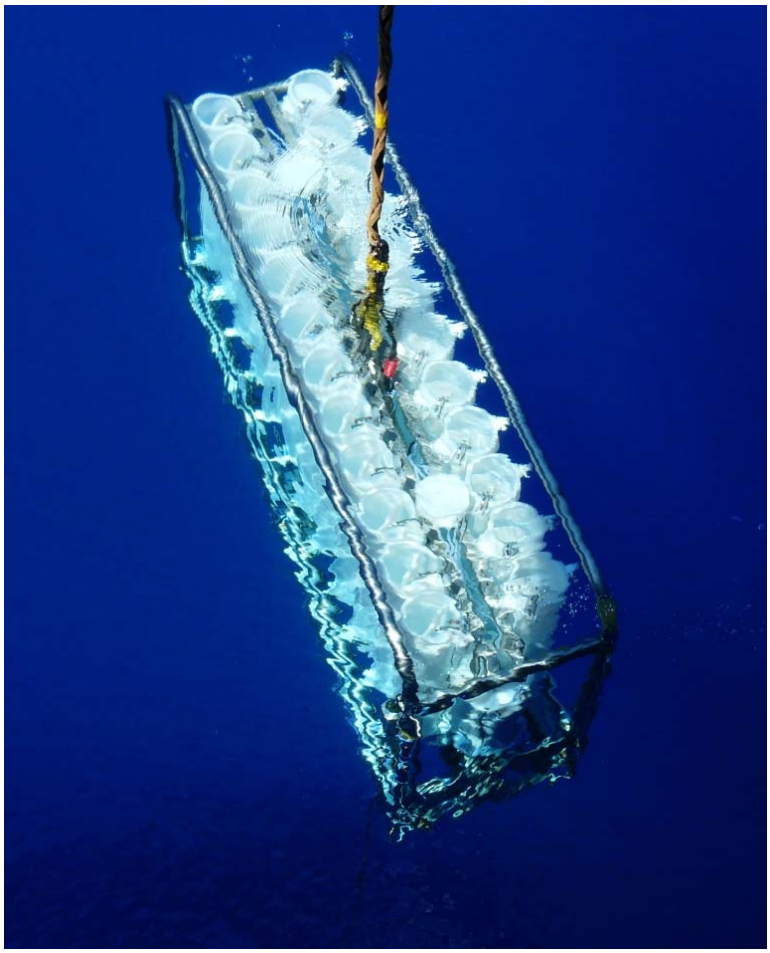
Cruise report 64 PE 321 on RV Pelagia

GEOTRACES West Atlantic leg 2

Bermuda 11-06-2010 to Fortaleza (Brazil) 08-07-2010

Micha J.A. Rijkenberg

With contributions of participants



Royal Netherlands Institute for Sea Research

Acknowledgements

On behalf of all participants I want to thank captain Bert Puijman for his help, advice and hospitality on his ship Pelagia. The crew of Pelagia consisting of Cynthia Everduin, Marco Frankfort, Roel van der Heide, Fred Hiemstra, Klaas Kikkert, Paul Lancel, Arend Nieboer, Ger Vermeulen, José Vitoria and Martien de Vries helped whenever and wherever necessary. They made our stay on Pelagia a very convenient and happy time. Also the help of the NIOZ ICT department during the cruise and the help with data management after the cruise by Hendrik van Aken and the data management group was appreciated. We acknowledge ZKO (project number 839.08.410) for funding of this work.

Front page: the new ultraclean CTD frame with 24 27L PVDF samplers with open butterfly lids underwater (picture of Micha Rijkenberg).

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Cruise summary

Research cruise

The Geotraces West Atlantic cruise leg 2; 64PE321 on RV Pelagia started 11 June 2010 departing from St George (Bermuda) and ended in Fortaleza (Brazil) on 07 July 2010 with Micha Rijkenberg (Royal NIOZ) as chief scientist.

Cruise narrative

During leg 2 of the Geotraces cruise a total of 22 stations were conducted of which 1 was a test station (st 20), 14 normal stations (st 22, 24, 25, 27, 28, 29, 31, 32, 34, 35, 37, 38, 39, 41), 4 superstations (st 23, 26, 33, 40) and 3 were hyperstations (st 21, 30, 36) (Figure 1). A test station was conducted to check system performance and to rinse the UC CTD. Normal stations typically consisted of 1 CTD 25L and 1 UC CTD to the bottom. Superstations were defined by the additional use of *in situ* pumps and the sampling of Pa/Th. Hyperstations consisted typically of 2 x CTD 25 L to the bottom, 2 x UC CTD to the bottom, 1 shallow (~500 m) CTD 25L cast and the use of the *in situ* pumps.

The ship stayed at UTC (-3) throughout the cruise. The slightly curved cruise track resulted from the optimization of the amount of station time relative to the amount of steaming time necessary to reach our final destination, Fortaleza (Brazil), while staying outside the exclusive economic zones of a large diversity of Caribbean and South American countries.

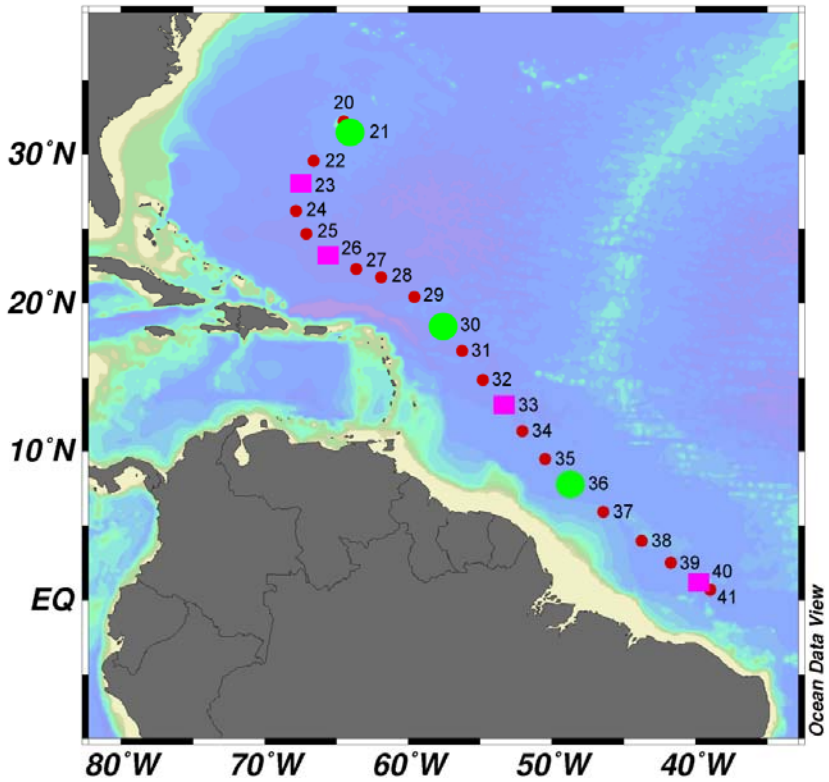

Figure 1: The cruise track of 64PE321, red circles indicate normal stations (station 20 was a test station), pink squares indicate superstations and green circles indicate hyperstations.

RV Pelagia departed from St George (Bermuda) on the 11th of June to take in fuel at Carcer (Bermuda). RV Pelagia left Bermuda on the 12th of June. That same afternoon a test station (st 20) was carried out to test both rosette systems and to clean the UC CTD. From experience during 64PE319 we knew that one rinse is sufficient to clean the UC CTD with respect to trace metals such as iron (Fe), aluminium (Al) and manganese (Mn). The first hyperstation (st 21), at the Bermuda Atlantic Time-series Study site (BATS), started that same day. BATS was originally planned for the first leg of Geotraces (64PE319) but was cancelled due to storm. The importance of station 21 (BATS) lay in its function as a cross over station for various GEOTRACES cruises resulting in opportunities for inter-comparison of a diverse set of parameters. Hyperstation 36 was a cross-over station with RV Meteor cruise M81/1 (GEOTRACES cruise A11, 4th February until 8th March 2010, chief scientist M. Frank, IFM-GEOMAR, Kiel). The location choice of hyperstation 30 was based on the equal distance between this station relative to station 21 and station 36. The location choice of the superstations, i.e. the use of *in situ* pumps, was simply based on the creation of a regular sampling pattern.

The weather conditions were excellent during the whole expedition. During the first week the wind force was about 3 Beaufort, see Figure 2. On 18/06/2010 we entered a region influenced by the trade winds with wind forces between about 4 and 5 Beaufort.

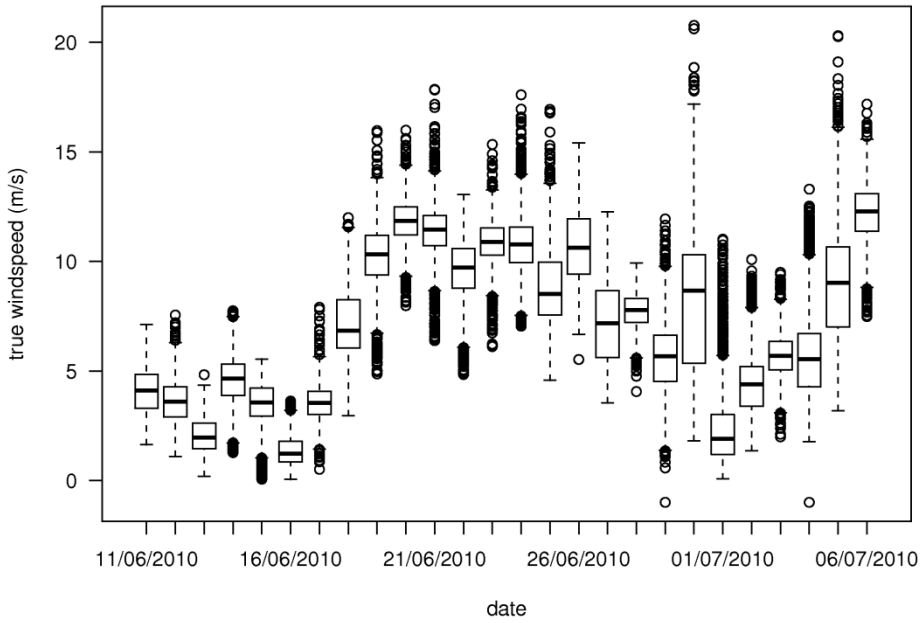

Figure 2: Boxplot of the true windspeed (m/s) during 64PE321.

The air temperature increased within a few days after the start of the cruise from about 23-24°C to about 28°C, see Figure 3. As a consequence high volume samples collected in inferior containers were lost due to leakage after a temperature related increase in pressure. To prevent further sample loss high volume samples were as much as possible stored inside air-conditioned parts of the ship or inside temperature controlled containers. In the future, it is advised that the quality of the high volume sample containers is tested before being used on board.

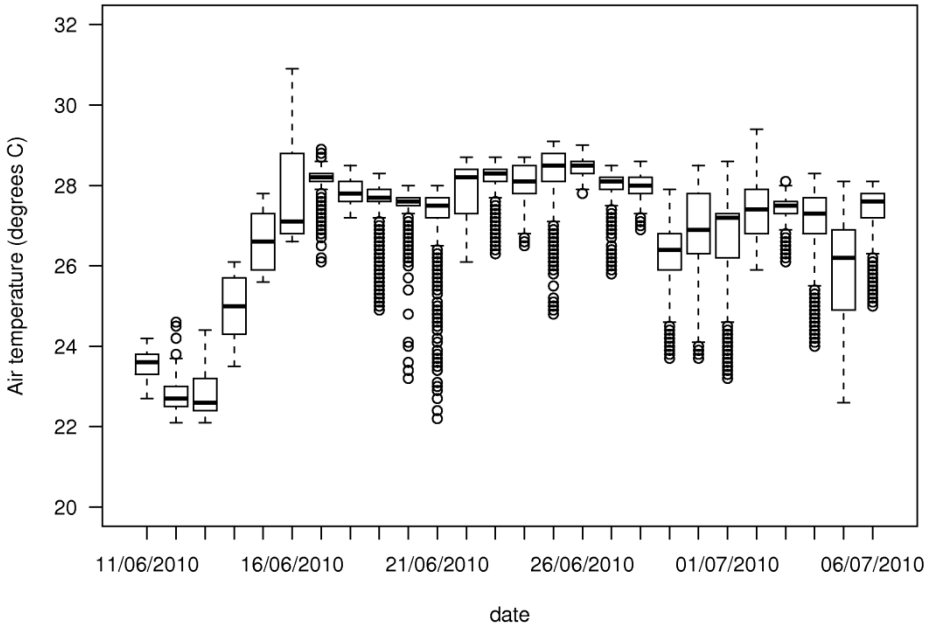

Figure 3: Boxplot of the air temperature (°C) during 64PE321.

An interesting aspect of leg 2 was our encounter with water masses consisting of seawater mixed with Amazon river water. Although the mouth of the Amazon is located at the equator, the first encounter of low salinity surface waters with a green-black color (Figure 4) was at latitude ~ 17°N - 13°N (st 31, 32, 33), see Figure 5. A second encounter with surface waters affected by Amazon river input was at latitude 6°N-4°N (st 37, 38).

Figure 4: On the left clear blue surface seawater at 28°05'N and 67°30'W and on the right the green black surface seawater affected by Amazon river outflow at 05°55'N and 46°25'W.

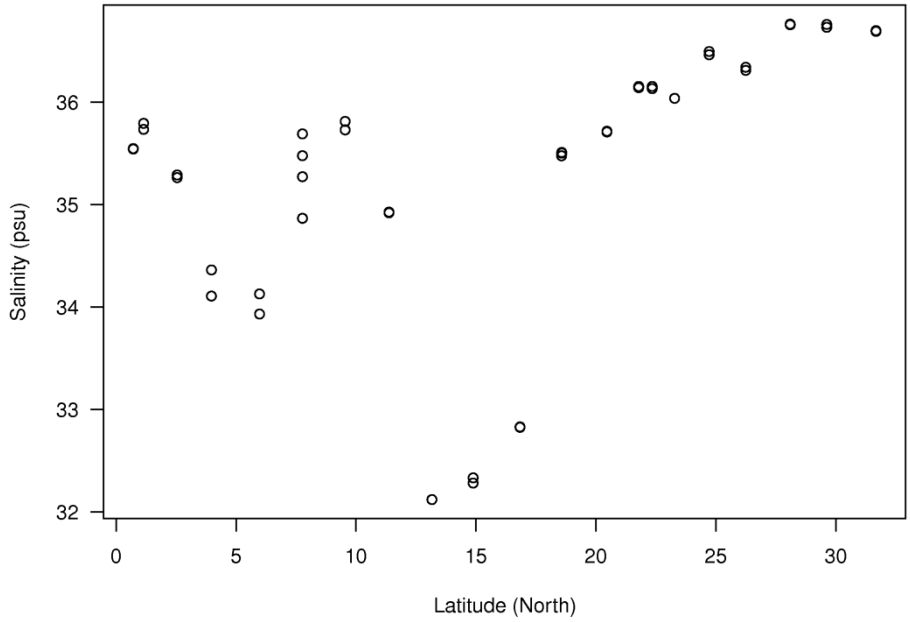

Figure 5: Salinity at 10 m depth in relation to latitude during 64PE321. Data from bottle #24 of the UC CTD and the CTD 25L frames.

Overall, the second leg of the Geotraces cruise with Pelagia was a successful cruise with many samples taken and all planned stations executed.

Description of sample equipment and deployment

On board we used two rosette systems. Both systems were deployed to deep ocean waters by a 17.7 mm diameter Kevlar hydrowire with seven independent internal signal/conductor cables (Cousin Trestec S.A.) that were controlled onboard. One rosette system was used for ultra clean trace metal sampling and consisted of an all-titanium frame with 24 sample bottles of 27 L each made of PVDF plastic (UC CTD; UCC in the cruise summary file). Sampling of the UC CTD occurred in a class 100 clean-room container (de Baar et al., 2008). The second rosette system consisted of 24 new Niskin-type samplers of 25L each mounted on a new stainless steel rosette sampler (CTD 25L, ROS in the cruise summary file). Seven *in situ* pumps (AWI) were used for the collection of particulate matter. Underway surface seawater sampling was executed by pumping seawater into a trace metal clean laboratory container using a Teflon diaphragm pump connected by an acid-washed braided PVC tubing to a towed fish positioned at approximately 3 m depth alongside the ship. The fish was deployed daily, typically just before or after a station. Other parameters measured underway were the navigation parameters, weather parameters and sea-surface water temperature. Salinity was measured but due to technical problems not logged in Casino (the ships monitoring system of underway parameters, e.g. wind, water & air temperature, salinity etc.) and as a consequence the data was lost. Aerosol samples were taken by two aerosol samplers on the top deck of Pelagia. For more details see section 2.2 for the list of parameters, and appendix 2 Station list and Devices list.

Challenges during the deployment of the equipment included: i) failing conductivity, temperature and oxygen sensors due to problems with a cable on the CTD 25L system (st 21, 23), ii) at station 24 the CTD 25L touched the bottom resulting in atypical nutrient values for some Niskin bottles, and iii) failing data logging of the SBE21 system by Casino from

11/07/2010 to 15/07/2010 and after electricity problems on 01-02/07/2010. Furthermore, due to the high centre of gravity of the UC CTD, a danger exists that the UC CTD frame topples sideways during rough weather. However, such adverse weather conditions were not encountered during the second leg of Geotraces.

1. General introduction of the GEOTRACES project

The goal of the GEOTRACES project is 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) Trace elements and isotopes of the international GEOTRACES program

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.

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

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.

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.**

The 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. Afterwards 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

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 an unrecognized source of dark ocean 'primary productivity'.

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.

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.

D) Ocean Biogeochemical Climate Modelling

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.

References

de Baar, H.J.W., Timmermans, K.R., Laan, P., De Porto, H.H., Ober, S., Blom, J.J., Bakker, M.C., Schilling, J., Sarthou, G., Smit, M.G. and Klunder, M., 2008. Titan: A new facility for ultraclean sampling of trace elements and isotopes in the deep oceans in the international Geotraces program. Marine Chemistry, 111(1-2): 4-21.

2. Participants and parameters

2.1. List of participants

1	**Micha Rijkenberg PI**	NIOZ; BIO-Chemical Oceanography
2	**Sander Asjes**	NIOZ; MTEC
3	**Karel Bakker**	NIOZ; GEO
4	**Merce Bermejo**	Universitat Autònoma de Barcelona
5	**Marie Boyé**	LEMAR IUEM
6	**Daniele de Corte**	NIOZ/RuG
7	**Santiago Gonzalez**	NIOZ; BIO-Chemical Oceanography
8	**Steven van Heuven**	Ocean Ecosystems, Univ.Groningen (RuG)
9	**Patrick Laan**	NIOZ; BIO-Chemical Oceanography
10	**Oliver Lechtenfeld**	AWI
11	**Rob Middag**	NIOZ; BIO-Chemical Oceanography
12	**Kerstin Olbrich**	University of Vienna
13	**Viena Puigcorbé**	Universitat Autònoma de Barcelona
14	**Lesley Salt**	NIOZ; BIO-Chemical Oceanography
15	**Patrick Schmidt**	University Bremen (UB)
16	**Veronique Schoemann**	NIOZ; BIO-Chemical Oceanography
17	**Eva Sintes**	University of Vienna
18	**Leon Wuis**	NIOZ; MTEC
19	**Taichi Yokokawa**	NIOZ; BIO-Chemical Oceanography

For complete addresses and email see Appendix 1

Figure 6: Scientists and crew of GEOTRACES leg 2 (64PE321) on the RV Pelagia in the East Atlantic Ocean.

2 .2. List of parameters

sample equipment & parameters	collected by	responsible for analysis and data
UC CTD (UCC)		
Library metals totals	P. Laan	P. Laan, H de Baar
Library metals dissolved	P. Laan	P. Laan, H de Baar
Nuts	K. Bakker	K. Bakker
unfiltered Fe	P. Laan	P. Laan, L Gerringa
Fe	P. Laan	P. Laan, M. Rijkenberg
Mn	R. Middag	R. Middag
Al	R. Middag	R. Middag
Fe ultra filtration	M. Rijkenberg	P. Laan, M. Rijkenberg
Fe Speciation	V. Schoemann, M. Rijkenberg	L. Gerringa
Ag	P. Laan	E. Achterberg
Pt	P. Laan	A. Cobelo
Co, Zn, Cd	M. Boye	M. Boye
Co-speciation	M. Boye	M. Boye
Cd Isotopes	P.Laan	M. Rehkamper
Nd	P.Laan	T. van Flierdt/M. Frank
234 Th	V. Puigcorbe	V. Puigcorbe, M. van der Loeff
210Pb and 210Po	V. Puigcorbe, M. Bermejo	P. Masque
DOM	O. Lechtenfeld	O. Lechtenfeld
Si-isotopes	P. Laan, R. Middag	L. Pichevin
T Fe and Zn isotopes	V. Schoemann	J. de Jong, V. Schoemann
DFe and Zn isotopes	V. Schoemann	J. de Jong, V. Schoemann
Fe, Cu, Zn	V. Schoemann	J. de Jong, V. Schoemann
14C/13C	S. van Heuven, L. Salt	H. Meijer

25 L CTD (ROS)

CFC	P. Schmidt		R. 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	O. Lechtenfeld		O. Lechtenfeld
DON / FDOM	S. Gonzalez		
Nutrients	K. Bakker		K. Bakker
nitrate isotopes	K. Bakker		D. Sigman
BA / Vir/ Abundance	D. De Corte		D. De Corte
3H-Leu / Bacterial prod.	T. Yokokawa		T. Yokokawa
14C-DIC / Archaeal Prod.	S. Gonzalez		T. Yokokawa
3H-FISH	T. Yokokawa		T. Yokokawa
14C-FISH	S. Gonzalez		T. Yokokawa
FISH	D. De Corte		T. Yokokawa
DNA	T. Yokokawa		T. Yokokawa
POC	T. Yokokawa		T. Yokokawa
Nitrification/NH3	T. Yokokawa		T. Yokokawa
Burst Size	D. De Corte		D. De Corte
Viral production/Decay	D. De Corte		D. De Corte
qPCR Nitrifiers	K. Olbrich		P. Berube
Enzymatic activity	E.Sintes/ K. Olbrich		E. Sintes
230Th and 231Pa	M. Bermejo		M. Rutgers van der Loeff
226 Ra	V. Puigcorbe, O. Lechtenfeld		M. Rutgers van der Loeff
Ac Ra, Cs (large-volume)	V. Puigcorbe, M. Bermejo	Ac	P. Masque, M. Rutgers vd Loeff, W. Geibert
		Ra	P. Masque, M. Rutgers vd Loeff
		Cs	P. Masque
Pu, Cs, Np (20L)	V. Puigcorbe, M. Bermejo		T. Kenna
I-129 and Tc	V. Puigcorbe, M. Bermejo		P. Masque

In Situ Pumps

230Th and 231Pa, partic.	O. Lechtenfeld, P. Schmidt	231Pa 230Th	M. Rutgers van der Loeff
we try to save a fraction for Nd		eps Nd	T. vd Fliert
		biogenic opal	M. Rutgers van der Loeff
		carbonate	M. Rutgers van der Loeff
226Ra/228Ra	O. Lechtenfeld, P. Schmidt		M. Rutgers van der Loeff

Dust collectors

Dust	P. Schmidt, R. Middag	Alex Baker

FISH

Pt	R. Middag	A. Cobelo
Pb-isotopes	R. Middag	M. Rehkamper

3. Analyses and measurements

3.1. General parameters and Data management

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 datafile and of sectionplots 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

Kley France winch

Leon Wuis

Although we did all stations and casts during the Geotraces cruise from Bermuda to Fortaleza there were still some technical problems with the Kley France winch. The first problem was the random loss of electricity caused by failure of an encoder on one of the HF motors. The function of the encoder was to check the turning direction and speed of the winch/motor. After replacement the winch functioned fine again. Another technical problem was the powerpack of the Kley France winch. As a result of problems with the air-conditioning resulting in temperatures over 60°C the electricity equipment failed. The problem with the air-conditioning was solved by thawing of the heat exchanger and removal of the air filters which blocked the air inlet. After these adaptations the powerpack worked fine during the rest of the voyage.

UC CTD and CTD 25L

Sander Asjes

There were several small problems with the seabird system in the beginning of the cruise. At station 21 cast 5 the seabird pump on the CTD 25L stopped working at several depths. The problem was a cable connector which was subsequently replaced. A second problem on 14 June (station 22) translated in several errors occurring in the seabird system of the CTD 25L. Replacement of the interconnection cable between the Kevlar cable and the probe solved these errors.

The UC CTD had no problems at all during the cruise. The CTD 25L didn't have any problems after the replacements of the cable connector and the interconnection cable for the remainder of the cruise.

3.1.3. Nutrient Measurements

Karel Bakker, Laboratory for Nutrient Analysis, Royal N.I.O.Z.

Summary

On this cruise, more than 1000 samples were analyzed on Phosphate, Silicate, Nitrate and Nitrite. Analyses typically were processed within three hours after sampling.

During the cruise there were about 4000 analysis processed on a Seal Analytical QuAAtro Auto-analyzer. The different nutrients were determined colorimetrical as described by Grashoff et all. (1983).

Methods

Samples were obtained from a CTD 25L sampler with 24 bottles of 25 Liter each and an UC CTD with 24 bottles of 27 Liter. All samples were collected directly after the DIC and DOC -sampling in 125 ml polypropylene bottles, and sub sampled unfiltered in the lab container for ^{15}N in glass vials which were immediately frozen at -18° C, (for Patrick Rafter) and for nutrients in 5 ml polyethylene vials. The nutrient samples were analyzed within 3 hours on a Quatro auto-analyzer. Calibration standards were prepared freshly every day diluted from stock solutions of the different nutrients in 0.2µm filtered low nutrient seawater (LNSW). The LNSW is surface seawater depleted for most nutrients, only containing some 0.10uM silicate as background. LNSW is also used as baseline water for the analysis in-between the samples. Each run of the system had a correlation coefficient for 9 calibration points of at least 0.9999. The samples were measured from the lowest to the highest concentration in order to keep carry-over effects as small as possible, so from surface to deep waters. Prior to analysis, in two hours all samples and standards were brought to room temperature of 23° C, concentrations were recorded in µM per Liter at this temperature.

In every run a daily freshly diluted mixed nutrient standard, containing silicate, phosphate and nitrate a so called nutrient-cocktail, was measured in triplicate. Secondly a natural sterilized Reference Nutrient Sample (RMNS Kanso, Japan) containing a known concentration of silicate, phosphate, nitrate and nitrite in Pacific Ocean water, was analyzed in triplicate every run. The cocktail and the RMNS were both used to monitor the performance of the analysis. Finally the RMNS was used to adjust all data to obtain the final data set, so all referred to the same RMNS values for each analysis, and made data comparable to the first leg of GEOTRACES and to other data.

From every station the deepest sample is sub sampled for nutrients in duplicate, the duplicate sample-vials were all stored dark at 4° C, and measured again with the next station, for statistics.

Chemistry

Silicate reacts with ammonium molybdate to a yellow complex, after reduction with ascorbic acid, the obtained blue silica-molybdenum complex is measured at 800nm. Oxalic acid is used to prevent formation of the blue phosphate-molybdenum.
Phosphate reacts with ammonium molybdate at pH 1.0, and potassium antimonyl-tartrate is used as an inhibitor. The yellow phosphate-molybdenum complex is reduced by ascorbic acid and measured at 880nm.
Nitrate plus nitrite (NOx) is mixed with an imidazol buffer at pH 7.5 and reduced by a copperized cadmium column to nitrite. The nitrite is diazotated with sulphanylamide and naphtylethylene diamine to a pink colored complex and measured at 550nm.
Nitrate is calculated by subtracting the nitrite value of the nitrite channel from the NOx value.
Nitrite is diazotated with sulphanylamide and naphtylethylenediamine to a pink colored complex and measured at 550nm.

Described by K. Grasshoff et al, 1983. Methods of seawater analysis. Verlag Chemie GmbH, Weinheim.

Statistics of the analysis of this cruise

In table below; the typical statistics of triplicate analysis on 4 depth-levels taken from the Last CTD Station 41, analyzed in one run:

	PO4	Si	NOx	NO2
UNIT	µmol/L	µmol/L	µmol/L	µmol/L
Surface Bottle 24				
AVERAGE	0.056	0.82	0.01	0.014
STDEV	0.001	0.00	0.00	0.002
CV %	2.05	0.19	44.1	10.4
Surface Bottle 20				
AVERAGE	0.076	0.84	0.07	0.066
STDEV	0.001	0.01	0.00	0.002
CV %	1.32	0.78	2.34	2.27
Bottle 16				
AVERAGE	1.522	9.84	22.93	0.019
STDEV	0.003	0.02	0.08	0.006
CV %	0.17	0.18	0.33	31.6
Bottle13				
AVERAGE	2.350	29.46	35.18	0.011
STDEV	0.004	0.02	0.05	0.001
CV %	0.19	0.08	0.15	5.41
Bottle 1				
AVERAGE	1.363	35.23	20.18	0.009

STDEV	0.002	0.06	0.04	0.002
CV %	0.11	0.17	0.22	27.0

The standard deviation and C.V. of RMNS in-between different runs:

PO4: 0.011 µM C.V. 0.66% of average concentration of 1.650 µM
Si : 0.37 µM C.V. 0.62% of average concentration of 59.86 µM
NOx: 0.122 µM C.V. 0.54% of average concentration of 22.60 µM
NO2: 0.009 µM C.V. 2.38% of average concentration of 0.389 µM

The CV of the duplicate samples (bottle 1's) in-between runs after correction with RMNS

PO4: 0.015 µM C.V. 0.92% at average concentration of 1.60 µM
Si : 0.39 µM C.V. 0.69% at average concentration of 59.95 µM
NOx: 0.12 µM C.V. 0.52% at average concentration of 23.60 µM
NO2: 0.010 µM C.V. 64.7% at average concentration of 0.015 µM

Problems during the cruise

Due to the high temperatures outside the lab container, the air-conditioning had to cool down much more intensively than during leg 1. Those temperature changes caused a long periodic sinus on the results of the first three days near Bermuda, both on the base line as on the measured peaks. By decoupling the contact airflow with the analyzer, by insulation and by blocking the internal fan of the instrument itself, the amplitude of the sinus was reduced to acceptable levels. For PO4 the amplitude went down from +/- 0.02 µM for PO4 and for NO2 to smaller than 0.007 µM, for silicate and nitrate this amplitude was less of a problem because of the observed higher values. However this means that the data of the first 5 stations would need a manual correction for this sinus, and this will be done later at NIOZ.

Remark:

To improve the analysis of the nutrients in the near surface waters (above 200 meter) even further we will use the lower part of the calibration line with the low nutrient standard additions to increase the accuracy.

3.1.4. Dissolved oxygen

Lesley Salt, Steven van Heuven

Water samples were taken from the CTD 25L at every station for the determination of concentrations of dissolved oxygen, in order to calibrate the CTD sensor of that CTD frame. Samples were taken from a minimum of three depths. Additional samples at three depths were taken from the UC CTD to verify the calibration of the UC CTD to the CTD 25L. 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 afterwards, 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 0.9999, with an average standard deviation of the residuals between the calibration line and the calibration standards of ±0.5 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. Technical malfunctions meant that samples from stations 26-29 were unable to be accurately analyzed.

At each station at least one sample was taken in duplicate. The standard deviation (1 S.D.) of circa 20 replicates was 0.85 μmol l^{-1}, after discarding 3 samples with unacceptable replicate differences of >2 μmol l^{-1}. The differences between additional samples taken from the UCC and those sampled from the same depths on the CTD 25L show a standard deviation of 4.7 μmol l^{-1}.

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 20l sample of deep-ocean water, brought to equilibrium with the atmosphere, were analyzed during the cruise. These ‘quality’ controls were measured during three series of analysis to confirm the stock KI concentration. The standard deviation of the difference between these samples and their theoretical values was 0.6 μmol l^{-1} indicating an average 100.4% recovery of oxygen in samples.

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

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 21 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. In addition, unfiltered samples from 12 stations were acidified and stored to determine the total Fe concentrations in the NIOZ laboratory after 6-12 months of dissolution. A cubic meter vessel was filled overnight at the 4th of July. This water will be brought back to NIOZ and can be used as medium for culture experiments or used as calibration water in the future.

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 during the 64PE321 cruise ranged from 66 pM in the oligotrophic surface waters up to 2.03 nM in the deep water and some high surface areas. The standard deviation varied between 0% and 12% (the latter being exceptional), but was on average 2.1% 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 0.008nM±0.009nM and was defined as a sample loaded for 5 seconds and measured daily. The average limit of detection was determined at 0.013nM±0.0nM and was defined as 3*standard deviation of the mean blank and measured daily. To better understand the day to day variation duplicate samples were measured after at least 24h 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 is uncorrected for this day to day variation. The consistency of the FIA system over the course of the day was verified using a drift standard. Drift has been observed and seemed to be variable from day to day. All data will be corrected for this daily drift after the cruise and all results so far are not corrected. A certified SAFe

standard (Johnson et al. 2007) for the long term consistency and absolute accuracy was measured on a regular basis.

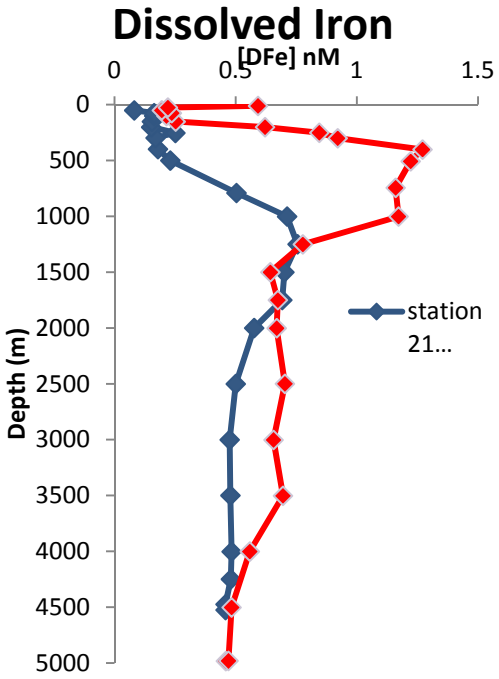

Figure 7: Profiles of dissolved iron versus depth.

Preliminary results

Figure 7 shows 2 depth profile obtained during the 64PE321 cruise. Station 21 is a profile sampled at the Bermuda Atlantic Time series Study (BATS) station. Low surface values and a minor subsurface maximum corresponding with the oxygen minimum zone. Station 33 is more south and has a surface maximum which corresponds to the low salinity Amazon outflow water. Also the oxygen minimum zone have been shifted more to the surface and increased relative to the BATS station.

We have had a lot of problems during the cruise with the temperature controlled laboratories and during this cruise drift in the analyses during the day was observed. Data presented here is not corrected yet for this drift. This will be done in the home laboratory. It is extremely important to maintain a constant temperature during the analyses.

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

DFe consists of several distinguishable and measurable fractions such as a truly soluble Fe fraction (Fe(III) and Fe(II)), a truly soluble organically complexed Fe fraction and a colloidal Fe fraction. 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 0.2 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 (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 at hyperstations (Table 1).

Table 1) Water column samples taken from the ultraclean titanium UC CTD at hyperstations

station	cast	bottles	filter	sampled for
21	1	2, 4, 6, 8, 9, 11, 14, 16, 20, 22, 24	0.02 & 0.2 µm	DFe
21	1	2, 4, 6, 8, 9, 11, 14, 16, 20, 22, 24	1000 kDa	DFe & FeL
30	1	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23	1000 kDa	DFe & FeL
36	1	1, 3, 5, 7, 9, 11, 13, 15, 17, 19, 21, 23	1000 kDa	DFe & FeL

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

Véronique Schoemann, Micha Rijkenberg, Patrick Laan and Loes Gerringa

Introduction

Iron limits primary production in up to 40% of open ocean waters. The distribution and biological availability of Fe in seawater is strongly controlled by its physical-chemical speciation, for which colloids and Fe-organic complexes are playing key roles. In order to study the distribution of chemical species of Fe, the chemical speciation is determined in two different size fractions, the <0.2 µm and the <1000kDa filtered fractions over the whole water column. Special attention was given to sample the Amazon plume during the present GEOTRACES Western Atlantic cruise leg 2 (64PE321).

Sampling

Samples were collected along the whole water column (12-14 depths from surface to bottom) with the NIOZ Titan ultraclean UC CTD at stations 21 (BATS station), 24, 26, 30, 32, 36, 38 and 40. Some additional surface water samples were taken with a towed fish and at station 37, where fresh water inputs were detected by decreased salinities. These samples are complementary to samples that have been processed during the previous GEOTRACES Western Atlantic cruise leg 1 (64PE319).

Method

The samples have been analysed on board of the RV Pelagia, except samples from station 40 and the ultrafiltered (<1000kDa) samples, which are kept frozen until analysis at NIOZ home laboratory. The natural ligand characteristics were determined by applying a complexing ligand titration with addition of iron (from 0 to 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 by cathodic stripping voltammetry (CSV) (Croot and Johansson, 2000). The electrical signal recorded with this method (nA) was converted to a concentration (nM), upon which the ligand concentration and the binding strength will be estimated using the non-linear regression of the Langmuir isotherm (Gerringa and al., 1995).

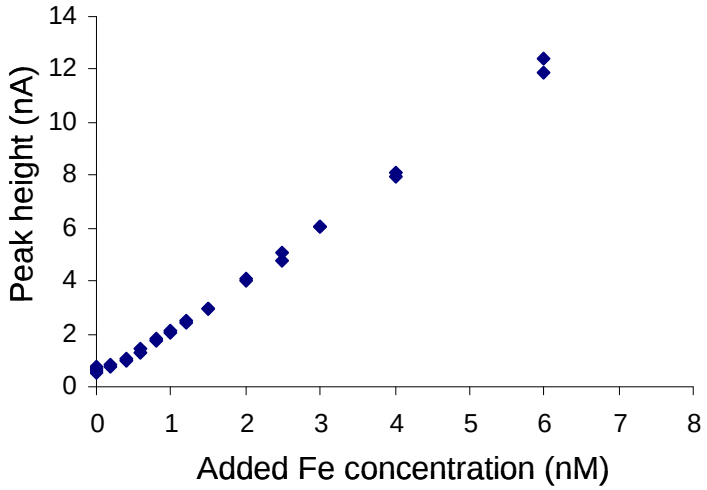
The voltammetric equipment consisted of a µAutolab potentiostat (Type II and III, Ecochemie, The Netherlands), a mercury drop electrode (model VA 663 from Metrohm) and

a new autosampler. All equipment was protected against electrical noise by a current filter (Fortress 750, Best Power).

Results

Results of a titration obtained at station 21 (BATS) is given as an example in Figure 8. The titration data will be further processed at the home laboratory in order to estimate ligand concentration and the conditional binding constant.

Figure 8: An example of titration obtained at station 21.



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3.2.A.4. Dissolved Al and Mn

Rob Middag

Introduction

Dissolved Al is a trace metal with a scavenged-type distribution and an extreme difference between the extremely low concentrations in the North Pacific and the elevated concentrations in the North Atlantic; varying by greater than two orders-of-magnitude (Orians

and Bruland, 1985). The distribution of dissolved Al in surface waters of the open ocean is influenced by atmospheric dust inputs (Measures et al., 2008) and variations in the intensity of removal by scavenging. The surface distribution of dissolved Al can potentially be a tracer of atmospheric Fe inputs. For Al there is no known biological function within the cell, but it has been shown Al is 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 liter 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 chemoluminescence 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 liter 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 high in the surface waters south of Bermuda (> 40 nM) and decreased in the southward direction towards the Amazon plume with values around~25 nM. There was an mid depth minimum of Al around 1000 m depth, followed by and increase with depth to concentrations of Al of around 25 nM. In the deepest bottom waters concentrations

of Al decreased again below 20 nM (see Figure 9). A subsurface maximum was observed in the northern part of the transect between 200 and 500 meter depth.

Concentrations of Mn were elevated in the surface waters with concentration >3 nM, also in the Amazon plume. With depth the concentrations of Mn decreased to low concentrations in the deep basin (see Figure 10). Lowest concentrations of Mn (<0.1 nM) were found in the deepest bottom waters.

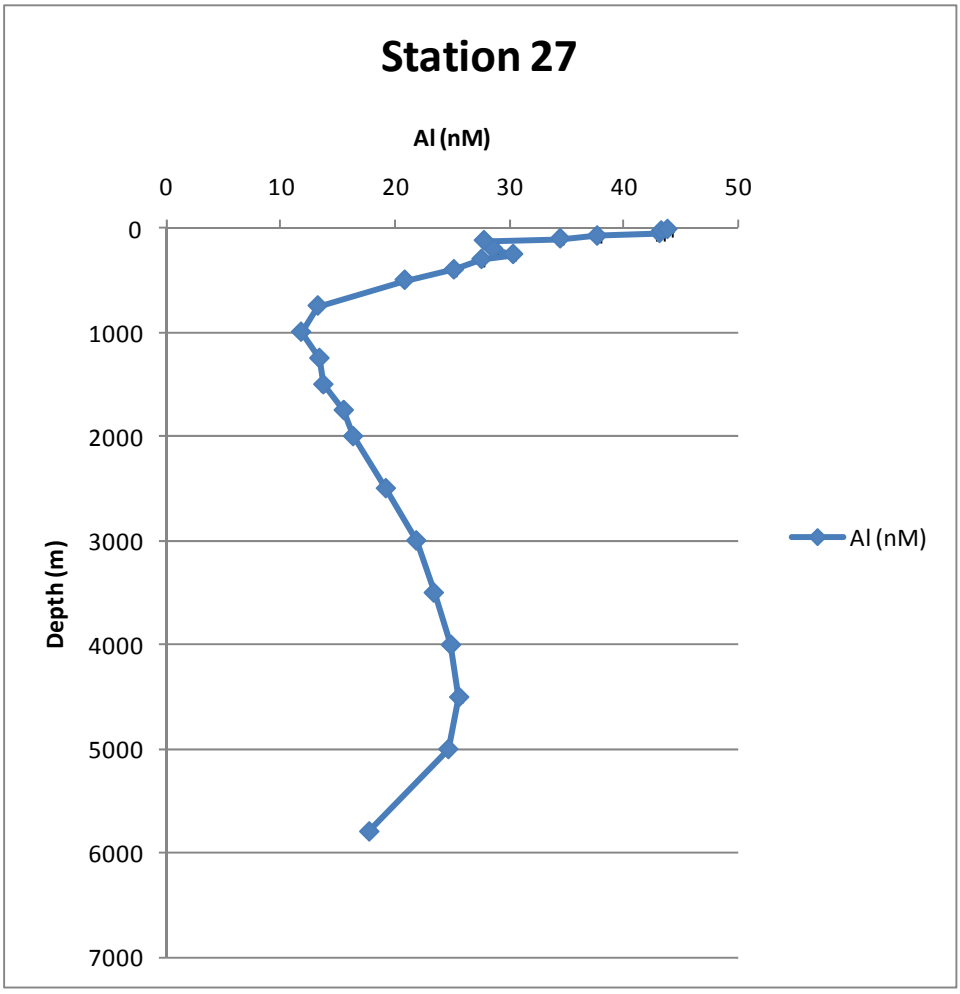

Figure 9. Dissolved Al (nM) versus depth (m) at station 27. Error bars represent standard deviation of triplicate measurement (~1%).

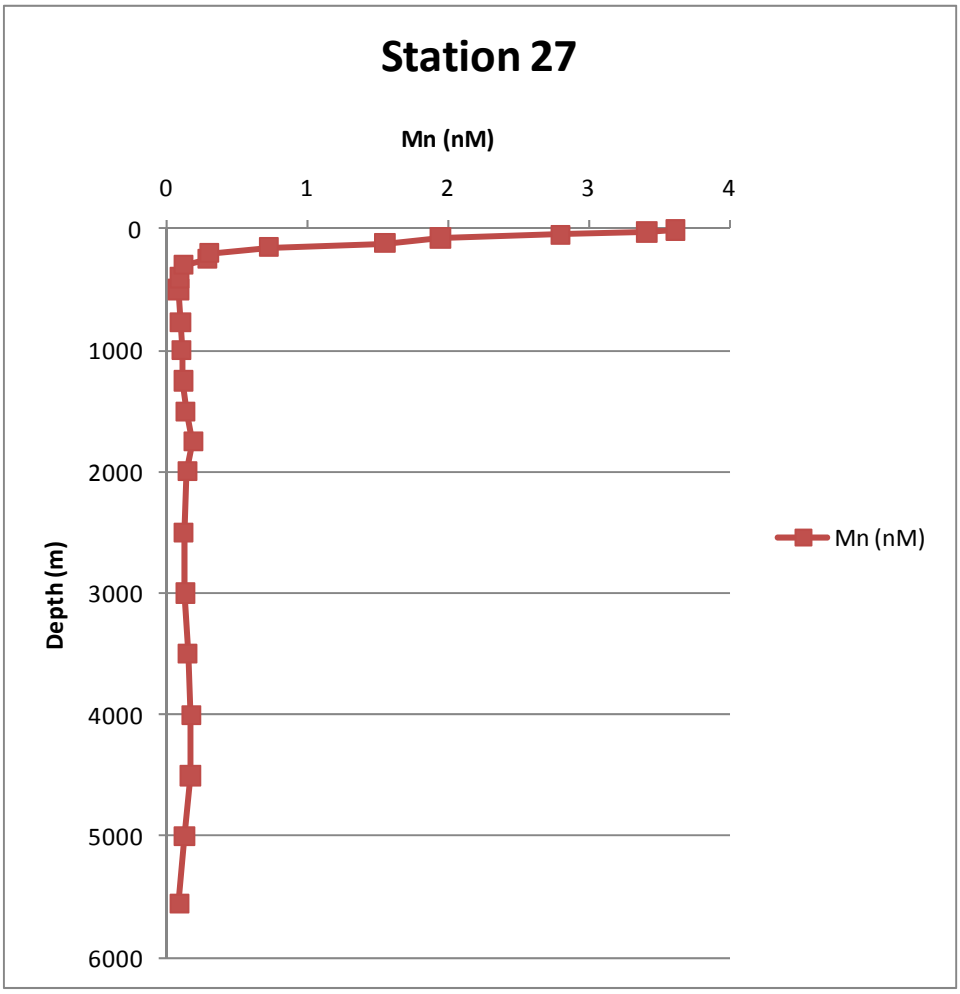

Figure 10. Dissolved Mn (nM) versus depth (m) at station 27. Error bars representing standard deviation of triplicate measurement are not visible on this scale (~1%).

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

Rob Middag

Introduction

The input of airblown 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

In total 22 trace metal and 22 major ion filters were collected.

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 °C freezer.

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

Véronique Schoemann[2], Jeroen de Jong[1,2], Nadine Mattielli[1],

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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 their 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.

In order to study the distribution and behavior of iron, zinc and their isotopes in seawater in the western North Atlantic, samples have been collected at three stations along a north-south transect during the GEOTRACES Western Atlantic leg 2 (64PE321) onboard the RV *Pelagia*. Those samples complement a set of samples previously taken during the GEOTRACES Western Atlantic leg 1 (64PE319). Iron and zinc concentrations will be measured along three whole water column profiles and iron and zinc isotopic composition will be determined at six selected depths of two of the 3 sampled stations. We hope to shed some light on isotopic signatures of biological processes e.g. autotrophic/heterotrophic uptake and remineralization; or abiotic processes, such as physico-chemically driven dissolution/precipitation processes associated with atmospheric input, river input, organic complexation, oxygen minimum, sediment redox processes. Special attention was given to sample Amazon influenced surface seawater.

Sampling for TM concentration measurement.

Water column samples were collected at 21 to 24 depths at stations (Nos. 21, 23 and 30) 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 closeable end caps.

Inside a class 100 clean air van, 250 mL sub-samples for total dissolvable (unfiltered) and dissolved (filtered) iron 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 liter of sample) with subboiling (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 µm pore size 142 mm diameter polycarbonate membrane filter with 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

TM concentrations. Iron and zinc concentrations will be measured 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 recently 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. The cobalt cycle in the North West Atlantic

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Introduction

Cobalt (Co) is among trace metals selected in the GEOTRACES Science Plan an essential micronutrient. Its internal cycle is described by combining a nutrient-like cycling like that of major nutrient phosphate, with additional (versus P) removal of Co from deep waters by a scavenging term (Saito and Moffett, 2002 ; Ellwood, 2008). At times it displays surface-water depletion indicative of biological utilization, such as in the oligotrophic central Atlantic (Saito and Moffett, 2002). It also correlates with phosphate there (Saito and Moffett, 2002) where the cobalt uptake relative to phosphate uptake is more than an order of magnitude higher in the surface waters than in the northeast Pacific (Martin and Gordon, 1988; Martin et al., 1989). This implies an increased biological importance of cobalt in the oligotrophic Atlantic. Its cycle in the deep ocean can be controlled by the competition between its scavenging removal on settling particles and its stabilization in solution by the complexation with organic Co(III)-binding ligands. In surface waters the organic complexation of cobalt may also serve to stabilize dissolved Co, preventing its microbial co-oxidation with manganese, an important removal pathway for cobalt in coastal environments (Moffett and Ho, 1996), and slowing down its scavenging process on settling particles. Among the potential external sources of Co in the section, the natural dust input may be an insignificant Co source in the Sargasso Sea (Saito and Moffett, 2002), unlike any input of anthropogenic aerosols (Thuróczy et al., 2010). Reversely the plume of the Amazon spreading northward is potentially an important source of Co into the surface waters of the section similarly to the Hudson River Estuary in the northeast American coast (Tovar-Sanchez et al., 2004). Furthermore increase of cobalt concentrations in the northward flow of the Gulf Stream along the south-eastern American continental shelf waters has been reported (Windom and Smith, 1972). Hence the transportation from continental shelf and slope waters towards the open ocean may be an additional external source of Co along the section. Next the deep section will reveal internal processes of the Co cycle such as remineralisation and scavenging, as well as external inputs by reductive dissolution within sediment and diffusion into overlying bottom waters. Finally the cobalt concentrations in the well characterized water masses crossed along the section, such as NADW, AAIW, AABW, will be compared to their levels in the source region of these waters. This will reveal Co dynamics over water-masses transportation in deep oceans.

Field work

Cobalt was sampled in the waters using the ultraclean sampling facilities of NIOZ for trace metals and several other variables, with ultraclean 24 large volume (27 L) samplers on TITAN a titanium frame with CTD and other sensors for oxygen, light transmission (inverse for particles abundance), and a clean container holding the UC CTD frame.

Dissolved cobalt was sampled at 15 deep casts among the 20 hydrocasts achieved along the section from Bermuda to the Equator. Unfiltered samples later used to estimate particulate Co (as the difference between unfiltered and filtered fractions) and samples to determine the organic speciation of cobalt were sampled at 9 hydrocasts. The vertical resolution for the three parameters was 12-14 depths throughout the whole water column.

Dissolved cobalt was measured directly on board at 9 deep casts in filtered (0.2 µm), acidified (pH~1.9-2) and UV-digested samples by FIA-Chemiluminescence method with toyopearl preconcentrating column and acidified ammonium acetate (pH 4) as a column conditioning step prior to the sample loading and the rinse steps, following the method adapted by Shelley et al., 2010 (after Cannizzaro *et al*., 2000). Concentrations were estimated by two daily calibrations made at the start and the end of a series of samples. The accuracy of the method was evaluated by determining dissolved cobalt in acidified North Pacific deep and surface seawater samples from the Sampling and Analysis of Iron (SAFe) program. The method yields mean values of 2 ± 0.2 pM in surface and 24.3 ± 3 pM in deep which is in excellent agreement with the SAFe consensus values of 2.7 ± 1.3 pM and 26.9 ± 4.7 pM, in surface and deep reference waters respectively. BATS station was sampled in the complete water column (e.g., 24 depths) where DCo will be analysed by J. Bown back to the home lab and intercalibrated with published distributions of cobalt recorded at this time serie (Saito and Moffett, 2001 ; Shelley et al., 2010 ; Milne et al., 2010).

Total dissolvable cobalt will be analysed in the unfiltered, acidified and UV-digested samples within the 6-12 coming months in the home lab by FIA-Chemiluminescence method (Shelley et al., 2010).

The organic speciation of Co will be measured in the home lab in filtered (0.2 µm) and frozen- stored samples (-20°C) by Cathodic Stripping Voltammetry after Ellwood *et al.* (2005; 2001).

Preliminary results

Dissolved cobalt distribution at depth suggested low surface value in the euphotic layer (<6 pM), an increase of cobalt concentrations in the oxygen minimum zone to maximum values at depth and either a decrease towards deep waters or an uniform concentration at around 55-60 pM.

The plume of Amazon may represent a significant source of dissolved cobalt in the thin surface layer of fresh waters offshore with a DCo signature of 15-20 pM (Figure 11) as compared to < 6 pM in surface at stations not impacted by Amazon waters. Furthermore it seemed to be no strong evidence of an atmospheric input of Co along the section.

DCo was typically ranging between 55 and 60 pM in the core of AAIW (Figure 11). In deeper waters DCo was about 50 pM in NADW (Figure 11), possibly without showing a meridian trend. In the Antarctic Bottom Waters DCo was lower than in overlying deep waters, typically of ~20 pM (Figure 11).

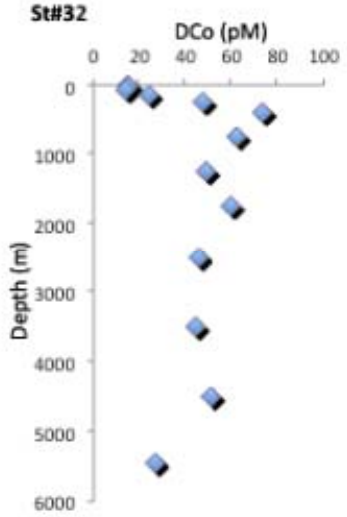

Figure 11 – Distribution of dissolved cobalt (pM) at depth (m) at Station#32.

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3.2.A.8. Natural and anthropogenic radionuclides.

Viena Puigcorbé, Mercè Bermejo, Oliver Lechtenfeld

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).

^{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 CTD 25L) 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 vd 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 fiber. 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 radionuclides

The anthropogenic radionuclides ^{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 behaviors 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

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

Total ^{234}Th: *Viena Puigcorbé*

The water samples were analyzed 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%). For stations 29 and 36 higher resolution profiles of 15 depths were done. 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. 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 27 we collected 5 deep samples (3000m) in order to be able to do the calibration. At this depth ^{234}Th and ^{238}U should be in secular equilibrium, which 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.

POC/^{234}Th ratios: *Oliver Lechtenfeld and Viena Puigcorbé*

For the determination of the POC/^{234}Th ratio on sinking particles we collected >50 µm particles at the export depth of 100m at all deployments of the in situ pumps. 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 CTD 25L from 100-150m 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.

Total ^{210}Po/^{210}Pb: *Viena Puigcorbé*

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 3 profiles of 10 depths each and 2 profiles of 15 depths. 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 10L cubitainers and, after tapping the water, they were acidified with 20 mL of hydrochloric acid (32%). A ^{209}Po spike was added, along with a Pb^{2+} spike and a Fe^{3+} carrier. After that we waited 12h for the equilibration before we raised the pH to 8.5 adding ammonia. After the precipitation, the water was removed until they were able to be transferred to a smaller bottles (250mL) and then they were stored until the arrival to Universitat Autònoma de Barcelona (UAB) were later processing steps will be realized and they will be measured by alpha spectrometry.

^{231}Pa and ^{230}Th : *Mercè Bermejo and Oliver Lechtenfeld*

Dissolved ^{231}Pa and ^{230}Th *Mercè Bermejo*

Samples for dissolved ^{231}Pa and ^{230}Th were collected at 7 stations from the CTD 25L. At each station we sampled 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 analyzed on a ICP-mass spectrometer.

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

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. 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 are very sensitive to moisture in the pump container positioned on deck. To avoid possible malfunctioning a 1.5 kW heater was installed in the container to make it drier. 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 filterhead containing one 0.8 μm supor filter. The programmed pumping duration was 2.5 h. The volume of water that was pumped through the filter was recorded by a flowmeter and varied between 238 and 768 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 filterheads were disassembled from the in-situ pumps and taken to the lab. Before opening the filterhead, the remaining water on the supor filter was sucked off with a water jet pump. Then the supor filter was taken out from the filterhead. Four subsamples were taken from each filter. To avoid contamination the subsampling 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 analyzed by isotope dilution as described in the previous section for dissolved samples.

^{228}Ra and ^{227}Ac: *Viena Puigcorbé, Mercè Bermejo*

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 stations 35 and 38. At 3 "hyper"stations (21, 30 and 36) we have collected large volume samples, varying from 75L at great depths to 125L at shallow depths with the CTD 25L. In addition, we collected at these stations a 120L surface water sample from the ship's seawater supply. To make data management easy and be able to relate the samples, which were collected from the ship's seawater supply, to the environmental parameters measured by the CTD's these samples have been given the cast name corresponding with the cast closets in time to this sample. The water was passed over MnO_2 coated acrylic fiber to adsorb radium and actinium. These samples will be analyzed for Ra isotopes and Ac by delayed coincidence counting and alpha and gamma spectroscopy in the home laboratories. The effluent of the fiber was used for analysis of anthropogenic radionuclides.

Anthropogenic radionuclides: *Viena Puigcorbé, Mercè Bermejo*

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

We collected 20L of unfiltered seawater samples for the analysis of these radionuclides at 5 stations (21, 25, 30, 36 and 39), 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 Texel where they will be sent to Columbia University where Tim Kenna is going to analyze them.

^{129}I

In order to analyze this anthropogenic radionuclide, 3L of water were collected at 10 depths over the water column at 4 stations (21, 25, 30, 36 and 39). The samples were stored without acidifying them.

^{137}Cs

The water used for the analysis of ^{137}Cs at UAB was the effluent of the fiber used to retain Ra and Ac isotopes (explained above). These samples were collected at 3 "hyper" stations (21, 30 and 36). The volume of the three shallower 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 2mL 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 analyzed in the home laboratory.

Preliminary results

^{234}Th activity on in situ pump filters: *Oliver Lechtenfeld*

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.

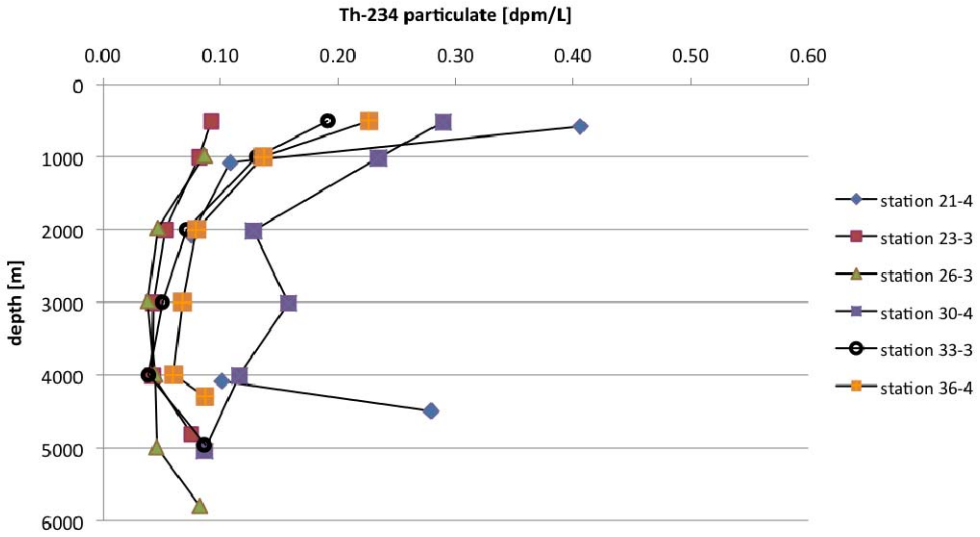

Figure 12. displays the particulate ^{234}Th activities in the water column of all 7 ISP stations. ^{231}Pa/^{230}Th will be determined on the same filter samples at the home lab.

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3.2.A.9. DOM & trace metals

Oliver Lechtenfeld

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 behavior 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 14 stations the Titan team collected for us 0.2 µm filtered samples from the UC CTD at 6 depths: 25 m, 75 m, 250 m, 1250 m, 2000 m and bottom. Once in a while a sample from the towed fish was taken to have an additional surface sample prior or after a CTD station. Total number of samples leg 2: 89. Each time one 0.5 L sample was collected in

LDPE bottles and frozen (-20°C) immediately for the RP-HPLC-ICP-MS study of complexation of trace metals by organic ligands at AWI. A second 0.5 L sample was acidified to pH=2 and passed over a PPL-column to extract DOM. These columns were stored frozen at -20°C for their later analysis with FT-ICR-MS for the molecular-level characterization of DOM. Sampling for DOM was generally coordinated with the sampling for DOC. Total number of DOC samples for leg 2: 331 duplicates.

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3.2.B. CO_2 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 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 a VINDTA 3C (Versatile INstrument for the Determination of Total Alkalinity, designed and built by Dr. L. Mintrop, Marine Analytics and Data, Kiel, Germany). DIC was measured simultaneously on two instruments, referred to as A and B (VINDTA #14 and #17, respectively), however with regard to TA, the majority of stations were only measured on B(17). 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 shallowest ~500m), the remainder of the profile was measured deep-to-shallow. This assured that any 'startup 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 report on the treatment of the carbon data will, in due time, be available as a separate report. On station 40, in addition to the regular sampling scheme, 6 depths were also sampled in triplicate. The samples were stored in 250ml borosilicate bottles and poisoned with 0.125ml of 50% saturated $HgCl_2$ for later, external and further internal, analysis. This will hopefully validate our data further.

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 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.

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. Acid samples were collected for post-cruise determination of acid strength.

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3.2.B.2. pH

Lesley Salt, Steven van Heuven

pH measurements were made spectrophotometrically, using a SAMI 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, which has a throughflow 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 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. At station 40, in addition to regular samples, six depths were taken in triplicate and given the same treatment as regular samples.

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 it is likely that most $^{14}CO_2$ was blown away by the wind. 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, acquired through Blockland Packaging, NL, 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, flushed with ~1-2 times their volume and capped with a ~3% headspace. After collecting, samples and sampling trays were rinsed off with about 2 liters 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 and sampling tubes stored in 0.1M HCl solution and rinsed before use.

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 ΔC14 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.

3.2.B.3. Chlorofluorocarbons

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 418 samples for chlorofluorocarbons (CFC-11 and CFC-12) distributed on 20 deep profiles along the entire section were taken. Water samples from the CTD 25L 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 is 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.

3.2.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

Leg 1 participant: *Thomas Reinthaler[1], Taichi Yokokawa[1,2], Daniele De Corte[1,3]*

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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).

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 CTD 25L bottles into acid rinsed polycarbonate bottles. Filtration and/or fixing of samples was done within 15 min after sampling the CTD 25L.

Particulate organic carbon (TR and TY)

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 (DDC)

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 (TR and Santiago Gonzales, NIOZ)

Immediately after the recovery of the CTD 25L, 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 [14C]-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 microcentrifuge method (TY)

^{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 radioassayed 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 (TR, SG and TY)

The relative abundance and activity of the major prokaryotic groups will be determined by MICRO-CARD-FISH analysis. Fifty milliliters were incubated with 3H-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.htm). 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 (TR and TY)

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 labeled forward and revers 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 (DDC)

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 ultrafiltration 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 (DDC)

To study the viral decay rates, the water samples were filtered through 0.2 μm by tangential flow ultrafiltration. 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.

Ectoenzymatic activity of prokaryotic communities (ES and KO)

The ectoenzymatic activity of prokaryotic organisms was determined adding a specific substrate attached to a fluorochrome to water samples of 6 or 24 different depths. The samples were incubated in the dark at *in situ* temperature during 24-96 h, depending on the expected enzymatic activity. The substrates used were 4-methylumberlliferyl (MUF)-alpha-glucoside, MUF-beta-glucoside, MUF-phosphate and 4-methylcoumarinyl-7-amide (MCA)-

leucineaminopeptide, to assess the ectoenzymatic activity of alpha-glucosidase, beta-glucosidase, phosphatase and leucine-aminopeptidase, respectively. Fluorescence is observed after enzymatic splitting of the substrate and the fluorochrome. The activity of the different enzymes is linearly related to the fluorescence and was detected on the spectrofluorometer using an excitation wavelength 365 nm and an emission of 445 nm. Fluorescence will be transformed to substrate concentrations by using a standard curve in which the fluorochromes (MUF and MCA) were added to 0.2 µm filtered sample water (Acrodisc® Syringe Filter) at concentrations ranging from 2.5 to 100 nM. The cleavage activity will be calculated from the change of each substrate concentration over time.

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.

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Appendix 2. Station list & devices deployment

CTD 25L is the high volume 25L CTD
UCCTD is the ultra clean CTD
ISP are *the in* situ pumps

Station_cast	Device	Action	Date	Time	Latitude	Longitude
20_1	CTD25L	Begin	12/06/2010	19:00:56	32.229178	-64.494357
20_1	CTD25L	Bottom	12/06/2010	19:03:09	32.228985	-64.494135
20_1	CTD25L	End	12/06/2010	19:06:56	32.228735	-64.493522
20_2	UCCTD	Begin	12/06/2010	19:30:48	32.228407	-64.492357
20_2	UCCTD	Bottom	12/06/2010	20:04:15	32.228343	-64.49225
20_2	UCCTD	End	12/06/2010	20:37:48	32.228878	-64.49175
21_1	CTD25L	Begin	13/06/2010	0:53:33	31.666667	-64.166997
21_1	CTD25L	Bottom	13/06/2010	2:07:45	31.666632	-64.166742
21_1	CTD25L	End	13/06/2010	3:37:25	31.666445	-64.166793
21_2	UCCTD	Begin	13/06/2010	3:47:54	31.666845	-64.166795
21_2	UCCTD	Bottom	13/06/2010	5:09:15	31.666875	-64.166407
21_2	UCCTD	End	13/06/2010	6:56:14	31.666765	-64.166395
21_3	CTD25L	Begin	13/06/2010	7:05:38	31.666568	-64.166455
21_3	CTD25L	Bottom	13/06/2010	7:21:02	31.666437	-64.16651
21_3	CTD25L	End	13/06/2010	7:44:48	31.666505	-64.166717
21_4	ISP	Begin	13/06/2010	7:59:14	31.666198	-64.166817
21_4	ISP	Pump started	13/06/2010	10:36:21	31.666537	-64.166395
21_4	ISP	Pump stopped	13/06/2010	13:10:35	31.666768	-64.166143
21_4	ISP	End	13/06/2010	14:59:46	31.666392	-64.166665
21_5	CTD25L	Begin	13/06/2010	15:29:41	31.667057	-64.166432
21_5	CTD25L	Bottom	13/06/2010	16:46:11	31.666657	-64.16657
21_5	CTD25L	End	13/06/2010	17:59:08	31.666578	-64.166558
22_1	UCCTD	Begin	14/06/2010	11:53:29	29.61562	-66.529925
22_1	UCCTD	Bottom	14/06/2010	13:20:28	29.615588	-66.52951
22_1	UCCTD	End	14/06/2010	15:09:36	29.615778	-66.529818
22_2	CTD25L	Begin	14/06/2010	15:19:30	29.615662	-66.529718
22_2	CTD25L	Bottom	14/06/2010	16:42:19	29.615608	-66.52949
22_2	CTD25L	End	14/06/2010	18:30:13	29.615672	-66.529517
23_1	UCCTD	Begin	15/06/2010	11:30:45	28.090858	-67.501617
23_1	UCCTD	Bottom	15/06/2010	12:56:01	28.09188	-67.500755
23_1	UCCTD	End	15/06/2010	14:32:52	28.090815	-67.501965
23_2	CTD25L	Begin	15/06/2010	14:52:07	28.090553	-67.50137
23_2	CTD25L	End	15/06/2010	16:10:01	28.090813	-67.501605
23_3	ISP	Begin	15/06/2010	16:42:11	28.090873	-67.501663
23_3	ISP	Pump started	15/06/2010	19:01:30	28.090752	-67.501462
23_3	ISP	Pump stopped	15/06/2010	21:33:21	28.090645	-67.501497
23_3	ISP	End	16/06/2010	0:10:11	28.090523	-67.50214

Station_cast	Device	Action	Date	Time	Latitude	Longitude
23_4	CTD25L	Begin	16/06/2010	0:22:45	28.090533	-67.501515
23_4	CTD25L	Bottom	16/06/2010	1:38:09	28.090753	-67.50206
23_4	CTD25L	End	16/06/2010	3:17:24	28.090778	-67.501593
24_1	UCCTD	Begin	16/06/2010	14:22:51	26.239138	-67.804632
24_1	UCCTD	Bottom	16/06/2010	15:45:13	26.238773	-67.804327
24_1	UCCTD	End	16/06/2010	17:36:11	26.238722	-67.804268
24_2	CTD25L	Begin	16/06/2010	17:48:28	26.238652	-67.804392
24_2	CTD25L	Bottom	16/06/2010	19:08:52	26.238472	-67.804122
24_2	CTD25L	End	16/06/2010	21:52:28	26.238785	-67.804018
25_1	UCCTD	Begin	17/06/2010	16:21:08	24.714485	-67.072785
25_1	UCCTD	Bottom	17/06/2010	17:52:42	24.714722	-67.072768
25_1	UCCTD	End	17/06/2010	19:49:07	24.714255	-67.072688
25_2	CTD25L	Begin	17/06/2010	19:56:29	24.714313	-67.072607
25_2	CTD25L	Bottom	17/06/2010	21:27:55	24.714622	-67.072758
25_2	CTD25L	End	17/06/2010	23:05:06	24.714745	-67.072838
26_1	UCCTD	Begin	18/06/2010	12:23:55	23.274647	-65.552702
26_1	UCCTD	Bottom	18/06/2010	13:52:59	23.274707	-65.553323
26_1	UCCTD	End	18/06/2010	16:06:49	23.275002	-65.552822
26_2	CTD25L	Begin	18/06/2010	16:13:38	23.274763	-65.552918
26_2	CTD25L	Bottom	18/06/2010	17:48:25	23.274755	-65.553068
26_2	CTD25L	End	18/06/2010	19:34:25	23.274832	-65.55348
26_3	ISP	Begin	18/06/2010	19:43:59	23.274903	-65.553448
26_3	ISP	Pump started	18/06/2010	22:33:08	23.274515	-65.552628
26_3	ISP	Pump stopped	19/06/2010	1:04:07	23.275227	-65.553447
26_3	ISP	End	19/06/2010	3:12:15	23.27468	-65.55336
27_1	UCCTD	Begin	19/06/2010	17:53:53	22.340743	-63.583362
27_1	UCCTD	Bottom	19/06/2010	19:32:32	22.34059	-63.583125
27_1	UCCTD	End	19/06/2010	21:32:26	22.34097	-63.583165
27_2	CTD25L	Begin	19/06/2010	21:44:01	22.341102	-63.583282
27_2	CTD25L	Bottom	19/06/2010	23:15:51	22.340878	-63.583352
27_2	CTD25L	End	20/06/2010	1:09:09	22.340692	-63.583965
28_1	CTD25L	Begin	20/06/2010	14:09:05	21.776198	-61.843225
28_1	CTD25L	Bottom	20/06/2010	15:42:01	21.776427	-61.84375
28_1	CTD25L	End	20/06/2010	17:41:34	21.776398	-61.843107
28_2	UCCTD	Begin	20/06/2010	17:52:04	21.77661	-61.843237
28_2	UCCTD	Bottom	20/06/2010	19:29:36	21.77681	-61.84336
28_2	UCCTD	End	20/06/2010	21:58:00	21.777135	-61.84297
29_1	UCCTD	Begin	21/06/2010	16:48:07	20.455577	-59.532287
29_1	UCCTD	Bottom	21/06/2010	18:14:40	20.454313	-59.530968
29_1	UCCTD	End	21/06/2010	20:14:01	20.454308	-59.530608
29_2	CTD25L	Begin	21/06/2010	20:21:57	20.45435	-59.530822
29_2	CTD25L	Bottom	21/06/2010	20:37:32	20.454195	-59.531023
29_2	CTD25L	End	21/06/2010	21:30:04	20.454407	-59.531003

Station_cast	Device	Action	Date	Time	Latitude	Longitude
30_1	CTD25L	Begin	22/06/2010	14:37:56	18.57224	-57.612363
30_1	CTD25L	Bottom	22/06/2010	14:53:37	18.572495	-57.612353
30_1	CTD25L	End	22/06/2010	15:25:17	18.572743	-57.61215
30_2	UCCTD	Begin	22/06/2010	15:46:57	18.572503	-57.612185
30_2	UCCTD	Bottom	22/06/2010	17:17:41	18.572402	-57.612063
30_2	UCCTD	End	22/06/2010	19:08:16	18.572293	-57.61234
30_3	CTD25L	Begin	22/06/2010	19:19:52	18.57246	-57.612313
30_3	CTD25L	Bottom	22/06/2010	20:42:36	18.572143	-57.612327
30_3	CTD25L	End	22/06/2010	22:34:03	18.572468	-57.611903
30_4	ISP	Begin	22/06/2010	22:52:48	18.572373	-57.612183
30_4	ISP	Pump started	23/06/2010	1:30:43	18.572582	-57.611887
30_4	ISP	Pump stopped	23/06/2010	4:01:01	18.572172	-57.612057
30_4	ISP	End	23/06/2010	5:51:34	18.572283	-57.612093
30_5	CTD25L	Begin	23/06/2010	6:07:21	18.572607	-57.612223
30_5	CTD25L	Bottom	23/06/2010	7:31:18	18.572323	-57.612155
30_5	CTD25L	End	23/06/2010	9:11:39	18.572052	-57.6117
30_6	UCCTD	Begin	23/06/2010	9:33:08	18.564638	-57.60612
30_6	UCCTD	Bottom	23/06/2010	11:07:32	18.56456	-57.60612
30_6	UCCTD	End	23/06/2010	13:13:52	18.56427	-57.605565
31_1	UCCTD	Begin	24/06/2010	11:16:52	16.830833	-56.268777
31_1	UCCTD	Bottom	24/06/2010	12:49:20	16.831883	-56.268383
31_1	UCCTD	End	24/06/2010	14:59:44	16.831218	-56.268187
31_2	CTD25L	Begin	24/06/2010	15:06:50	16.831188	-56.268535
31_2	CTD25L	Bottom	24/06/2010	16:39:29	16.831547	-56.268853
31_2	CTD25L	End	24/06/2010	18:30:00	16.831512	-56.268637
32_1	UCCTD	Begin	25/06/2010	11:37:17	14.880428	-54.802502
32_1	UCCTD	Bottom	25/06/2010	13:01:47	14.879442	-54.803318
32_1	UCCTD	End	25/06/2010	15:00:51	14.879848	-54.802807
32_2	CTD25L	Begin	25/06/2010	15:12:42	14.879908	-54.802893
32_2	CTD25L	Bottom	25/06/2010	16:37:19	14.880128	-54.802965
32_2	CTD25L	End	25/06/2010	18:27:35	14.879842	-54.80308
33_1	UCCTD	Begin	26/06/2010	9:08:54	13.161565	-53.420695
33_1	UCCTD	Bottom	26/06/2010	10:30:42	13.16181	-53.421037
33_1	UCCTD	End	26/06/2010	12:18:22	13.162215	-53.421695
33_2	CTD25L	Begin	26/06/2010	12:25:46	13.16227	-53.421497
33_2	CTD25L	Bottom	26/06/2010	14:35:57	13.161895	-53.420862
33_2	CTD25L	End	26/06/2010	16:31:31	13.16181	-53.42125
33_3	ISP	Begin	26/06/2010	16:51:54	13.161803	-53.421365
33_3	ISP	Pump started	26/06/2010	19:01:29	13.161728	-53.421158
33_3	ISP	Pump stopped	26/06/2010	21:34:35	13.161952	-53.420718
33_3	ISP	End	26/06/2010	23:38:07	13.1619	-53.42102
34_1	UCCTD	Begin	27/06/2010	14:02:17	11.372247	-52.045452
34_1	UCCTD	Bottom	27/06/2010	15:18:53	11.372933	-52.045477

Station_cast	Device	Action	Date	Time	Latitude	Longitude
34_2	CTD25L	Begin	27/06/2010	17:27:08	11.372305	-52.045123
34_2	CTD25L	Bottom	27/06/2010	18:46:52	11.372443	-52.045398
34_2	CTD25L	End	27/06/2010	20:30:46	11.37286	-52.045057
35_1	UCCTD	Begin	28/06/2010	11:09:28	9.54559	-50.468612
35_1	UCCTD	Bottom	28/06/2010	12:23:39	9.545913	-50.469465
35_1	UCCTD	End	28/06/2010	14:07:08	9.546245	-50.468992
35_2	CTD25L	Begin	28/06/2010	14:16:57	9.546235	-50.46864
35_2	CTD25L	Bottom	28/06/2010	15:56:51	9.545448	-50.468977
35_2	CTD25L	End	28/06/2010	17:18:01	9.546268	-50.46935
36_1	UCCTD	Begin	29/06/2010	11:15:49	7.765993	-48.882982
36_1	UCCTD	End	29/06/2010	12:22:55	7.766165	-48.88343
36_2	UCCTD	Begin	29/06/2010	14:14:35	7.766273	-48.88266
36_2	UCCTD	Bottom	29/06/2010	15:25:18	7.766425	-48.883542
36_2	UCCTD	End	29/06/2010	17:05:56	7.766245	-48.88365
36_3	CTD25L	Begin	29/06/2010	17:13:48	7.766358	-48.883647
36_3	CTD25L	Bottom	29/06/2010	18:22:45	7.766662	-48.883463
36_3	CTD25L	End	29/06/2010	19:59:01	7.766253	-48.883463
36_4	ISP	Begin	29/06/2010	22:37:13	7.76588	-48.883563
36_4	ISP	Pump started	29/06/2010	22:37:20	7.76591	-48.883582
36_4	ISP	Pump stopped	30/06/2010	0:53:23	7.766973	-48.88386
36_4	ISP	End	30/06/2010	2:31:01	7.76635	-48.884183
36_4	ISP	End	30/06/2010	2:42:27	7.766008	-48.883045
36_5	CTD25L	Begin	30/06/2010	2:52:35	7.76646	-48.88298
36_5	CTD25L	Bottom	30/06/2010	3:05:12	7.766247	-48.882778
36_5	CTD25L	End	30/06/2010	3:47:48	7.766263	-48.883457
36_6	UCCTD	Begin	30/06/2010	3:58:54	7.766438	-48.883467
36_6	UCCTD	Bottom	30/06/2010	5:10:56	7.766467	-48.88349
36_6	UCCTD	End	30/06/2010	6:55:13	7.766585	-48.883703
36_7	CTD25L	Begin	30/06/2010	7:08:03	7.766793	-48.883785
36_7	CTD25L	Bottom	30/06/2010	8:21:26	7.766402	-48.88335
36_7	CTD25L	End	30/06/2010	9:41:25	7.766038	-48.883773
37_1	UCCTD	Begin	01/07/2010	11:11:51	5.977332	-46.416647
37_1	UCCTD	Bottom	01/07/2010	12:12:36	5.978762	-46.416803
37_1	UCCTD	End	01/07/2010	13:47:57	5.978568	-46.417473
37_2	CTD25L	Begin	01/07/2010	13:56:18	5.978832	-46.417543
37_2	CTD25L	Bottom	01/07/2010	14:58:30	5.977388	-46.41675
37_2	CTD25L	End	01/07/2010	16:30:54	5.977325	-46.41649
38_1	CTD25L	Begin	02/07/2010	16:52:22	3.977483	-43.755627
38_1	CTD25L	Bottom	02/07/2010	17:57:32	3.974895	-43.752653
38_1	CTD25L	End	02/07/2010	19:37:13	3.973565	-43.751973
38_2	UCCTD	Begin	02/07/2010	19:45:06	3.973302	-43.751487
38_2	UCCTD	Bottom	02/07/2010	20:55:16	3.973583	-43.751058
38_2	UCCTD	End	02/07/2010	22:30:26	3.972892	-43.750657

Station_cast	Device	Action	Date	Time	Latitude	Longitude
39_1	UCCTD	Bottom	03/07/2010	15:22:55	2.544362	-41.699655
39_1	UCCTD	End	03/07/2010	17:02:59	2.544683	-41.699692
39_2	CTD25L	Begin	03/07/2010	17:11:07	2.545127	-41.700307
39_2	CTD25L	Bottom	03/07/2010	18:18:48	2.544697	-41.699588
39_2	CTD25L	End	03/07/2010	20:02:08	2.545995	-41.700032
40_1	UCCTD	Begin	04/07/2010	12:50:09	1.1472	-39.686865
40_1	UCCTD	Bottom	04/07/2010	13:57:11	1.146613	-39.686022
40_1	UCCTD	End	04/07/2010	16:05:08	1.147298	-39.686748
40_2	CTD25L	Begin	04/07/2010	16:18:57	1.147228	-39.686035
40_2	CTD25L	Bottom	04/07/2010	17:28:22	1.147232	-39.686442
40_2	CTD25L	End	04/07/2010	19:08:25	1.147462	-39.686582
40_3	ISP	Begin	04/07/2010	19:17:28	1.147342	-39.686158
40_3	ISP	Pump started	04/07/2010	21:40:24	1.146535	-39.685978
40_3	ISP	Pump stopped	05/07/2010	0:13:09	1.147108	-39.685765
40_3	ISP	End	05/07/2010	1:48:10	1.147213	-39.68628
41_1	UCCTD	Begin	05/07/2010	9:20:42	0.71611	-38.967057
41_1	UCCTD	Bottom	05/07/2010	10:15:50	0.715548	-38.966903
41_1	UCCTD	End	05/07/2010	11:59:56	0.71614	-38.967853
41_2	CTD25L	Begin	05/07/2010	12:11:35	0.714798	-38.966255
41_2	CTD25L	Bottom	05/07/2010	13:18:23	0.715753	-38.966023
41_2	CTD25L	End	05/07/2010	15:01:22	0.716275	-38.965972

Appendix 3. Samples taken from FISH

Samples taken from the fish:

A = dissolved platina group metals
B = total platina group metals
C = total Pb
D = dissolved cadmium
E = dissolved Nd

Operation ID station book	Latitude (North) (3)	Longitude (West) (3)	Date	Time (UTC)	Time (ship time)	sampled for
321_FISH13	-	-	13/06/10	18:30	15:30	A, B, C, D
- (2)	29°42,30	66°26,10	14/06/10	11:00	08:00	A, C
321_FISH14	-	-	16/06/10	03:50	00:50	A, C
321_FISH16	-	-	16/06/10	23:40	20:40	A, C
321_FISH16	-	-	17/06/10	11:00	08:00	A, B, C
321_FISH17	-	-	18/06/10	11:25	08:25	A, C
321_FISH18	-	-	19/06/10	17:00	14:00	A, C
321_FISH19	-	-	20/06/10	13:40	10:40	A, C
321_FISH20	-	-	21/06/10	(1)	(1)	A, C
321_FISH21	-	-	22/06/10	12:55	09:55	A, C, D
321_FISH22	-	-	24/06/10	19:15	16:15	A, B, C, E
321_FISH23	-	-	25/06/10	19:10	16:10	A, C
321_FISH24	-	-	26/06/10	23:55	20:55	A, C
321_FISH25	-	-	27/06/10	12:45	09:45	A, C
321_FISH26	-	-	28/06/10	17:45	14:45	A, C
- (2)	-	-	30/06/10	10:20	07:20	A, B, C, D
321_FISH28	-	-	01/07/10	17:05	14:05	C, E
- (2)	04°10,99	44°01,82	02/07/10	13:40	10:40	A, C
- (2)	02°36,71	41°47,91	03/07/10	13:15	10:15	C
- (2)	01°10,64	40°43,77	04/07/10	12:00	09:00	A, B, C, D
321_FISH31	00°41,99	38°57,95	05/07/10	15:15	12:15	C

(1) To recover the time that the FISH sample was taken on 21/06/10 we have to wait till the samples are back from Pelagia. The sample would have been taken between 14:34 (321_FISH20) and 16:30 (Station 29_1) on 21/06/10.
(2) No entries in Casino logbook.
(3) Due to problems with the network and Casino it was sometimes decided to include the latitude and longitude.