begin/End-319_UCCTD21 End END 23-05-10 13:52 STATION19
64pe319-FISH FISH
64pe319-FISH FISH-Start/End
64pe319-FISH FISH-Start/End-319_FISH1 Start BEGIN 30-04-10 14:58 PROFILE1
64pe319-FISH FISH-Start/End-319_FISH1 End END 02-05-10 14:40 PROFILE2
64pe319-FISH FISH-Start/End
64pe319-FISH FISH-Start/End-319_FISH2 Start BEGIN 03-05-10 14:19 PROFILE3

64pe319-FISH FISH-Start/End-319_FISH2	End END	03-05-10 19:57	PROFILE3
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH3	Start BEGIN	04-05-10 11:10	STATION4
64pe319-FISH FISH-Start/End-319_FISH3	End END	04-05-10 14:11	STATION4
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH4	Start BEGIN	08-05-10 15:35	PROFILE4
64pe319-FISH FISH-Start/End-319_FISH4	End END	08-05-10 17:04	PROFILE4
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH5	Start BEGIN	09-05-10 13:06	PROFILE5
64pe319-FISH FISH-Start/End-319_FISH5	End END	09-05-10 14:30	PROFILE5
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH6	Start BEGIN	10-05-10 15:14	PROFILE6
64pe319-FISH FISH-Start/End-319_FISH6	End END	10-05-10 16:15	PROFILE6
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH7	Start BEGIN	12-05-10 15:37	PROFILE7
64pe319-FISH FISH-Start/End-319_FISH7	End END	12-05-10 16:54	PROFILE7
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH8	Start BEGIN	17-05-10 14:21	PROFILE8
64pe319-FISH FISH-Start/End-319_FISH8	End END	17-05-10 16:16	PROFILE8
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH9	Start BEGIN	19-05-10 13:48	PROFILE9
64pe319-FISH FISH-Start/End-319_FISH9	End END	19-05-10 15:05	PROFILE9
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH10	Start BEGIN	21-05-10 16:56	PROFILE10
64pe319-FISH FISH-Start/End-319_FISH10	End END	22-05-10 09:59	PROFILE10
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH11	Start BEGIN	22-05-10 15:55	PROFILE101
64pe319-FISH FISH-Start/End-319_FISH11	End END	22-05-10 17:09	PROFILE11
64pe319-FISH FISH-Start/End			
64pe319-FISH FISH-Start/End-319_FISH12	Start BEGIN	23-05-10 16:58	PROFILE12
64pe319-FISH FISH-Start/End-319_FISH12	End END	23-05-10 18:13	PROFILE12
64pe319-Situ Pump ISP			
64pe319-Situ Pump ISP-Begin/End			
64pe319-Situ Pump ISP-Begin/End-319_ISP1	Begin BEGIN	03-05-10 00:24	STATION2
64pe319-Situ Pump ISP-Begin/End-319_ISP1	End END	03-05-10 07:02	STATION2
64pe319-Situ Pump ISP-Begin/End			
64pe319-Situ Pump ISP-Begin/End-319_ISP2	Begin BEGIN	05-05-10 14:52	STATION6
64pe319-Situ Pump ISP-Begin/End-319_ISP2	End END	05-05-10 21:43	STATION6
64pe319-Situ Pump ISP-Begin/End			
64pe319-Situ Pump ISP-Begin/End-319_ISP3	Begin BEGIN	07-05-10 19:05	STATION8
64pe319-Situ Pump ISP-Begin/End-319_ISP3	End END	08-05-10 01:37	STATION8
64pe319-Situ Pump ISP-Begin/End			
64pe319-Situ Pump ISP-Begin/End-319_ISP4	Begin BEGIN	11-05-10 22:30	STATION11
64pe319-Situ Pump ISP-Begin/End-319_ISP4	End END	12-05-10 05:29	STATION11
64pe319-Situ Pump ISP-Begin/End			

64pe319-Situ Pump ISP-Begin/End-319_ISP5	Begin BEGIN	14-05-10 00:51	STATION13
64pe319-Situ Pump ISP-Begin/End-319_ISP6	End END	14-05-10 07:40	STATION13
64pe319-Situ Pump ISP-Begin/End			
64pe319-Situ Pump ISP-Begin/End-319_ISP7	Begin BEGIN	19-05-10 01:46	STATION15
64pe319-Situ Pump ISP-Begin/End-319_ISP7	End END	19-05-10 09:01	STATION15