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The Expedition of the Research Vessel "Polarstern" to the Antarctic in 2008 (ANT-XXV/1)

Edited by
Gerhard Kattner and Boris Koch
with contributions of the participants

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ANT-XXV/1

31 October - 3 December 2008

Bremerhaven - Cape Town

Chief scientist
Gerhard Kattner

Coordinator
Eberhard Fahrbach

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ANNEX

1. ZUSAMMENFASSUNG UND FAHRTVERLAUF

Gerhard Kattner
Alfred-Wegener-Institut

Der Fahrtabschnitt ANT-XXV/1 begann am Freitag, den 31. Oktober nachmittags, in Bremerhaven und führte zunächst nach Rotterdam zum Bunkern. Während des gesamten Fahrtabschnitts wurde ständig Seewasser an Bord gepumpt, um kontinuierlich chemische, biologische und ozeanografische Messungen durchführen zu können. Das Seewasser wurde über das fest installierte Bordwassersystem und durch ein zusätzlich installiertes Pumpsystem im Brunnenschacht gefördert. Außerdem wurde noch Wasser mit Hilfe eines so genannten „Fischs“ an Bord gepumpt, der ständig seitlich neben dem Schiff in der Wasseroberfläche geschleppt wurde.

Eine große interdisziplinäre Gruppe von Wissenschaftlern aus mehreren Nationen befasste sich mit der Zusammensetzung und der chemischen Charakterisierung der gelösten organischen Substanzen im Meer in den verschiedenen Klimazonen. Parallel dazu wurde die chemische Zusammensetzung des Aerosols untersucht. Spurenelemente und der Fluss von elementarem Quecksilber zwischen Wasser und Atmosphäre wurden kontinuierlich während der gesamten Fahrt bestimmt. Ein weiteres Projekt befasste sich mit der Bestimmung von mehrfach fluorierten Verbindungen ebenfalls im Oberflächenwasser und in der Atmosphäre. Der Kohlenstoffkreislauf im Oberflächenwasser wurde mit dem Ziel untersucht, ein autonomes System zur Messung der verschiedenen Kohlenstoffkomponenten zu entwickeln. Außerdem gehörte die Bestimmung von Dimethylsulfid (DMS) in der Wasseroberfläche und in der Atmosphäre zum Messprogramm. Um die globale marine Primärproduktion aus Satellitendaten besser abschätzen zu können, wurden optische *in-situ* Messungen durchgeführt und die Zusammensetzung des Phytoplanktons und des partikulären, organischen Kohlenstoffs bestimmt. Eine weitere Arbeitsgruppe befasste sich mit den Strahlungseigenschaften der Atmosphäre, insbesondere Aerosolen, deren Ergebnisse ebenfalls in die Fernerkundung und Klimamodelle eingehen sollen.

Am 3. November wurden die ersten Messungen im Ärmelkanal auf Höhe der Normandie vorgenommen. Am 6. November, vor der Nordspitze Spaniens, wurde ein längerer Posidonia-Test durchgeführt. Danach wurde ein Scanfish getestet, ein geschlepptes Gerät, das auf dem 3. Fahrtabschnitt eingesetzt werden soll. Am 12. November stiegen 12 Teilnehmer in Las Palmas auf Gran Canaria ab. Neben den kontinuierlich laufenden Messungen wurden täglich CTD-Stationen bis zu 200 Metern Tiefe und insgesamt 8 tiefe CTD-Stationen bis zum Meeresboden im Mittelmeerausstrom und in den tiefen Becken vor der afrikanischen Küste durchgeführt, um die verschiedenen Wassermassen des Atlantiks zu beproben. Am 29. November fand die letzte Probenahme im Kapbecken, das über 4600 Meter tief ist, statt, wo sich in der bodennahen Wasserschicht bereits Antarktisches Bodenwasser mit Temperaturen von nur noch 0,7° C befindet. Am 30. November wurde mittags die letzte Station bis 200 m Tiefe durchgeführt. Am 3. Dezember morgens endete der Fahrtabschnitt in Kapstadt (Fig. 1.1).

Abb. 1.1: Kurskarte der Polarstern Reise ANT-XXV/1
Fig. 1.1: Cruise track of RV Polarstern during the expedition ANT-XXV/1

ITINERARY AND SUMMARY

The cruise leg started in Bremerhaven in the afternoon on 31 October. The first stop was in Rotterdam for refuelling. During the entire cruise seawater was continuously pumped on board to measure chemical, biological and oceanographic parameters. The ship has a permanently deployed seawater supply, which was continuously used. Another source of seawater was a pumping system in the moonpool and additionally, an online water sampling device, the so-called “Fish” or “Iron Fish”, was deployed alongside the vessel to continuously pump water on board from the ocean surface.

A detailed interdisciplinary study focused on the molecular characteristics of dissolved organic matter (DOM) in the Atlantic surface ocean to relate the DOM data to different climatic, hydrographical, biological and meteorological regimes. In parallel, aerosol samples were taken for the determination of the chemical composition of the organic matter. Trace elements and the flux of mercury between water and atmosphere were continuously measured. Another project focused on the determination of per- and polyfluorinated compounds (PFCs) to characterize the distribution of PFCs in the atmosphere and seawater. The marine carbon cycle in the surface ocean was investigated to provide operational approaches for unattended operation. In addition, dimethylsuphide (DMS) measurements were conducted in the surface waters and the atmosphere. *In-situ* measurements of ocean optics and samples for the determination of phytoplankton composition and pigments and particulate organic matter were taken to improve estimates from remote sensing data of global marine primary production and distribution of major phytoplankton functional groups. Another project aimed at observing both the radiation budget and the state of the atmosphere, in particluar aerosols, as accurate as possible to provide realistic atmosphere-radiation relationships for use in climate models and in remote sensing.

On 3 November, we stopped to perform the first measurements using the CTD profiler and water samplers in the English Channel. On 6 November, off the northern tip of Spain, the Posidonia system was intensively tested. A “Scanfish”, a towed system, which will be used during leg 3, was also deployed and tested. On 12 November a group of 12 participants disembarked at Las Palmas, Gran Canaria. In addition to the continuous measurements, CTD stations were performed daily to a depth of 200 m and a total of 8 deep CTD stations to the bottom at the Mediterranean outflow and in the deep basins along the African coast were carried out to sample the various water masses of the Atlantic Ocean. On the 29 November, the last deep CTD cast was performed to take water samples from great depths of the Cape Basin, which is 4,600 m deep. There at depth, the Antarctic bottom water is already present with temperatures of 0.7° C. On 30 November, the last CTD station took place. The cruise leg ended on 3 December in Cape Town (Fig. 1.1).

2. WEATHER CONDITIONS

Klaus Buldt
Deutscher Wetterdienst

RV *Polarstern* set sail on 31 October 2008 and at this time a low over Gotland moved north-east while another low over Brittany developed. During the night the last-mentioned low moved towards south-west France. This constellation caused light to moderate winds from eastern directions while leaving the harbour of Bremerhaven. Later in the night the wind slightly increased to 5 - 6 Bft.

During the following days this low over southern France moved back north and was found over the English Channel on 2 November. This constellation brought us increasing fresh to strong easterly winds on the first part of the leg from Bremerhaven to Rotterdam, reaching 8 Bft on the approach of Hoek van Holland. While the low over the English Channel filled on 3 November, a new depression which had developed over south-west France during 2 November moved to the inner Bay of Biscay. Its warm front dominated our weather on this day with little rain, reduced visibility, strong wind from north-east up to 7 Bft. This sequence of events repeated several times until 5 November: Several lows developed over south-west France/northern Spain and moved within 48 hrs towards the English Channel where they filled. This situation caused permanent easterly to north-easterly winds of 4 - 5 Bft, occasional rain as well as some showers.

On 5 November a strong cyclone developed west of Iceland. Its frontal system extended during the following days to the southern parts of the Bay of Biscay / Cape Finisterre. Already in the morning of 6 November its warm front crossed our position. Overcast sky and upcoming light rain together with wind shifting to south-west and increasing to force 7 marked this event. After frontal passage around noon the wind turned north-west and decreased rapidly to 4 - 5 Bft. Several showers were observed in the afternoon. A swell of about 3 m built up and rolled in from north-west. It even increased to about 4 m during the next day due to a strong current generated by a new low west of Ireland which was developing during the night to 7 November.

Within the next days the high pressure area over the Azores influenced the weather on our track. Until 9 November it moved towards the Iberian Peninsula while intensifying. West of the Azores a shallow depression formed but hardly moved. The westerly winds of 4 - 5 Bft turned again east and decreased to 3 Bft during the day. Decreasing swell, scattered sky and temperatures around 18° C gave us the first almost sunny day on this cruise. However, already in the afternoon of 9 November the field of high clouds belonging to the low mentioned above came up. Thus, the next day brought us similar conditions as far as wind and temperature are concerned, but the sky remained mainly broken to overcast.

During the following two days this low moved towards Morocco while filling. Its widely spreading field of clouds influenced the weather on our course until early 11 November. Temperatures around 20° C and a slight wind first from south-east and later from east were measured.

Meanwhile a new high pressure area had developed slightly north of the Azores. In the morning of 12 November its ridge extended down to the Canary Islands. At 07:00 we approached the roadstead of Las Palmas. Disembarking of 12 persons took place in a freshly blowing wind from north-east, a swell of about 2 m, temperatures around 20° C and a broken to overcast sky. Just an hour later we were on our way again. Already next day we sailed into the area of the north-easterly trade winds. The high pressure area mentioned intensified during the next days and moved to the northern part of the Bay of Biscay. Along its southern boundary the trade winds blew with up to 7 Bft, decreasing slowly not before midnight of 14 November.

At about the same time just along 20°N a pretty strong subtropical jet stream developed as can be seen in the attached satellite image (Fig. 2.1). Wind speed in the layer of 200 hPa reached up to 100 kn. But this phenomenon could only be observed for a short period. Already 24 hrs later its massive band of clouds had disappeared. Even in the radio sounding of the following day there was no outstanding wind speed measured in this layer.

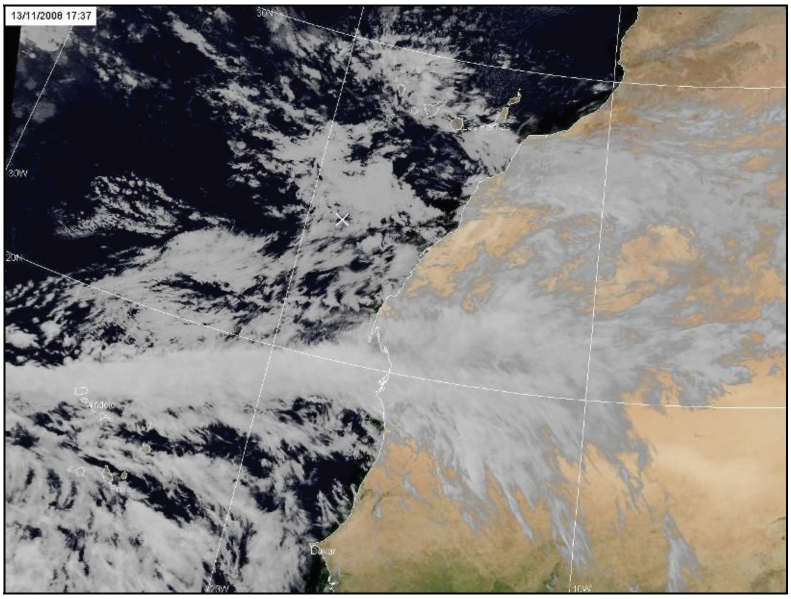

Fig. 2.1: A strong subtropical jet stream on 14 November

We crossed 20°N during the night from 14 to 15 November. Almost clear sky, decreasing north-easterly trade winds of 4 - 5 Bft and temperatures of 21° C were observed. During the next three days the wind decreased very slowly and turned to North on 17 November. Along with scattered sky mainly consisting of clouds in medium and high layers, air temperature raised up to 28° C and water temperature up to 29° C.

From 17 to 21 November we sailed through the Innertropical Convergence (ITC) which stretched along 7°N from Sierra Leone to French Guyana. This area normally well known for intense rain showers and heavy thunderstorms happened to be extremely calm. Only one very light rain shower was observed in a distance of more than 3 nm away from the ship in the evening of 19 November. Partly clouded sky (mainly cumulus humilis with a coverage of 3/8 and less), temperatures of around 28° C, a relative humidity of about 80 % and light winds from various directions together with a swell of about 2 m marked the predominating weather during these days.

On 18 November, 08:00 UTC at 8°30'N, 19°30'W we had a rendezvous with the German research vessel *Maria S. Merian*. A boat shuttle was arranged so that crew and scientists of both vessels had the chance to visit each other until noon. This action took place under a clear sky, temperatures of around 28° C, northerly winds of 2 Bft and a swell rolling in from south-east of about 2 m.

Crossing the equator on 21 November, 12:45 UTC at 12°04'W temperatures had gone down to 26° C. Wind blowing from south-east with 5 Bft indicated the approach to the region of south-easterly trade winds. Cloudiness increased in the afternoon but even this very last day in the ITC went by without any precipitation.

Entering the forecast area of *Ascension* the subtropical high pressure system over the South Atlantic governed the upcoming weather. South-easterly trade winds blew constantly with 4 - 5 Bft, temporarily 5 Bft. Along with this, scattered to broken sky was observed. Heading further south the trade wind inversion became predominant. In the early morning mainly broken to overcast sky was observed, but short before noon it became fair. This sequence recurred until the end of November. Crossing the Greenwich meridian on 26 November at 14°36'S temperatures had already dropped to 20° C, while wind and sea conditions remained unchanged.

Approaching the forecast area *Trades* additional to the subtropical high mentioned above a low over Namibia/Botswana influenced the weather on our course. Between both systems an almost cloud free area along the west coast of South Africa/Namibia gave us some bright and sunny days with temperatures around 18° C. However, on 29 November the gradient between both systems intensified which caused increasing south-easterly winds up to 7 Bft. This situation lasted until early morning of 1 December. Isolated showers and a sea state of up to 4 m were observed during 30 November.

Until the end of the expedition on 3 December there were hardly any changes in this weather situation. The south-easterly wind decreased to 5 - 6 Bft in the morning of 2 December but increased again during this last day at sea. Along with that mainly broken skies were observed while temperatures remained around 18° C.

3. SOURCES AND SHORT-TERM MOLECULAR CHANGES OF DISSOLVED ORGANIC MATTER IN THE ATLANTIC SURFACE OCEAN: IMPACT OF CLIMATIC ZONES

Boris P. Koch, Gerhard Kattner
Alfred-Wegener-Institut

Introduction

Dissolved organic matter (DOM) in the oceans contains about the same amount of carbon as the total global biomass or atmospheric CO_2 and exhibits an average age of several thousand years. Source, diagenesis and preservation mechanisms of DOM remain elemental questions in contemporary marine sciences and represent a missing link in models of global elemental cycles. One of the most important aspects to understand the global fluxes of marine DOM is to resolve the molecular mechanisms which convert fresh, labile biomolecules into semi-labile and refractory organic compounds in the ocean.

Organic carbon preservation is determined by resistance or susceptibility to decomposition primarily by microbes and photochemical degradation. Thus, it is crucial to couple DOM characterization with its biological and physico-chemical fate. Previous work along the transect of this cruise (*Polarstern* expedition ANT-X/1) provided the first high resolution comparison of bacterial and primary production on a meridional transect (Hoppe et al., 2002). The authors suggested that the observed net heterotrophy required bioavailable organic matter subsidies from:

- equatorial upwelling of pre-aged dissolved organic carbon (DOC),
- transport of DOC via currents from spatially remote upwelling systems and rivers,
- temporal transfer as a semi-labile degradation product of primary production.

As an additional source we suggest: deposition of labile atmospheric DOC.

The major aim of this study was to employ an interdisciplinary approach to complement detailed molecular characteristics of DOM in the Atlantic surface ocean to relate the data to different climatic, hydrographical, and (micro-) biological regimes as well as to terrestrial input from riverine and atmospheric sources. We also examined whether the input of aerosols can explain the occurrence of thermogenic compounds which were recently identified in marine DOM. Our goal was to achieve a high spatial resolution data set for the characterization of the sources and transformation processes of DOM from the North to the South Atlantic. We hypothesize that:

The majority of the molecular changes in DOM are taking place in the uppermost water column. This conversion occurs almost instantaneously after release by primary production or atmospheric input and is mediated by microbial and photochemical processes. After this quick process the reworked material is more similar to the refractory deep-sea DOM than to the fresh initial DOM.

An interdisciplinary group of more than 20 international scientists contributed to this project enabling us measuring most of the parameters which are important in the field of DOM characterization. This included the analyses of particulate and dissolved organic carbon (POC, DOC), amino acids, carbohydrates, dissolved and particulate lipids, chitin, organic acids and inorganic nutrients. DOM will be further characterized by ultrahigh resolution Fourier Transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), nuclear magnetic resonance (NMR), reversed-phase chromatographic separation, size exclusion chromatography, excitation emission matrix spectroscopy (EEMS) and carbon isotope composition (^{13}C, ^{14}C). In addition, various studies addressed parameters which are directly related to the composition and diagenesis of DOM such as bacterial abundance and activity, phytoplankton and zooplankton abundance, aerosol input and composition, radiation in the atmosphere and the water column, and pCO_2. Hydrogen peroxide measurement using acridinium ester flow injection analysis was applied onboard to relate the concentration of highly reactive hydroxyl radicals to changes in the molecular DOM signature. We will also study the interaction of DOM with trace elements. For this, liquid chromatography coupled to inductively coupled plasma mass spectrometry (ICP-MS) will be applied.

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3.1 Dissolved organic matter in the Atlantic Surface Ocean: bulk and detailed chemical characterization

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Objectives

To determine sources of DOM a major analytical focus will be molecular characterization by FT-ICR-MS. This technique can be applied to solid-phase extracts of marine DOM and has recently delivered first extensive molecular insights into the polydisperse and complex nature of this material (Koch et al., 2005).

From the exact masses derived by FT-ICR-MS molecular formulas for each compound can be calculated. The comparison between e.g., marine and terrestrial molecular formulas in DOM revealed differences which are suitable to distinguish between both DOM sources. In a recent study using FT-ICR-MS we found indications that the formation of semi-labile (or even refractory) compounds derived by fresh biomass might occur relatively fast on time-scales of days to weeks.

The FT-ICR-MS analyses of marine DOM also revealed the presence of hydrogen deficient compounds with extraordinarily low H/C ratios and therefore very high numbers of unsaturations which were identified as large oxidized polyaromatic hydrocarbons (PAHs, Koch and Dittmar, 2006) and may significantly impact global biogeochemical cycles (Dittmar and Koch, 2006). Most likely these molecules are derived from thermogenic processes and are mobilized from these apolar, insoluble sources by (microbial) oxidation.

All samples will be classified according to different climatic zones (temperature, radiation, etc.), primary production and extend of aerosol input. DOC concentration and composition will be related to the nutrient and oxygen situation, i.e. oligotrophic in open ocean or subeutrophic at shelf fronts, in samples from and below the euphotic zone to assess, e.g. the influence of photodegradation. The results will be also related to the isotopic signature of particulate and dissolved components, which in turn will reflect the adaptation of phytoplankton and heterotrophic bacterioplankton to the predominant nutrient regime.

In addition, the relation of hydrogen peroxide to DOM (see chapter 3.4.), chlorophyll and wet/dry deposition under open ocean conditions will be examined. Hydrogen peroxide levels may also be related to changes in the molecular quality of the DOM pool. A comparison of hydrogen peroxide to molecular characteristics determined by FT-ICR-MS may reveal additional information about hydrogen peroxide production or decay in the open ocean.

Links will be established to the investigations on aerosols (see chapter 3.2.) as a possible external source of these compounds. We also aim to define the typical marine-source fingerprint of aerosols as a function of various weather conditions and compare the structural features of marine aerosols and marine surface water samples. The Atlantic is an extremely good testing ground for this work as a transect from Bremerhaven to Cape Town covers the high dust region of the Sahara, the low dust regions south of the equator and thus allowing a wide scale look at the effects of dust supply, phytoplankton activity and the impact of DOM on metal speciation.

Work at sea

DOM sampling was carried out taking water from the Teflon "Fish" sampler, from the ships moon pool and the carousel water sampler (24 x 12-liter bottles) connected to the CTD on daily shallow (200 m) and occasional deep stations to the bottom. Water was filtered through Whatman GF/F filters. Salinity, water temperature and meteorological parameters, such as air temperature and radiation were continuously recorded by the ship devices. Satellite images for surface chlorophyll and continuous fluorescence measurements (see chapter 7.) in the moon pool provided complementary data in high spatial resolution. Aerosols were continuously collected at the observation deck.

In total, we extracted 150 samples with sorbent cartridges and retrieved over 200 samples for the analysis of bulk parameters such as DOC and POC. Sampling for most parameters was concertedly performed daily at 7:00, 13:00, 19:00 and 23:00 using the "Fish" sampler. Determination of bacterial abundance and production, hydrogen peroxide measurements and phytoplankton and zooplankton abundance was tightly coupled to the general DOM sampling scheme. Solid phase extraction (SPE) was carried out for the enrichment and desalting of DOM. Each day at 7:00, 13:00 and 19:00, 5 l of filtered seawater were extracted using sorbent cartridges. In addition, each day at 13:00 five liters of water were extracted from 200 m, the depth of the fluorescence maximum and 20 m depth. Approximately every third day 50 l of seawater were extracted from the surface. Extracted DOM samples from the deep CTD stations will be taken as a reference for the old refractory deep ocean DOM background.

Preliminary results

During the cruise we experienced two larger phytoplankton blooms which were reflected in high fluorescence values (Fig. 3.1). Most biogeochemical parameters will be measured after the cruise in the laboratories of the various international participants. Radiocarbon data will be used to assess the residence time of bulk DOC and specific DOM components.

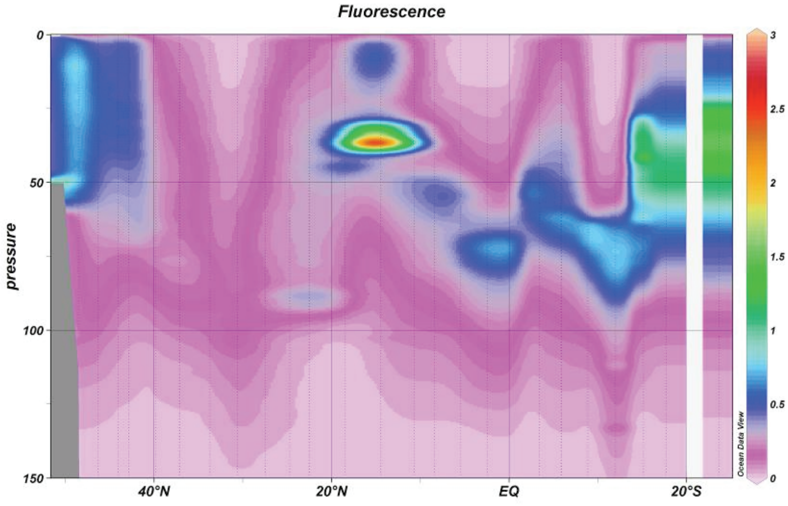

Fig. 3.1: Fluorescence distribution from shallow and deep CTD casts along the cruise track

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3.2 Molecular characteristics of aerosols, surface waters and surface-active substances

Philippe Schmitt-Kopplin, Norbert Hertkorn
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Objectives

Aerosols are likely external sources for marine DOM, and it is therefore important to compare structural features of aerosols and DOM in surface water samples. The dust regions of the Sahara contribute considerable amounts of material to the Atlantic Ocean strongly influencing the composition of marine aerosols and DOM.

Over the continents organic aerosols have been identified as major constituents of fine aerosols and secondary organic aerosols (SOA), which dominate especially in summer because of more extensive photochemistry. Even if most of the SOA form from biogenic precursors, SOA formation involves photooxidants whose levels have been strongly enhanced by human activities and accordingly, most of the supposedly biogenic SOA should be considered anthropogenic by origin. Marine aerosol measurements in 2007 on a north-south Chinese/Australian/Antarctic transect indicated intense influence on marine aerosol composition by human activity from ship exhausts (on main ship routes), terrestrial contributions (biomass burning and industry) and open ocean bursting events (close similarity among chemical footprints of surface water burst and aerosol fractions).

Trapped air bubbles in seawater considerably increase exchange surfaces between the bulk seawater and the atmosphere. Bubbles drag and enrich surface-active organic compounds along their path through the liquid bulk, to reach the sea surface and eventually burst and eject droplets into the atmosphere.

Work at Sea

During ANT-XXV/1, enrichment of organic surfactant materials was investigated at the water-air boundary across the entire transect by daily collection of the organic components in “Fish” surface water as well as by collection of the aerosol with a high volume air sampler installed on the front deck of the *Polarstern*. In parallel, bursting jets were generated and collected in the *Polarstern* laboratory. These complex mixtures of organic molecules will be analyzed with ultrahigh resolution organic structural spectroscopy back in the laboratory in Germany to finally result in a molecular distribution map indicating transfer from the ocean to the atmosphere.

In total, 66 aerosol filter samples were collected in 12 hours time intervals considering day and night events to follow diurnal effects. Its desalted water extracts (SPE by C18 cartridges) will be analyzed using ultrahigh resolution FTICR mass spectrometry. Source assignments will be attempted based on exact mass analysis, determination of elemental composition and data mining using in-house developed tools.

Based on their loading, the filters can be already visually classified into the following groups:

03.11. to 06.11.: dark colour and extensive filter load influenced by heavy ship traffic in the British Channel;
07.11. to 11.11.: low loaded filters influenced by the open sea;
12.11. to 17.11.: Sahara sand load;
18.11. to 21.11.: dark dust load (land influence? biomass burning?);
22.11. to 03.12.: white filters with low load, mainly due to ocean burst.

In addition to the described and processed bursting jet samples, CTD samples from 200 m depth and all deep stations were systematically extracted with SPE C18 cartridges resulting in a total of additional > 94 samples. For about six particular stations large amounts of water (up to 300 L per station) were extracted by means of multiple resins (Varian: PPL, C2, C8, C18, CN-E, ENV, PH) to finally enable systematic multidimensional NMR and FTICR mass spectral analyses for in-depth molecular-level characterization.

The photochemical transformation of these organic molecules in the near surface vertical gradient was followed with on-deck photochemical studies using 5 l samples at various depths. Organics were concentrated on SPE PPL cartridges and will be assessed by means of FTICR mass spectrometry. On boat H_2O_2 and DMS analyses already indicated ongoing DOM photo-transformations. More photo-degradation studies will be performed back in the home lab in collaboration with the consortium.

The comprehensive characterizations of these materials in conjunction with the surface water, the bursting and the aerosols samples will enable a molecular-level characterization of higher molecular weight (> 120 amu) organic compounds within the ocean and the atmosphere and will allow deriving transfer functions of these molecules across the water-air boundary.

In addition to these studies, methanol extracts of daily filter-cakes containing bacteria, phytoplankton or zooplankton resolved according to filter cut-off (> 0.2 μm, < 20 μm, > 20 μm, > 50 μm) were obtained. These will be exhaustively analyzed by means of FTICR mass spectrometry, database and data-mining under consideration of all novel biological information obtained within this cruise to reveal metabolome-wide relevant biological descriptors/biomarkers all over the entire transect.

The relationships between identified pathway-specific molecules under given sample conditions and the complex DOM compositions derived from equal or similar environments will be analyzed with respect to turnover and incorporation of small biomolecules into oceanic DOM.

Preliminary results

No result could be derived directly from the work done onboard. After the return of *Polarstern* at the end of May they will be analyzed in 2009 with FTICR-MS and NMR-spectroscopy.

Already from December 2008, back in the laboratories at Helmholtz Zentrum München, ultrahigh resolution mass spectrometry analyses of the 500 ml water C18 extracts could be conducted. First results of the surface samples showed thousands of signals corresponding to thousands of CHONS elementary compositions. The data were analyzed with a principal component analysis (PCA), and groupings of the variables (days) present a differentiation in various ecozones as illustrated in Fig. 3.2. These preliminary results are very promising and will allow to extract differentiating mass signals that can correspond to ecozone biomarkers, among them from natural and anthropogenic origin.

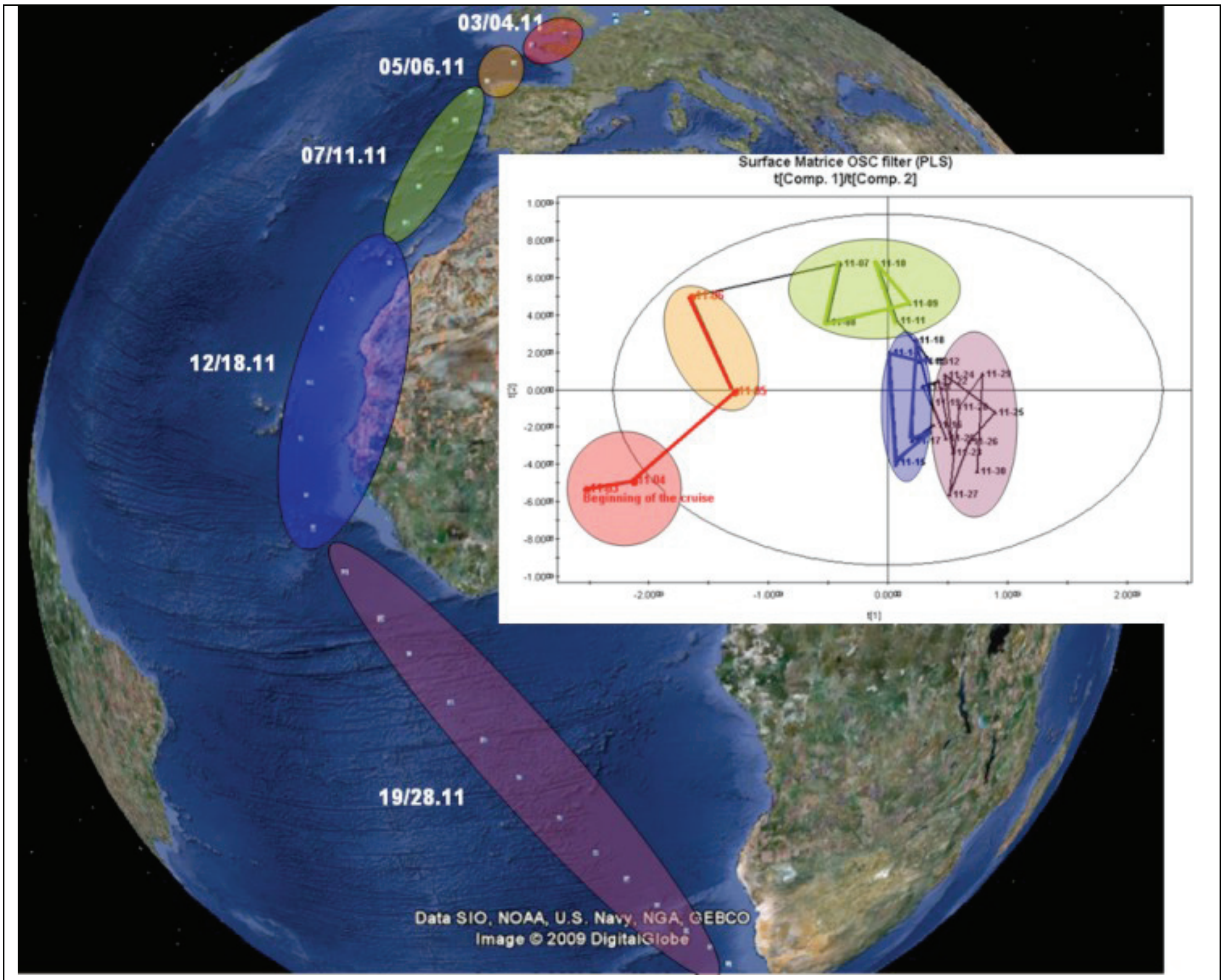

Fig. 3.2: Different ecozones along the transect reveal by ultrahigh resolution mass spectrometry of organic components in surface water

3.3 Hexane extraction of lipophilic substances and particulate lipids

Zhuoyi Zhu
East China Normal University

Objectives

The nonpolar lipophilic fraction of the marine DOM is only insufficiently covered by the extraction using styrene divinyl benzene polymer type sorbents (e.g. PPL). Therefore seawater will be extracted with hexane to separate nonpolar compounds. Thus, we will have an independent analytical approach to work on the chemical characterization of DOM. In addition, we will determine lipids in the particulate material. Back in the laboratory we will analyze the samples for total lipids and quantify how much dissolved lipid carbon contributes to the total dissolved organic carbon pool. Furthermore we will quantify lipid classes, and after hydrolysis we will use gas chromatography coupled to mass spectrometry to identify lipid biomarkers such as sterols, triterpenols or fatty acids and alcohols. These compounds can be used to identify sources and transformation processes of organic matter.

Work at sea

Generally, routine „Fish“ samples and shallow CTD samples were taken on board, usually 20 l seawater and filtered through precombusted GF/F filters. The 20 l samples were extracted with 100 ml n-hexane using a shaker (20 min). After shaking, the bottles were filled up with pre-extracted seawater derived from the previous extraction. After 30 min of phase separation, a separation unit was used to transfer the n-hexane extract into a glass bottle. The extract was concentrated to 1 - 2 ml using a rotation evaporator. This extract was transferred into a pre-combusted ampoule and evaporated to dryness using nitrogen. Particulate lipids were sampled in parallel to the dissolved lipid samples. Typically 4-10 l of seawater were filtered through GF/F filters. All samples were labelled (Table 3.1) and stored at -20° C.

Tab. 3.1: Sample list for dissolved lipids (DL) and particulate lipids (PL)

Sample No.	Date 2008	Time UTC	DL volume extracted(L)	n-hexane extract (mL)	PL volume filtered (mL)
001	03.11.	13:12	20.0	80	
004	04.11.	07:00	20.0	86	2000
005	04.11.	12:35			2000
007	04.11.	13:21	20.0	81	
009	04.11.	19:00	20.0	76	3500
011	05.11.	07:00	20.0	84	6500
012	05.11.	11:13	20.0	90	5000
017	05.11.	14:13	16.4	90	7000
020	06.11.	07:00	20.0	89	8000
022	06.11.	13:22	20.6	75	8300

3.3 Hexane extraction of lipophilic substances and particulate lipids

Sample No.	Date 2008	Time UTC	DL volume extracted(L)	n-hexane extract (mL)	PL volume filtered (mL)
024	07.11.	13:12	16.7	78	8700
026	07.11.	19:11	20.3	80	8700
028a	08.11.	07:00	18.4	81	8000
028b			20.4	76	
032	08.11.	13:22	20.0	82	9300
034	08.11.	19:00	20.0	81	9000
036a	09.11.	07:46	20.4	86	6500
036b			20.0	81	
038	09.11.	09:35	17.85	86	5800
041	09.11.	13:20	21.2	86	6800
043	09.11.	18:55	20.0	79	9000
045	10.11.	07:11	20.0	89	8000
049	10.11.	13:57	18.45	88	8200
051	10.11	19:25	20.0	88	7800
052	11.11.	07:00	20.0	92	7900
054	11.11.	13:11	21.25	88	9000
056	11.11.	16:00	20.0	82	7000
058a	12.11.	12:50	20.4	81	8200
058b			20.0	81	
059	12.11.	12:50	20.6	80	3800
061	12.11.	13:13	20.0	86	9000
063	12.11.	19:00	20.0	75	8000
065a	13.11.	07:00	20.4	79	8000
065b			20.0	84	
068	13.11.	13:14	20.0	84	8000
070	13.11.	19:00	20.0	74	8000
072	14.11.	07:00	20.0	66	9000
074	14.11.	09:47	20.0	82	8000
076	14.11.	12:07	19.0	84	10000
079	14.11.	19:35	20.0	88	8000
081	15.11.	07:00	20.0	90	8700
085	15.11.	13:18	20.0	65	8000
087	15.11.	19:00	20.0	75	8000
089	16.11.	07:00	20.0	77	8300
091	16.11.	13:13	20.0	76	7600
105	16.11.	19:00	20.0	56	3100
107	17.11.	07:00	20.0	70	8500
109	17.11.	12:58	20.0	75	9000
117	18.11.	07:00	20.0	87	7300
119	18.11.	13:15	17.3	86	8000
123	18.11.	19:00	20.0	89	8000
125	19.11.	07:00	20.0	85	9700

128	19.11.	13:13	20.0	90	8000
130	19.11.	19:00	20.0	90	8000
132	20.11.	07:00	20.0	89	8000
134	20.11.	13:18	20.5	91	6000
138	20.11.	15:27	20.0	93	6800
(no No.)	20.11	19:00	20.0	90	
142	21.11.	07:00	20.0	88	
144	22.11.	07:00	20.5	88	6500
146	22.11.	13:12	17.75	86	10600
150	23.11.	08:50	20.0	92	7600
153	23.11.	10:42	21.75	85	8000
155	23.11.	12:50	20.0	90	8000
159	24.11.	07:00			8800
160	24.11.	12:50	20.0	88	8000
162	24.11.	13:13	20.0	88	8000
167	25.11.	13:55	20.0	88	6000
169	25.11.	13:14	20.0	91	8000
171	25.11.	19:00	20.0	90	4600
174	26.11.	12:45	20.0	92	6000
177	26.11.	13:14	20.0	88	6600
179	26.11.	19:00	20.0	86	4800
181	27.11.	08:50	20.0	88	8000
182	27.11.	10:49	20.0	92	6000
184	27.11.	10:49	20.0	90	6000
186	27.11.	13:17	20.0	94	5000
195	28.11.	14:20	20.0	84	5000
192	28.11.	13:14	20.0	85	6000

3.4 Hydrogen peroxide and high resolution UV/Vis measurements across the Atlantic Ocean

Michael Gonsior, William J. Cooper (not on board)
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Objectives

Hydrogen peroxide is produced by photochemical reactions involving dissolved organic matter (DOM) (Cooper and Zika, 1983) as well as by wet and dry deposition (Kieber et al., 1999a,b). A biological source has been also suggested (Palenik and Morel, 1988). The acridinium ester flow injection analysis (FIA) of hydrogen peroxide determination has been previously optimized and successfully used in the Southern Pacific Ocean off the New Zealand Coast.

High resolution UV/Vis data are important to track the chromophoric dissolved organic matter (CDOM). The high resolution UV/Vis measurements (every 5 min and

1 m path length) and specific wavelength ratios may help to track specific DOM components produced by e.g. algal blooms.

A major goal of this study was to examine the relation of hydrogen peroxide to DOM, chlorophyll, temperature, and irradiation under open ocean conditions and to further test the flow injection analysis system. Hydrogen peroxide levels may also be related to changes in the quality of the DOM pool. A comparison of hydrogen peroxide concentrations to molecular characteristics determined by ESI-FT-ICR-MS may reveal additional information about hydrogen peroxide production/decay in the open ocean. Additionally, the hydrogen peroxide concentration measured from samples of the CTD casts can be combined with the salinity and temperature data to estimate the active mixing in the upper water column.

The goal of the UV/Vis measurements was to investigate small spatial changes of CDOM with the potential to find specific wavelength ratios which are indicative for sources of CDOM (e.g. to track CDOM produced by algal blooms).

Work at Sea

During ANT-XXV/1, samples were collected from daily CTD casts to a maximum depth of 200 m, from deep CTD casts every 4 days and 4 times daily from the surface ocean water. In general, 4 depths were sampled during the shallow (200 m) CTD casts and additional three depths for the deep CTD casts. The shallow CTD casts always included samples from the fluorescence maximum. The UV/Vis system was supplied with a continuous flow of clean seawater.

Hydrogen peroxide (H_2O_2) can be determined at nano-molar levels in natural waters using a chemiluminescent method involving the reaction of hydrogen peroxide with an acridinium ester (10-methyl-9-*p*-formylphenyl-acridinium carboxylate trifluoromethanesulfonate). This flow injection analysis system is simple, rapid, requires no catalyst or metal ion complexes, and has an analytical precision of 4 % RSD at typical natural water concentrations (Cooper et al., 2000). The method was further optimized and successfully applied on open ocean water samples.

The UV/Vis spectra were measured using an Ocean Optics USB4000 UV/Vis detector attached via fibre optic cables to a World Precision Instrument (WPI) 1 m path length wave capillary guard. A WPI D2H light source was used to supply sufficient light intensities between 265 nm and 700 nm. The water was pumped through the capillary using a Rainin peristaltic pump and a flow rate of 1 ml min^{-1}. Milli-Q water was frequently pumped through the system as a blank control.

Preliminary Results

H_2O_2 was measured at 24 CTD stations including 8 deep casts to the sea floor located in the major basins along the transect (Fig. 3.3). The measurements at the fluorescence maximum did not support the production of H_2O_2. However, at one station with extremely high chlorophyll fluorescence, a slight increase at the fluorescence maximum was observed (Fig. 3.4). The correlations between temperature, sunlight intensities, chlorophyll, etc. and surface hydrogen peroxide concentrations is part of the data processing after this research cruise.

The UV/Vis data has not yet been processed either. However, Fig. 3.5 gives a raw and processed UV/Vis spectrum to show the format of UV/Vis data available within the next few months. A Matlab routine has been established to correct the spectra and also to calculate several wavelength ratios. During the cruise, fluctuation of the light intensities generated by the light source occurred and the data needs to be corrected to address this problem.

References

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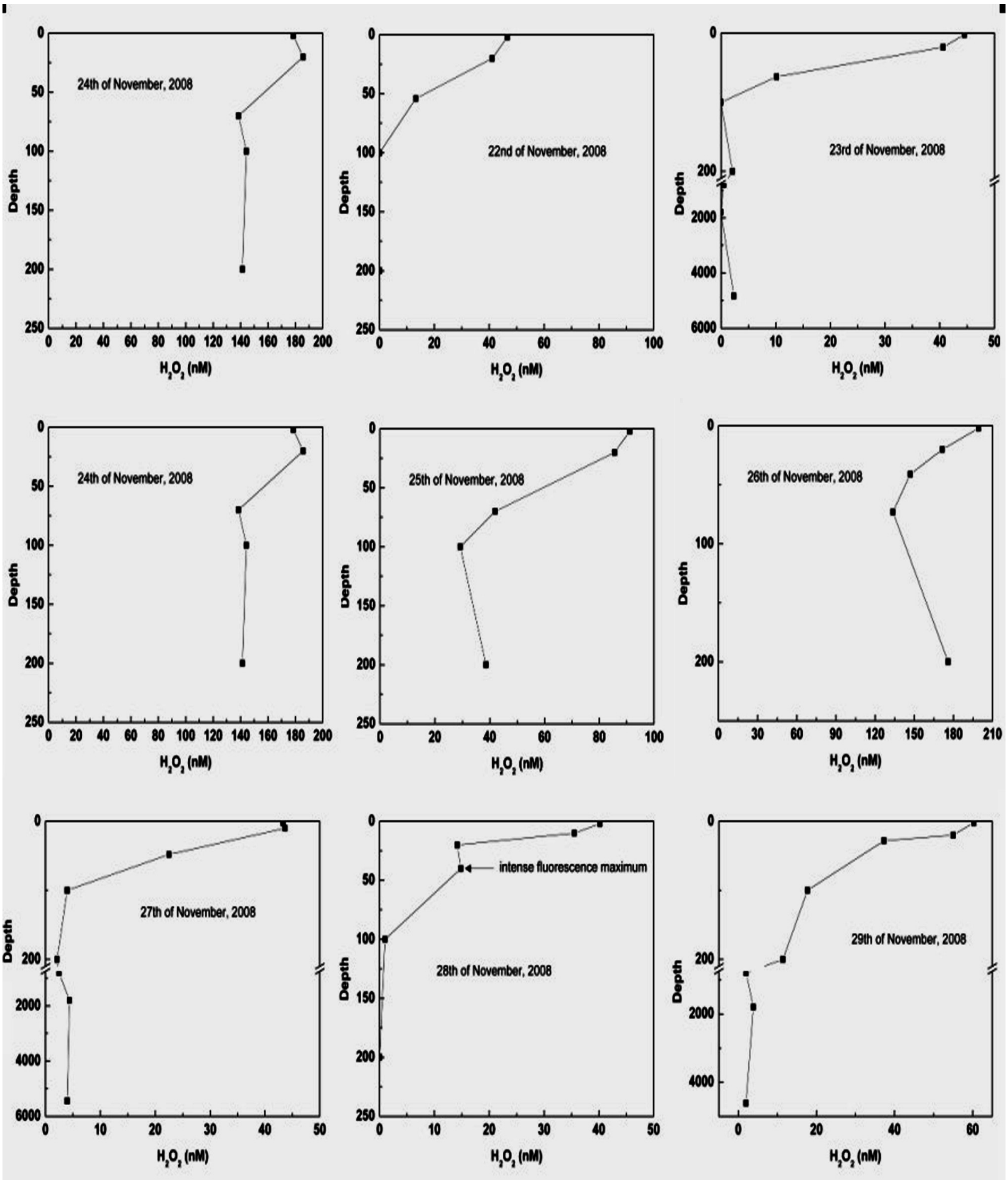

Fig. 3.3: Vertical hydrogen peroxide levels of samples collected during the daily CTD casts

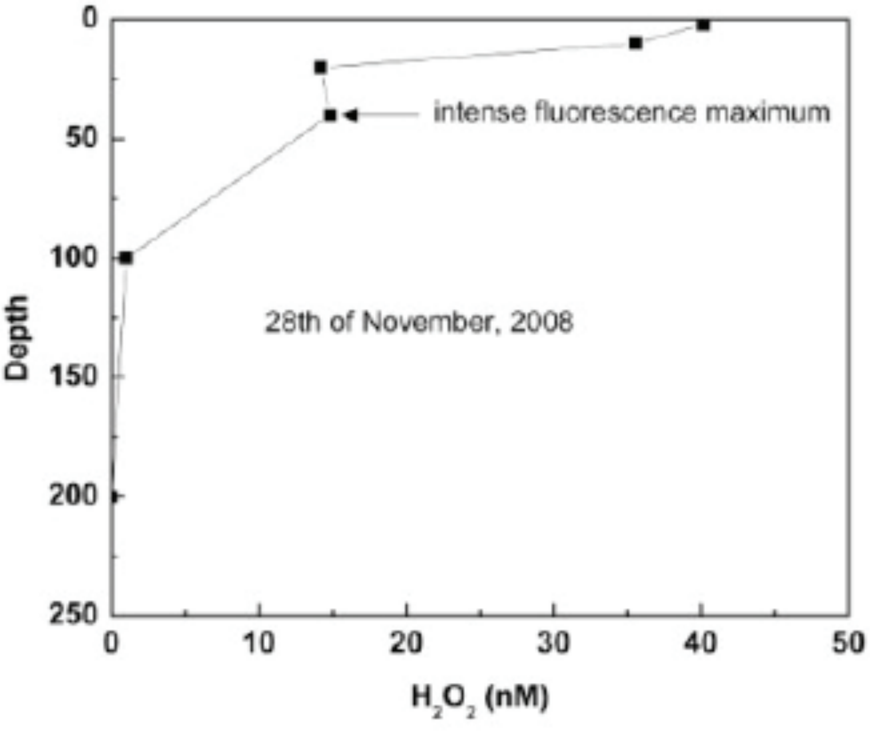

Fig. 3.4: The influence of an intense fluorescence maximum on the hydrogen peroxide concentration

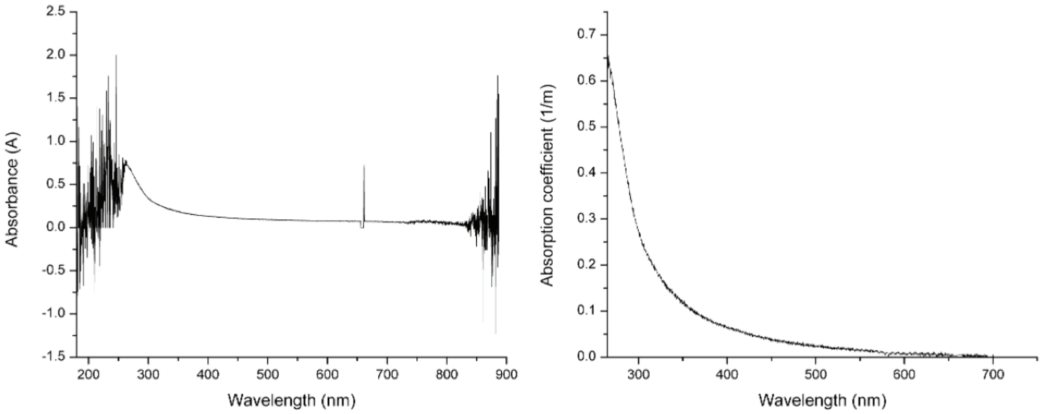

Fig. 3.5: UV/Vis spectra of raw and processed data

3.5 Low-molecular weight organic acids and the role of chitin in the DOM cycle

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Objectives

Little is known about the role of low-molecular weight organic acids in the cycling of dissolved organic matter (DOM) in the ocean. Therefore, the determination of monomeric organic acids by ion chromatography was incorporated as part of the investigations of the DOM group. In addition, the particulate organic matter (POM) will be analyzed with special emphasis on the main refractory component, chitin, and its relationship to the C/N ratio of POM. In this context, studies are conducted on microorganisms that possess the necessary enzymes (chitinases) to degrade chitin and are thus able to use it as C and N source. Especially the halophilic bacteria of the genus Vibrio have this ability and are thus a focus of the microbiological investigations. It is uncertain to what extent the degradation products of chitin enter the DOM cycle. This is particularly relevant since chitin is one of the most common organic substances in the marine environment but is seldom found in sediments.

Work at sea

Water and plankton samples were inoculated on marine agar, TCBS agar (for Vibrio) and MacConkey agar (for *E. coli*) to get direct counts (abundance) of cultivable bacterial population. In addition, bacterial samples were concentrated by filtration and then enriched in selective media (alkaline peptone water and trypticase soy broth) to obtain cultivable *Vibrio* and *E. coli* in abundant numbers. The bacterial colonies grown on the plates were stocked as mix culture in soft agar. These mixed isolates will be segregated to have a pure culture stock. The isolated bacterial strains will be subjected to 16S rRNA gene sequencing for reliable identification, and the diversity of the bacterial population will be analyzed. Selected strains of targeted species (e.g., *V. cholerae, V. parahaemolyticus, V. vulnificus, E. coli*, etc.) will be characterized biochemically. Genetic fingerprintings will be carried out to understand the relationship (phylogenetic distance) among the strains. The susceptibility of these strains to various antibiotics will be also checked. Specific PCRs will be carried out to detect the presence of toxigenic genes among the selected strains. Processed samples were also preserved for plankton identification and enumeration. The non-cultivable bacterial population will also be analyzed to understand its abundance and variations in different parts of the ocean. Samples are preserved for DAPI staining and counting, fluorescent antibody detection (for *V. cholerae*), as well as fluorescent *in-situ* hybridization analysis for specific bacterial groups (e.g. Vibrio, Gammaproteobacteria, etc.). Samples were also treated with specific chemicals and nutrients for detection of viable and dead cells among the total bacterial population. The environmental DNAs from all the samples were also preserved with ethanol. These DNA samples will be amplified, cloned and then gene sequencing will also be carried out to understand the diversity and abundance of non-cultivable bacterial population. A portion of each of the oceanic samples was also preserved for the analysis of various metabolites. It will be interesting to check the presence of various molecules (e.g. those responsible for bacterial signalling) to understand the stress condition of bacteria under different environmental settings.

Since the microbiological samples could not always be taken simultaneously with the sampling of the DOM group, additional samples were taken for the determination of seston weight, POC, PON, chitin, stable C and N isotopes, inorganic nutrients, DOC and DON from seawater, zoo- and phytoplankton concentrates and the fraction containing particles $< 20\ \mu$m.

Furthermore, samples for chitin determination were taken from a CTD cast at 20 m, at the fluorescence maximum and at 200 m depth. A total of 9,000 l of seawater were fractionated with plankton nets, and the POM was concentrated 10,000 times. During the first half of the expedition, the low performance of the water pump did not allow to process the planned amount of samples, since one plankton sampling of that type took about 7 hours. During the second half of the trip the POM fractionation could be optimized to only 4 hours.

In parallel to the microbiological samplings, 200 filter samples were taken for chitin, POC and stable isotopes and 40 water samples were collected for the determination of nutrients, DOC and DON. Further 100 POM samples were collected on filters for the DOM group and 400 for the microbiological studies. About 1,200 Petri dishes with different media were used and 300 bacteria enrichments in nutrient solutions were carried out.

Due to electronic problems of the ion chromatograph, the determination of organic acids in the extracts from the DOM group had to be postponed. Regarding the DOM-enrichment performed by solid phase extraction, besides the standard elution with methanol, an additional elution with ammonium hydroxide will be carried out in order to increase the recovery of low-molecular weight organic acids.

3.6 Bacterial abundance, production and community structure along the Atlantic Meridional Transect

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Objectives

In our study we aim at collecting a high resolution dataset of bacterial abundance and production to provide a metabolic context for the organic matter transformation work and pCO_2 concentrations. We will measure the radiocarbon age of DOC in water masses of varying origin to assess the oceanic residence time of differing sources of organic matter. The bacterial community composition using 454 sequencing will be assessed and related to different biogeochemical, hydrographical, and meteorological regimes.

Work at sea

Bacterial biomass: Samples (2 mL) for bacterial abundance were preserved with 0.2 μm filtered 25 % glutaraldehyde diluted to a final concentration of 2 %. Bacterial cell numbers will be enumerated using a Becton-Dickinson FACS caliber benchtop flow-cytometer and the nucleic acid stain Syto-13 following the methods of del Giorgio et al. (1996). Bacterial cells and microspheres will be separated in a log-log cytogram of green fluorescence intensity and side scatter. Samples will be run for 30 seconds or until a minimum of 20,000 events were counted. Bacterial cell numbers in the sample will be calculated using microspheres as an internal standard.

Bacterial production: Bacterial productivity was measured by ^{3}H-leucine (Kirchman et al., 1985) incorporation as modified by Smith & Azam (1992). A sample aliquot (1.5 mL) was added to a screw-top microcentrifuge tube, followed by addition of ^{3}H-leucine at saturating concentration. Procedural blanks consisted of simultaneous additions of sample water, ^{3}H-leucine, and 100 μL 100 % trichloroacetic acid (TCA). Triplicate live samples and a single blank were run for each assay. Tubes were incubated in the dark at *in-situ* temperatures and then terminated by the addition of 100 μL of 100 % TCA. Microcentrifuge tubes were placed in scintillation vials and radioassayed in a liquid scintillation counter.

Microbial community structure: Large volume water samples (> 30 l) were collected from surface and depth along the transect from the „Fish“, moonpool and CTD. Water was prefiltered through 3.0 μm teflon filters. Filtrate was subsequently filtered onto 0.2 μm teflon filters. Filters were stored in buffer at -80° C and will be processed at VCU.

References

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3.7 Radium isotopes

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Objectives

Since radium isotopes are non-particle reactive, they are readily transferred in the ocean by water movement and removed from water column only via radioactive decay. Ra nuclides, in particular long-lived ^{226}Ra ($t_{1/2}$ = 1,600 yr) and ^{228}Ra ($t_{1/2}$ = 5.7

yr) may be a suitable tracer for the study of water movement in the ocean because they are sufficiently long lived relative to the oceanic circulation. Using radium isotopes as passive conservative tracers, we will study the water movement in Atlantic Ocean. However, since there was obvious additional influence from Sahara, we will discriminate the contribution from dust. During this expedition, we will determine the radium isotopes in surface and several deep water layers in Atlantic Ocean. Considering the ratio of radium isotopes as inner-clock, the water age and dispersion coefficient will be estimated.

Work at sea

Large volume (> 200 l) of surface seawater was pumped from subsurface (ca. 3 - 4 m) using the „Fish“. Two deep water samples (1,800 m depth) were taken with CTD bottles. Details of the sampling locations and the ancillary data are given in Table 3.2.

Radium isotopes were pre-concentrated with a pre-cartridge (pore size 0.5 µm) to remove particles followed by two MnO_2-coated cartridges connected in a series to concentrate Ra. Then the MnO_2-fibres were detached from the cartridge and will be taken back to lab to ignite at 550° C for more than 6 hrs in a furnace. After cooling, the ashes will be weighed and transferred into a plastic vials for determination of γ-spectrometry (Model: Canberra GCW-2523). The extraction efficiency of Ra from seawater will be calculated from the relative efficiency of the two MnO_2-fibres. Assuming that no difference in extraction efficiency exists between the two MnO_2-fibre cartridges, the extraction efficiencies (η) can be calculated as: $\eta=1-A_2/A_1$, where A_1 and A_2 are measured Ra isotope activities of the first and second cartridge filters.

Tab. 3.2: Samples for the analyses of radium isotopes (samples were taken from the surface („Fish“) and 23/11 and 29/11 from 1,800 m)

Date dd/mm 2008	**Time hh:mm (UTC)**	**Position (Lat.)**	**Position (Long.)**	**Salinity**	**Water temp. (°C)**	**Volume filtration (L)**
04/11	14:15	06.151 W	48.510 N	35.29	13.36	249
05/11	12:04	07.840 W	46.337 N	35.63	14.65	244
06/11	13:18	10.300 W	44.047 N	35.89	15.93	249
07/11	19:45	11.794 W	42.345 N	35.84	16.16	281
08/11	18:20	12.770 W	39.144 N	36.22	17.94	281
09/11	09:20	13.340 W	37.130 N	36.27	18.41	280
10/11	10:40	14.255 W	33.991 N	36.69	19.79	280
11/11	16:18	14.989 W	30.221 N	36.74	21.25	280
12/11	13:45	15.598 W	27.453 N	36.71	20.80	277
13/11	11:18	18.182 W	24.883 N	36.89	22.39	280
14/11	08:27	20.504 W	22.499 N	36.88	23.02	312
15/11	11:09	20.741 W	18.808 N	36.59	24.38	281
16/11	10:56	20.995 W	14.831 N	35.61	27.19	280
17/11	10:49	20.200 W	10.943 N	35.39	28.88	280
18/11	13:44	19.350 W	08.279 N	34.43	29.28	280
19/11	11:39	16.923 W	05.597 N	34.28	29.16	280
20/11	13:37	14.150 W	02.470 N	34.66	28.51	281
22/11	09:13	09.590 W	02.938 S	36.03	26.07	280
23/11	15:00	07.027 W	05.965 S	34.94		217
23/11	23:08	06.113 W	07.044 S	36.06	24.82	279
24/11	19:37	03.893 W	09.648 S	36.01	23.43	249
25/11	13:37	01.864 W	12.008 S	36.40	22.48	280
26/11	11:01	00.651 W	14.911 S	36.15	20.19	279
27/11	09:39	03.127 E	17.731 S	35.89	19.39	281
28/11	10:20	05.426 E	20.304 S	35.74	19.32	280
29/11	18:30					200
30/11	08:47	10.278 E	25.6 S	35.32	18.44	249

4. ELEMENTAL MERCURY SEA-AIR FLUX

Joachim Kuss, Hildegard Kubsch, Klaus-Peter Wlost (until Las Palmas, Gran Canaria), Bernd Schneider (not on board)
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Objectives

The objective of the study is to determine the elemental mercury (Hg^0) sea-air flux in various geochemical provinces of the Atlantic Ocean in the frame of a project funded by the German Science Foundation (DFG). The cruise ANT-XXV/1 from Bremerhaven to Cape Town in November 2008 is the first study and will be complemented by the transect from Punta Arenas to Bremerhaven in April/May 2009 (ANT-XXV/5) for a seasonal intercomparison. The spatial variability of the Hg^0 flux will be investigated in relation to prevailing biological conditions and physical forcing factors like wind and solar radiation.

Mercury mobilized by anthropogenic activity is introduced into the sea by wet and dry deposition and by river drainage. However, the sea could also become a significant source because of Hg^0 sea-air gas exchange. Transformation of ionic mercury to volatile Hg^0 is possibly caused by direct photon-induced reactions and/or by biotic processes in surface waters. The spatial and seasonal variability of the Hg^0 emission has been shown for the Baltic Sea in 2006 (Kuss and Schneider 2007) and is investigated in the Atlantic Ocean during the two cruises of *Polarstern*. The following questions are attempted to be answered during the study:

- How do the atmospheric and oceanic circulations and thus the biogeochemical regimes determine the Hg^0 concentration in surface waters?
- Is the Hg^0 concentration in surface water related to biological processes?
- Do enhanced Hg^0 concentrations occur mainly in regions with predominance of primary production or of heterotrophic respiration?
- Is the elemental mercury (Hg^0) emission of the Atlantic Ocean variable in space and time?
- Is the release of Hg^0 controlled by latitudinal-dependent solar radiation?

Work at sea

During the transect seawater from the clean-seawater supply system of *Polarstern* was sampled. It was continuously analyzed for elemental mercury and carbon dioxide. Four times a day samples were filtrated for chlorophyll a, phaeopigments and dissolved and particulate organic carbon measurements.

Elemental mercury: The Hg^0 concentration in Atlantic surface water was determined at high resolution. This was achieved by a new method that rely on measurements of air that is equilibrated with surface seawater with respect to Hg^0 (Hg^0_{equ}). Clean seawater was continuously dispersed into the headspace of a 20 L gas bottle by a shower head and is released close to the bottom. After 1 hour the Hg^0 in the equilibrated headspace air (Hg^0_{equ}) was measured by cold-vapour atomic fluorescence spectroscopy after preconcentration by gold amalgamation. About 350 duplicate measurements of Hg^0_{equ} have been done. In addition, a total of about 5,000 samples of Hg^0_{atm} in the marine atmosphere were measured. The air samples were drawn via a Teflon tubing from the front of the top deck.

In addition, a new software “QueckIOW” was developed for the retrieval and storage of the mercury data from the spectrometer. Moreover, the software enables preliminary data processing steps by the synthesis of data distributed by the “DAVIS SHIP” system of *Polarstern* with the measurements.

Carbon dioxide: The partial pressure of CO_2 in surface water was recorded each minute. We used a non-dispersive infrared spectrometer coupled to a small bubble-type equilibrator (0.5 L) with a temperature probe. For comparison also the CO_2 concentration in the atmosphere was measured about twice a day, if the relative wind direction was from outside the ships’ sector.

Organic carbon: About 100 water samples were taken and subjected to filtration for the determination of dissolved and particulate organic carbon (DOC/POC), Chlorophyll a, and phaeopigments. Filters and filtrates are immediately cooled to -80° C and were then stored deep-frozen at -20° C until analyses in the laboratories of the IOW.

Trace metals: About 70 samples for reactive and total mercury determinations (Hg^{reac}/Hg^{tot}) and about 50 samples for other trace elements have been taken from a towed „Fish“ clean pumping system in collaboration with the trace metal group of the IOW (Dr. Christa Pohl and Ursula Hennings). The samples were acidified for later analysis in the trace metal lab of the IOW.

Preliminary results

Elemental mercury in water and air: First results (Fig. 4.1a) showed a clear regional variability of elemental mercury in surface water (Hg^0_{equ}). Elevated levels of 3-6 ng/m³ were measured along Europe in comparison to a relatively constant atmospheric concentration of 1.3 ng/m³. Hg^0_{equ} then decreased steadily with direction south until its concentration started to significantly increase again at a latitude of 15°N. Between 10°N and 2°N the concentration remained high at roughly 15 ng/m³ and then dropped sharply to about 4 ng/m³. Until 10°S the concentration declined to about 1.5 to 2.5 ng/m³ and remained in that range until 18°S. The atmospheric Hg^0 in the southern hemisphere was clearly lower compared to the northern hemisphere and was in the range of Hg^0_{atm} = 0.8-1 ng/m³. Between 18°S and 25°S Hg^0_{equ} was equal to the atmospheric concentration.

The data set requires further validation before it can be used for the sea-air flux (F_{Hg0}) calculation: $F_{Hg0}=k^*(Hg^0_{equ}-Hg^0_{atm})/H$. A prerequisite for gas exchange is a sea-air concentration difference ($Hg^0_{equ}-Hg^0_{atm}$) but the flux is also controlled by the dynamics at the sea surface. The gas exchange transfer velocity (k) that is dependent on wind speed accounts for the turbulence at the water surface. H is the Henrys' Law constant of Hg^0. Likely the emission by the sea was enhanced along Europe and in the area close to the ITCZ. Near Europe moderate sea-air concentration difference (ΔHg^0) but high wind speeds in autumn probably lead to enhanced fluxes. In the transition area between the seasonal variable ITCZ and the trade winds, high ΔHg^0 coincides with increased wind speeds that also could result in strong emission fluxes.

Carbon dioxide: The concentration of CO_2 in the marine atmosphere (CO_2^{atm}) was relatively constant in comparison to surface water values. It was slightly above 380 ppm (in dry air) north of 20°N. Further south the concentration declined to between 375 ppm and 380 ppm and approximately remained at that level.

The development of the partial pressure of CO_2 in the water ($pCO_2^{wat.}$) during the transect showed a strong variability (Fig. 4.1b). In the beginning of the cruise the pCO_2^{wat} was clearly below the atmospheric pCO_2^{atm}=380 μatm, indicating net primary production in this area. Between 35°N and 10°N increased pCO_2^{wat} is interrupted by strong depletion events of $pCO_2^{wat.}$=315 μatm, probably indicating local algae blooms. Then, between 10°N and 2°N pCO_2^{wat} was continuously depleted in comparison to pCO_2^{atm}. At 2°N the pCO_2^{wat} had increased to ~ 420 μatm sharply above the atmospheric value. Since also a clear drop in the surface water temperature was recorded (Fig. 4.1c) it probably indicated an upwelling area. Further south the pCO_2^{wat} declined smoothly to below the atmospheric value. Afterwards we passed water masses that were characterized by variable pCO_2 in the range of about ±30 μatm deviation from the atmospheric pCO_2 (Fig. 4.1b). Also the CO_2 data set is preliminary and has to be validated and interpreted in relation to other data sets. A comparison is attempted with other CO_2 recordings during the ANT-XXV/1.

References

Kuss J, Schneider B (2007). Variability of the gaseous elemental mercury sea-air flux of the Baltic Sea. Environmental Science & Technology 41, 8018-8023.

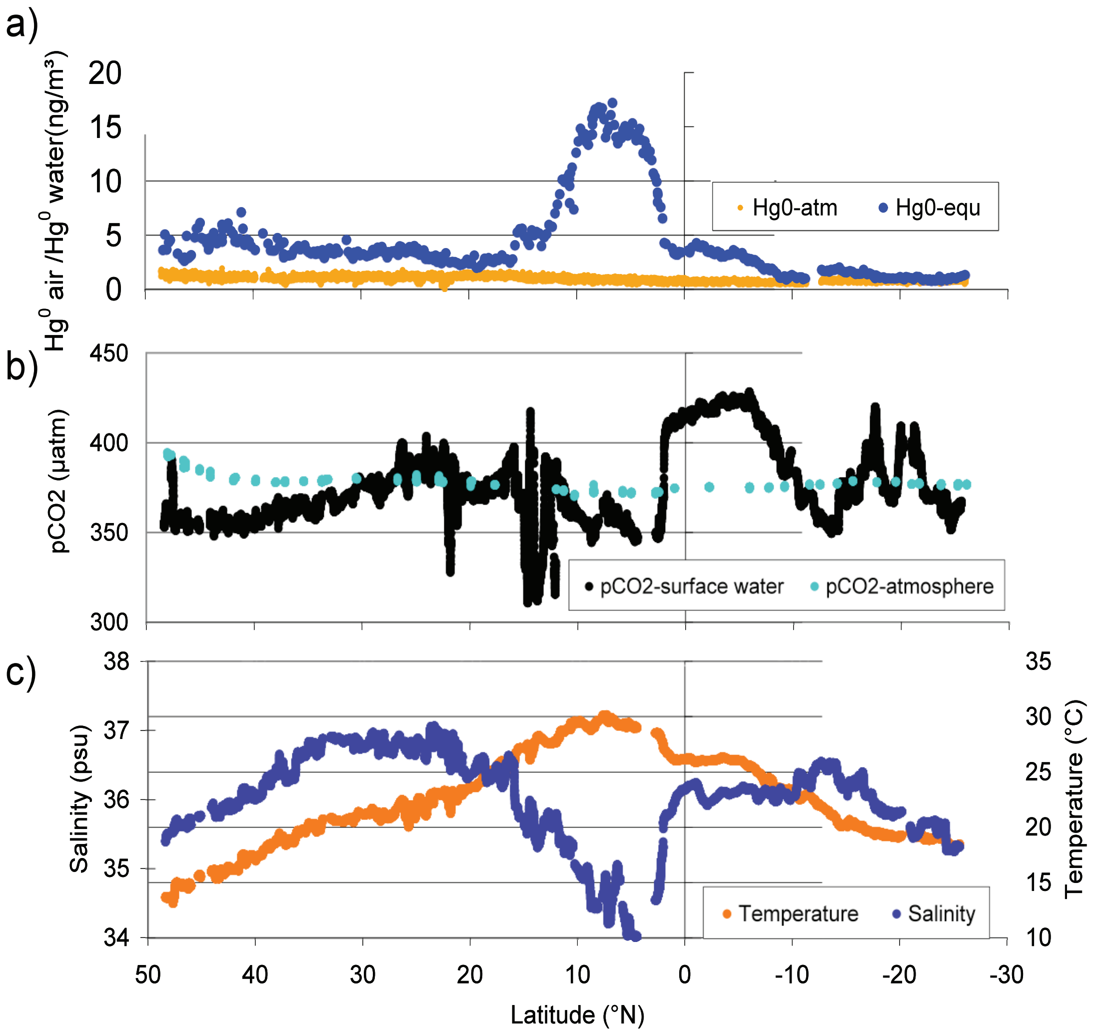

Fig. 4.1: Recordings of a) elemental mercury in the atmosphere and in equilibrium with water, b) pCO_2 in air and water and c) of temperature and salinity in surface water

Link to other projects

A broader view on the processes and inspiring information is expected by a joint interpretation of the data sets obtained during ANT-XXV/1. Especially with forthcoming data from the trace metal group of IOW (Dr. Christa Pohl), the bio-optics group of the AWI (Dr. Astrid Bracher), the meteorological group (Katharina Lengfeld and Timo Hanschmann) and the international DOM-Group (Prof. Gerhard Kattner).

We especially like to thank the captain and the crew of *Polarstern* for excellent support during the campaign and the DFG and AWI for funding.

5. DIMETHYLSULFIDE (DMS) MEASUREMENTS

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Objectives

The volatile sulphur compound dimethylsulfide (DMS) is produced in the oceans biologically via the cleavage of its precursor dimethylsulfoniopropionate (DMSP). The ocean is oversaturated with DMS, hence DMS is emitted into the atmosphere. DMS rapidly oxidizes in the atmosphere and can form cloud condensation nuclei (CCN). CCN can both directly and indirectly affect the radiative budget of the atmosphere by reflecting radiation back to space or by increasing the cloud albedo.

DMSP is produced in the ocean by specialized algae, such as dinoflagellates and coccolithophorids. DMSP is released into the water column by processes that cause phytoplankton cell lysis (e.g. grazing, stress). After release into the water column, DMSP can be taken up by other algae species or several bacteria groups. DMSP serves as an important nutrient and can be converted into biomass. However, DMSP can also be cleaved into DMS and acrylate. This chemical reaction is used as an energy source.

Due to the complex cycle of DMS and DMSP, it is difficult to predict the concentration of these sulphur compounds in the ocean and their influence on the climate. Further measurements of DMS and DMSP in the ocean during different seasons are needed to receive a better understanding of this complex cycle.

The first goal of this cruise was to measure the DMS and DMSP concentrations in surface sea water from the English Channel to Cape Town in order to investigate the distribution of these compounds in different climate regions. The second goal was to compare measured DMS concentrations from two different instruments: 1) purge and trap gas chromatograph coupled to a flame photometric detector (GC/FPD) and, 2) atmospheric pressure chemical ionization mass spectrometer (API-CIMS). The GC-FPD is a more traditional method used to measure DMS discretely. The API-CIMS coupled to a seawater equilibrator is a relatively new technique that could be used to continuously measure DMS. This technique has the potential to run autonomously as part of the OCEANET network, but needs to be tested for accuracy by comparison to other techniques, such as GC-FPD. A first attempt at measuring isoprene with an equilibrator coupled to API-CIMS was also made.

Work at sea

GC-FPD: DMS and DMSP were measured by using a purge and trap system which is attached to a gas chromatograph (GC) and flame photometric detector (FPD). Fig.

5.1 illustrates the setup schematically. The purge unit consisted of a vial which was filled with sample water. The DMS was sparged out of the sample via a helium stream and was pre-concentrated on a liquid nitrogen trap. The gas stream was dried before entering the cold trap via potassium carbonate (K_2CO_3). The pre-concentrated DMS was released onto the GC by heating the trap in hot water. DMS was separated in a capillary column and detected by burning in a hydrogen/air flame in the FPD. The detector signal was recorded using the software ‘Chrom Star’.

DMSP was determined after chemical conversion into DMS. DMSP is converted to DMS by alkaline hydrolysis in the seawater sample with sodium hydroxide pellets. The resulting DMS was measured as described above.

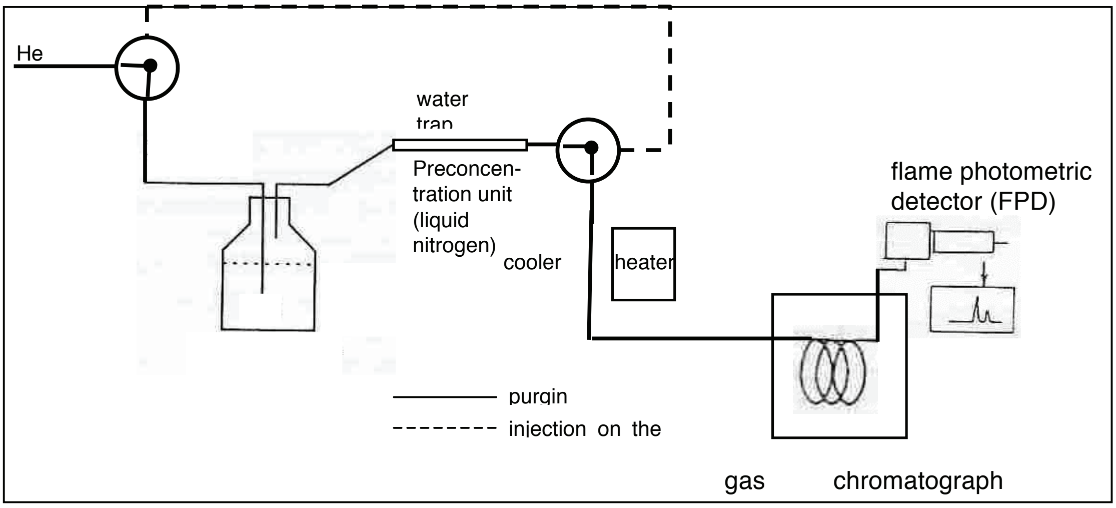

Fig. 5.1: Purge and trap system connected to gas chromatograph (GC) and Flame Photometric Detector (FPD) to measure DMS and DMSP

API-CIMS: DMS was also measured by atmospheric pressure chemical ionization mass spectrometry (API-CIMS). In the chemical ionization source water vapour is protonated (hydronium ion, H_3O^+) via ion molecule interactions with ionized air. The hydronium ion donates its proton to DMS, creating $DMSH^+$. $DMSH^+$ is detected by the mass spectrometer at m/z 63. DMS has a higher proton affinity than the hydronium ion but lower proton affinity than protonated higher order water clusters. Therefore, the amount of water vapour in the ionization source needs to be optimized for DMS. This is done by drying and heating the air stream entering the source. An isotopically labelled internal standard (trideuterated DMS, d_3-DMS, 2.4 ppm) is continuously monitored in conjunction with ambient DMS. The standard is ionized to d_3-$DMSH^+$ and monitored by the mass spectrometer at m/z 66. Isoprene is detected as protonated isoprene, m/z 69.

The API-CIMS is a single quadrupole instrument, modified from a Stanford Research Systems RGA 300 residual gas analyzer (Fig. 5.2). The system consists of an ionization source at atmospheric pressure and two vacuum chambers built at University of California, Irvine, in the lab of Eric Saltzman. The ionization source is a

^{63}Ni foil that is rolled and placed into the end of a ¼” glass lined stainless steel tube. The glass lined tube is heated with a coiled 300 W heater (Watlow) that fits over the tube. Air can be either drawn or pushed through the source and exits via 2 ¼” OD ports on either side of the source. The ions in the source are electrostatically steered through a 255 μm pinhole into the first vacuum chamber. The pressure in the first chamber is 1 Torr and is pumped by an Edwards 28 rotary vane pump. The ions are then steered through 2 cone lenses into the second vacuum chamber. This chamber is pumped down to 1x10-5 Torr by a Varian Navigator 550 turbomolecular pump that is backed by the same Edwards rotary vane pump that pumps the 1 Torr region. This chamber consists of 5 lenses, the quadrupole, and the electron multiplier. The signal generated at the electron multiplier is amplified by an electrometer housed in a compact electronics box that is affixed directly to the quadrupole flange. The signal is transferred as amps to a Windows computer running National Instruments software via an RS-232 connection.

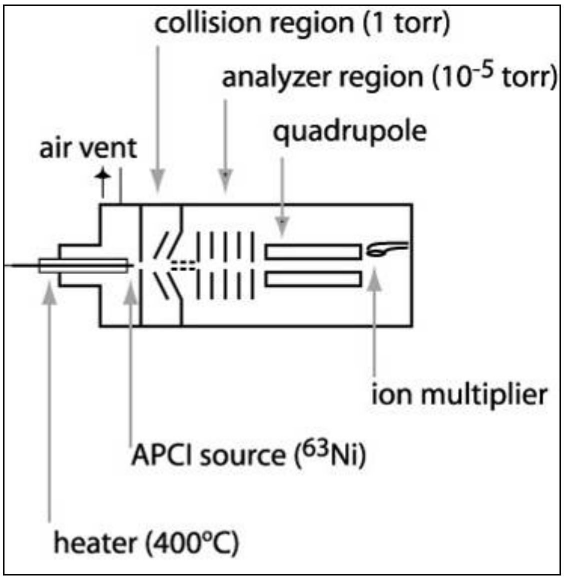

Fig. 5.2: API-CIMS schematic

GC-FPD sampling plan: Samples were taken from the „Fish“ system in different intervals. For comparison, samples were taken from the CTD. Additionally, 4 deep CTD stations were sampled. The sample plan is listed in Table 5.1.

Tab. 5.1: Sampled CTD stations

Date	CTD	Depth(m)	Bottle No.
09.11.2008	Deep	3498	6
09.11.2008	Deep	2500	7
09.11.2008	Deep	1099	8
09.11.2008	Shallow	surface	21
14.11.2008	Deep	bottom	5

Date	CTD	Depth(m)	Bottle No.
14.11.2008	Deep	2000	14
14.11.2008	Deep	1300	19
14.11.2008	Shallow	fluor. max	6
14.11.2008	Shallow	20	23
16.11.2008	Shallow	surface	21
16.11.2008	Shallow	20	19
16.11.2008	Shallow	fluor. max	11
17.11.2008	Shallow	200	3
17.11.2008	Deep	bottom	
17.11.2008	Deep	1300	7
17.11.2008	Deep	800	13
17.11.2008	Deep	20	23
29.11.2008	Shallow	surface	23
29.11.2008	Shallow	fluor.max	10
29.11.2008	Shallow	200	5

API-CIMS sampling plan: Surface seawater from the “Fish” was continuously pumped at a flow rate between 1-3 L min^{-1} to a Liqui-Cel membrane equilibrator (Fig. 5.3). The “Fish” was at approximately 2 m below the surface. Clean dry air was generated with a Dominick Hunter air purifier and directed to the equilibrator at 100 sccm in counter flow to the seawater. The clean air equilibrated with the gases in the seawater, was mixed with 2 sccm of isotopically labelled standard and 1.5 L min^{-1} flow of clean dry air, and then analyzed by the API-CIMS. Every 12 hours blanks for m/z 63, 66, and 69 were measured and the sensitivity of the instrument for isoprene was determined by standard addition. Approximately 5 sccm of 3 ppm unlabelled isoprene standard is added for 3 min intervals 3 times. Each mass is measured for approximately 2 seconds.

Several experiments were conducted to test the system. The Liqui-Cel equilibrator was compared to 2 homemade membrane equilibrators to test for biofouling in the Liqui-Cel. Also, 2 shallow profiles with the “Fish” were performed to determine if there are chemical gradients in the upper 14 m of the sea surface. Preliminary data analysis suggests that biofouling did not occur in the equilibrator and that there were no DMS or isoprene gradients in the upper 14 m.

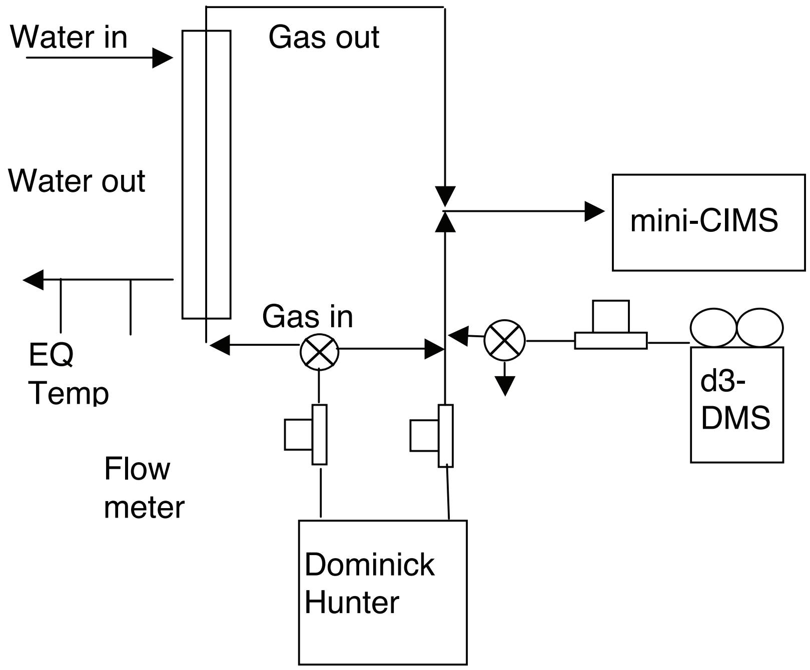

Fig. 5.3: API-CIMS and equilibrator sampling schematic

Preliminary results

DMS was below the detection limit of the GC-FPD during most times of the cruise. Between 15-17 November and 25-30 November, DMS was detectable with GC-FPD. The API-CIMS instrument was able to detect DMS over the whole cruise track. During most of the cruise the DMS levels were between 0.5 and 2.5 nM. Conditions along the cruise track were mostly oligotrophic. However, during the two time periods noted above higher chlorophyll and biological production were observed. An example of the DMS analysis intercomparison from one of the more productive regions is shown in Fig. 5.4. It is clear that there is disagreement between the two DMS measurement techniques. Full data analysis over the entire cruise track is needed before we can determine the reason for this discrepancy. So far CTD samples, DMSP, DMSO and isoprene data have not been analyzed.

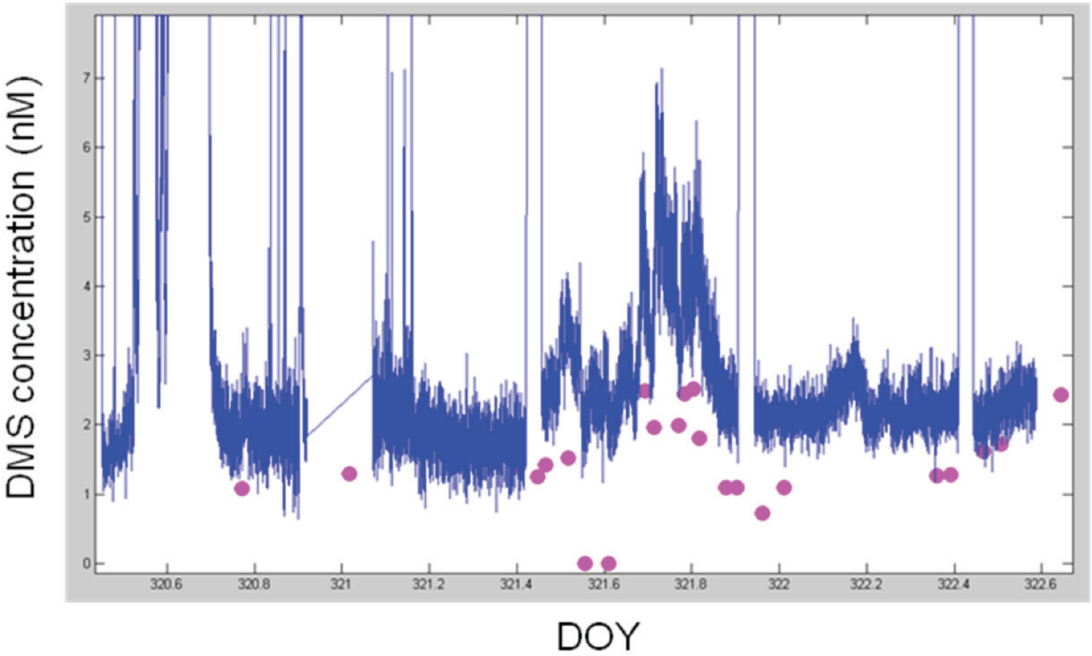

Fig. 5.4: Seawater DMS concentrations plotted against day of year from 15-17 November, 2008. Pink dots are GC-FPD measurements and blue line is API-CIMS measurement

6. INVESTIGATION OF POLYFLUORINATED SUBSTANCES IN THE ATLANTIC OCEAN

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GKSS Research Centre

Objectives

The proposed project is focused on the occurrence and atmospheric transport mechanisms of novel persistent organic pollutants (POPs) in the Atlantic Ocean, which include perfluoro alkyl sulfonamide and N-substituted sulfonamides (PFASs) and fluorotelomer alcohols (FTOHs). Based on the investigations for the novel POPs present in different environmental compartments the north-south transect through the Atlantic Ocean, the aims of the project are: (1) characterization of the concentrations of PFASs in the atmosphere and surface water; (2) evaluation of the air-sea gas exchange process using the Whitman two-film model to elucidate the transport of PFASs from the source region to the remote ocean. This project will improve the understanding of the fate of organic fluorinated substances in the Atlantic Ocean.

Per- and polyfluorinated compounds (PFCs), e.g. perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS), PFASs and FTOHs have been produced in large quantities for several decades and are widely used to produce consumer products such as polymerisation aids, stain repellents in carpets, textile, and leather and paper products. Scientific concern about PFCs increased due to their global distribution and ubiquitous detection in the environment, fish and marine mammals, as well as in human blood. Some PFCs have been shown to cause developmental delays and cancer in lab animals. Recent studies conducted in the presence of PFCs in wildlife from the Arctic have demonstrated that these chemicals are widespread in these regions and accumulate in the food chain. More studies are required to resolve how PFCs are transported from the sources to the coast and marine environment.

Semivolatile FTOHs, N-methyl perfluorooctane sulfonamidoethanol (N-MeFOSE), N-ethyl perfluorooctane sulfonamidoethanol (N-EtFOSE), N-methyl perfluorooctane sulphonamide (N-MeFOSA) and N-ethyl perfluorooctane sulphonamide (N-EtFOSA) have been reported in the atmosphere in the Arctic, Atlantic Ocean and in Asian and western U.S. air masses. The atmospheric residence times for FTOHs were estimated to range between 50 and 80 days. These evidences clearly indicated that semi-volatile PFCs undergo atmospheric long-range transport to remote regions.

ANT-XXV/1 was quite optimal for these investigations as it ranged from the likely sources (European continent) to remote areas without direct inputs. By combining short-term atmospheric samples and the collections of reprehensive water samples across different regions of the North and South Atlantic Ocean, findings are sought as to whether atmospheric transport or ocean currents are controlling the transport and setting flux of these organic pollutants.

Work at sea

Air sampling: Air samples were collected using a high-volume air sampler operating at a constant flow rate of 200-500 L min^{-1}. The ship-borne air samples were collected on the observation deck of *Polarstern*. Typically the collected air sample volume was 600-1,000 m^3. The high volume air sampler consisted of a high volume pump (ISAP 2000, Schulze Automation & Engineering, Asendorf, Germany), a digital flow meter, a metal filter holder and a PUF/XAD-2 column. GF/F 8 filter was used to collect atmospheric particles. Table 6.1 represents samples collected using PUF/XAD-2 columns. Apart from the gas/particle samples, total suspended particulates (TSPs) were also collected during the cruise (Table 6.2). Samples will be used to investigate the concentrations of some non-volatile perfluorinated compounds such as PFOA and PFOS, and the bulk concentration of organic carbon. Field blanks were prepared by shortly exposing the PUF/XAD-2 column to the sampling site. Air samples were stored at -20 ° C in a cooling room.

Water sampling: Water samples were collected using the keel (11 m depth) *in-situ* pump and filled in 2 L propylene bottles. The *in-situ* pump was connected to the ships sea water system (stainless steel pipe/Klauss pump). A glass cartridge packed with PAD-2 was used to enrich the analytes in the dissolved phase, and a glass fibre filter (GF/F 52) was used to collect suspended particulate matter (SPM). Each sample continually ran for 20 hours to achieve a sample volume of ~1,000 L (Table 6.3). Moreover, 33 water samples (2 L) were collected to determine the distribution of PFOA and PFOS across the Atlantic Ocean (Table 6.4). Water column samples are stored at 0° C, and the bottles and SPM samples were stored at -20° C in a cooling room.

Sample preparation and analysis: The samples will be further handled in a clean-lab at GKSS Research Centre. PUF/XAD-2, PAD-3 cartridges and GF filters will be extracted with organic solvents (hexane, dichloromethane, acetone, and methanol) or a mixture of solvents for ~16 h. Two liter water samples will be extracted using wax cartridges and eluted with 15 mL acetonitrile. Extracts will be further concentrated with a rotation evaporator and nitrogen blower down to a total extract volume of 100 μL.

Semi- and volatile PFASs will be quantified by an Agilent 6890 gas chromatograph (GC) coupled to a 5973 mass spectrometer (MS). PFOS and PFOA will be determined using liquid chromatography coupled with tandem mass spectrometers (LC-MS-MS). Data obtained from this cruise will set up a background of PFCs in the Atlantic Ocean. Furthermore, the air-sea gas exchanges of PFASs will be investigated to discover the importance of atmospheric transport for the occurrence of these organic fluorinated substances in remote oceans.

Tab. 6.1: High volume air samples for the determination of semi-volatile PFCs

Sample I.D.	Date	Time	Lat.	Long.	Volume (m^3)	T_{air} (°C)	Humidity (%)
ANT-XXV-1 A1	02.11.08	14:00:00	52.050	-5.786	687	9.9	80
ANT-XXV-1 A2	04.11.08	15:50:00	48.388	-11.623	911	12.3	87
ANT-XXV-1 A3	05.11.08	10:30:00	46.338	-11.623	857	13.7	81
ANT-XXV-1 A4	07.11.08	15:20:00	42.822	-13.361	640	14.0	64
ANT-XXV-1 A5	07.11.08	15:20:00	42.822	-16.207	2237	14.0	64
ANT-XXV-1 A6	09.11.08	14:00:00	37.129	-16.207	986	17.9	79
ANT-XXV-1 A7	12.11.08	19:00:00	26.841	-20.744	1101	20.2	81
ANT-XXV-1 A8	12.11.08	19:00:00	26.841	-20.744	1209	20.2	81
ANT-XXV-1 A9	16.11.08	12:30:00	14.580	-14.154	968	26.7	81
ANT-XXV-1 A10	20.11.08	13:30:00	2.469	-7.063	877	26.9	78
ANT-XXV-1 A11	23.11.08	14:00:00	-5.925	3.127	1303	24.0	78
ANT-XXV-1 A12	27.11.08	15:00:00	-17.740	8.519	522	19.4	78
ANT-XXV-1 A13	29.11.08	13:20:00	-23.705	13.605	610	18.7	79

Tab. 6.2: Particle samples for the determination of total suspended particulates and ionic PFCs

Sample I.D.	Time	Date	Lat.	Long.	Volume (m^3)	T_{air} (°C)	Humidity (%)
ANT-XXV-1 PF1	13:00:00	04.11.08	52.050	-3.615	1301	9.9	80
ANT-XXV-1 PF2	16:20:00	07.11.08	48.317	-6.286	1724	12.3	87
ANT-XXV-1 PF3	15:20:00	09.11.08	42.822	-11.643	1233	14.0	64
ANT-XXV-1 PF4	10:00:00	12.11.08	37.129	-13.363	1965	17.9	79
ANT-XXV-1 PF5	19:00:00	15.11.08	26.841	-16.217	1519	20.2	81
ANT-XXV-1 PF6	12:30:00	20.11.08	14.580	-20.964	2453	26.7	81
ANT-XXV-1 PF7	13:30:00	23.11.08	2.469	-14.153	1826	26.9	78
ANT-XXV-1 PF8	14:00:00	27.11.08	-5.925	-7.063	2457	24.0	78
ANT-XXV-1 PF9	15:00:00	29.11.08	-17.740	3.127	1248	19.4	78
ANT-XXV-1 PF10	13:20:00	01.12.08	-23.705	8.521	522	19.4	78

Tab. 6.3: High volume water samples for the determination of semi-volatile PFCs

Sample I.D.	Date	Time	Lat.	Long.	Volume (L)	T_{water} (°C)	T_{air} (°C)	Salinity
ANT-XXV-1 W1	02.11.08	16:40:00	51.917	2.681	409	13.8	10.7	35.07
ANT-XXV-1 W2	03.11.08	7:54:00	50.245	-1.361	1000	14.4	11.4	35.17
ANT-XXV-1 W3	04.11.08	8:30:00	48.967	-5.657	1000	12.4	13.4	35.36
ANT-XXV-1 W4	05.11.08	8:10:00	46.440	-7.760	1035	14.7	13.8	35.64
ANT-XXV-1 W5	06.11.08	8:30:00	44.521	-9.765	1073	15.4	14.8	35.74
ANT-XXV-1 W6	07.11.08	9:30:00	42.852	-11.638	1088	15.87	13.9	35.90
ANT-XXV-1 W7	08.11.08	8:28:00	40.519	-12.356	835	17.23	15.9	36.35
ANT-XXV-1 W8	09.11.08	10:18:00	37.129	-13.361	992	18.4	17.9	36.27
ANT-XXV-1 W9	10.11.08	8:30:00	34.303	-14.166	1463	19.7	18.8	36.69
ANT-XXV-1 W10	11.11.08	9:10:00	31.173	-14.866	1262	20.8	20.0	36.87
ANT-XXV-1 W11	12.11.08	7:50:00	28.118	-15.348	1296	21.03	19.8	36.78
ANT-XXV-1 W12	13.11.08	8:50:00	25.155	-17.898	1350	21.54	20.6	36.79
ANT-XXV-1 W13	14.11.08	16:08:00	22.133	-20.524	950	22.54	21.5	36.76
ANT-XXV-1 W14	16.11.08	8:15:00	15.295	-20.967	919	27.16	25.7	35.74
ANT-XXV-1 W15	17.11.08	9:15:00	11.203	-20.254	1041	28.6	27.4	35.23
ANT-XXV-1 W16	18.11.08	12:30:00	8.446	-19.404	1120	29.23	28.7	34.47

Sample I.D.	Date	Time	Lat.	Long.	Volume (L)	T_{water} (°C)	T_{air} (°C)	Salinity
ANT-XXV-1 W17	19.11.08	9:30:00	5.871	-17.165	925	29.13	27.9	34.57
ANT-XXV-1 W18	20.11.08	9:00:00	2.950	-14.583	1015	28.5	27.2	34.50
ANT-XXV-1 W19	21.11.08	8:00:00	0.696	-12.656	935	26.1	25.7	36.06
ANT-XXV-1 W20	20.11.08	9:50:00	-3.006	-9.532	705	26.08	25.7	36.04
ANT-XXV-1 W21	23.11.08	9:10:00	-5.929	-7.060	1000	25.48	23.6	36.15
ANT-XXV-1 W22	24.11.08	9:30:00	-8.445	-4.920	750	23.61	22.6	35.97
ANT-XXV-1 W23	25.11.08	8:30:00	-11.412	-2.380	1000	22.91	20.9	36.19
ANT-XXV-1 W24	26.11.08	8:30:00	-14.577	0.361	1110	20.0	20.0	36.17
ANT-XXV-1 W25	29.11.08	9:30:00	-23.232	8.086	1000	19.05	18.6	35.48
ANT-XXV-1 W26	30.11.08	9:21:00	-25.672	10.346	790	18.44	18.0	35.32

Tab. 6.4: Two liter water samples for the determination of ionic PFCs

Sample number	Volume (L)	Date	Time	Lat.	Long.	T_{water} (°C)	Salinity
ANT-XXV-1 LW1	2	02.11.08	16:00:00	52.000	2.805	13.7	35.07
ANT-XXV-1 LW2	2	02.11.08	23:58:00	50.885	1.253	13.81	35.21
ANT-XXV-1 LW3	2	03.11.08	07:52:00	50.246	-1.356	14.1	35.17
ANT-XXV-1 LW4	2	03.11.08	11:15:00	50.125	-2.071	14.41	35.17
ANT-XXV-1 LW5	2	03.11.08	17:49:00	49.951	-3.042	14.0	35.21
ANT-XXV-1 LW6	2	03.11.08	23:04:00	49.625	-3.958	13.7	35.26
ANT-XXV-1 LW7	2	04.11.08	08:30:00	48.969	-5.654	12.4	35.36
ANT-XXV-1 LW8	2	04.11.08	11:15:00	48.690	-5.986	13.0	35.28
ANT-XXV-1 LW9	2	04.11.08	18:30:00	48.038	-6.508	13.7	35.51
ANT-XXV-1 LW10	2	05.11.08	09:15:00	46.338	-7.836	14.61	35.65
ANT-XXV-1 LW11	2	05.11.08	18:20:00	46.117	-8.009	14.85	35.71
ANT-XXV-1 LW12	2	05.11.08	21:50:00	45.789	-8.308	14.7	35.69
ANT-XXV-1 LW13	2	06.11.08	08:20:00	44.548	-9.735	15.4	35.74
ANT-XXV-1 LW14	2	06.11.08	12:33:00	44.099	-10.242	16.0	35.92
ANT-XXV-1 LW15	2	06.11.08	21:50:00	43.856	-10.516	16.1	35.88
ANT-XXV-1 LW16	2	07.11.08	09:15:00	42.852	-11.631	15.89	35.87
ANT-XXV-1 LW17	2	07.11.08	23:00:00	41.860	-11.945	16.08	35.86
ANT-XXV-1 LW18	2	08.11.08	23:00:00	38.438	-12.979	18.54	36.35
ANT-XXV-1 LW19	2	10.11.08	00:20:00	35.517	-13.824	19.8	36.70
ANT-XXV-1 LW20	2	10.11.08	17:27:00	33.593	-14.455	20.5	36.86
ANT-XXV-1 LW21	2	12.11.08	07:40:00	28.121	-15.347	21.0	36.78
ANT-XXV-1 LW22	2	13.11.08	09:30:00	25.000	-18.283	22.63	36.80
ANT-XXV-1 LW23	2	15.11.08	08:50:00	19.200	-20.716	23.95	36.58
ANT-XXV-1 LW24	2	16.11.08	09:58:00	15.000	-20.983	27.12	35.71
ANT-XXV-1 LW25	2	17.11.08	23:57:00	9.643	-19.833	29.55	34.89
ANT-XXV-1 LW26	2	19.11.08	18:15:00	4.857	-16.267	29.1	33.90
ANT-XXV-1 LW27	2	21.11.08	14:30:00	-0.251	-11.857	26.17	36.18
ANT-XXV-1 LW28	2	23.11.08	09:20:00	-5.929	-7.060	25.47	36.15
ANT-XXV-1 LW29	2	24.11.08	23:30:00	-10.186	-3.433	23.11	36.04
ANT-XXV-1 LW30	2	26.11.08	12:20:00	-15.083	0.802	20.31	36.14
ANT-XXV-1 LW31	2	29.11.08	09:25:00	-23.221	8.075	19.01	35.69
ANT-XXV-1 LW32	2	30.11.08	22:20:00	-27.365	11.318	18.13	35.43
ANT-XXV-1 LW33	2	01.12.08	15:13:00	-29.431	13.498	18.05	35.41

7. BIO-OPTICAL MEASUREMENTS: GROUND-TRUTHING FOR SATELLITE OBSERVATIONS

Erika Allhusen, Anja Theis, Astrid Bracher (not on board)
Alfred-Wegener-Institut

Objectives

It has been estimated that marine phytoplankton contributes 30 to 60 % to the global primary production. The large uncertainty range is a result of the lack of global information on phytoplankton absorption and light penetration depth, which cannot be supplied by the current ocean colour satellite sensors. The spectral resolution of these sensors is not sufficient to extract the relevant information. The variation of phytoplankton absorption in ocean waters also affects the retrieval of chlorophyll *a* concentrations (a measure of phytoplankton biomass) derived from satellite data, which are important input data used in primary production models. Results by Bracher et al. (2006) show that specific phytoplankton absorption spectra as well as information on the light penetration depth can be derived by combining information from measurements of the two satellite instruments, MERIS with high spatial, and SCIAMACHY with high spectral resolution (both operating on board of the European environmental satellite ENVISAT).

Besides the analysis of satellite data and applied model studies, field measurements in the open ocean of phytoplankton pigment composition, optical characteristics of phytoplankton and other water constituents, reflectance and underwater light measurements are highly precise input parameters for the validation of results from the analyses of satellite data and modelling.

Thus the aim of this research project is to improve estimates of global marine primary production and the distribution of major phytoplankton functional groups by using remote sensing data in combination with *in-situ* measurements of ocean optics, phytoplankton productivity and composition and particulate organic carbon (POC). In particular, data will be collected during this cruise to improve our understanding of the oceans variability in optical properties and to improve/develop remote sensing algorithms for the investigated research area. Algorithms to retrieve POC from space are still very basic, but are of great importance for studies concerning biogeochemical cycles and the biological pump within the world’s oceans because carbon and not chlorophyll are the bases for those studies. Through a better knowledge of the sinks and sources of CO_2 in the ocean a contribution will be made to a better understanding of changes in the world's climate as well as to the understanding of the marine food web.

Work at sea

Water sampling: Water samples were taken every morning at 7 am from beneath the ship (moon pool) and at about 1 pm from the CTD (three different depths: surface, fluorescence maximum and 100 m). Sampling times were closely coordinated with the other groups to allow analysis of possible correlations between our data in the future. Water samples were processed for various analyses:

- Nearly 2,300 L of water samples were filtered through GF/F and CN filters for analysis of pigments, total suspended matter, and particulate absorption measurements.
- Water samples were preserved for flow cytometry measurements later in the laboratory in Bremerhaven.
- Particulate absorption in suspension and absorption of Gelbstoff were measured during the cruise using the point-source integrating-cavity absorption meter (PSICAM) (Röttgers et al. 2005).

Online and *in-situ* optical measurements

- A FastTracka Fast Repetition Rate Fluorimeter (FRRF) was used in a flow-through system with water continuously pumped from the moon pool to provide online data of chlorophyll fluorescence during the cruise.
- During the stations radiances were measured firstly from onboard the ship with a set of three radiometers and secondly in the water column (0-160 m) at the stations.

Preliminary results

Data from FRRF and PSICAM: At the start of the cruise, after crossing the English Channel, we measured higher chlorophyll concentrations. Later, concentrations rapidly decreased to near detection limit of our equipment. At about 25°N we encountered the first phytoplankton bloom as it could be seen in satellite images (Fig. 7.1) and fluorescence of particles peaked for some time. Some days after crossing the equator (21.11.08) chlorophyll concentrations started to rise again probably due to upwelling systems in the region and did not diminish until the end of the sampling on board. The absorption measurements with the PSICAM corroborate generally with the FRRF data.

Additionally, water samples were filtered and the frozen or dried filters will be transported to the home laboratories for further analyses of pigments by high-performance liquid chromatography (HPLC) and fluorometry, particulate absorption and total suspended matter (TSM). Water samples were also preserved for the analysis by flow cytometry.

Combined with satellite pictures of the sampling sites, this range of analyses and *in-situ* measurements will hopefully give a detailed picture of the surface phytoplankton community in the Northern and Southern Atlantic Ocean.

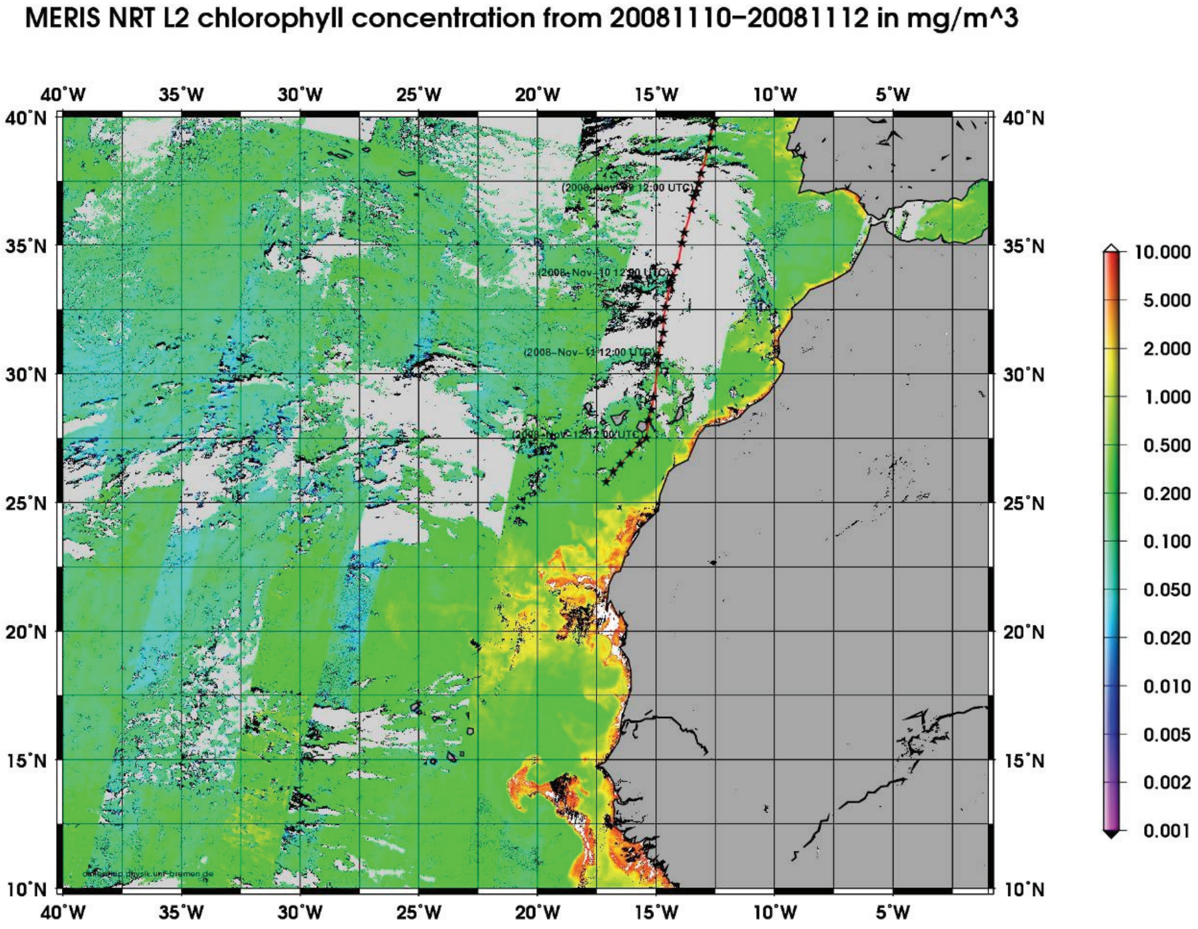


Fig. 7.1: Chlorophyll concentration during the Polarstern cruise ANT-XXV/1, MERIS/ESA data visualized by T. Dinter and A. Sadeghi (AWI-IUP group PHYTOOPTICS)

References

Bracher A, Vountas M, Dinter T, Röttgers R, Doerffer R, Burrows JP (2006). Retrieval of phytoplankton distribution and light absorption from space borne SCIAMACHY data using Differential Optical Absorption Spectroscopy. Proceedings of the Ocean Optics XVIII, 9-13 Oct 2006, Delta CentreVille, Montreal, Canada.

Röttgers R, Schönfeld W, Kipp P-R, Doerffer R (2005). Practical test of a point-source integrating cavity absorption meter: the performance of different collector assemblies. Applied Optics, 44, 5549-5560.

8. OCEAN COMPONENT OF THE OCEANET PROJECT – MEASUREMENTS OF CO_2 PARTIAL PRESSURE, TOTAL GAS TENSION AND OXYGEN

Peer Fietzek, Tobias Steinhoff, Arne Körtzinger (not on board)
IFM-GEOMAR

Objectives

The OCEANET project aims at further development and at testing autonomous instrumentation for measurement of energy and matter exchange between the atmosphere and the surface ocean. At first, the instruments were tested and installed aboard *Polarstern*. Since the processes under investigation require both a rather comprehensive observational approach as well as high spatial and temporal coverage, unattended operation of the multi-parameter instrumentation aboard "Voluntary Observing Ships" is the long term goal of this initiative.

The oceanic component of this study places a strong focus on the marine carbon cycle in the surface ocean which is of high climatic relevance but at the same time susceptible to climate change. The surface ocean's CO_2 source/sink function is maintained by a complex interaction of physical, chemical and biological processes. Therefore its understanding requires measurement of various different parameters.

During this second OCEANET cruise the work carried out during the first *Polarstern* transit (ANT-XXIV/4) was continued. This time the focus was on the autonomous measurement of CO_2 partial pressure (pCO_2) with underway flow-through as well as submersible systems, whose feasibility was assessed via intercomparison measurements. Data for dissolved oxygen (O_2) concentration as well as total gas tension were measured as additional and relevant chemical parameters. For a more detailed data analysis physical parameters measured by the ship's system (temperature, salinity) will be considered as well. For the investigation of coherences between the measured chemical and biological parameters, the data collected by other participants of this cruise might be included into the analysis (DMS, DMSP, chlorophyll, DOC, etc.).

Work at sea

During the cruise ANT-XXV/1 we operated several submersible as well as underway instruments in the wet laboratory of *Polarstern*. The intercomparison exercises of sensors for the measurement of CO_2 partial pressure (pCO_2) in seawater, which were started during the preceding transit ANT-XXIV/4, were continued. A total of three different systems were run. Two of them were prototypes which were tested for the first time on this cruise: the submersible HydroC™ (CONTROS Systems and Solutions GmbH, Kiel, Germany), and an underway unit by Franatech GmbH

(Lüneburg, Germany). The GO/Neill underway $p\mathrm{CO}_2$ measurement system (General Oceanics Inc., Miami, Florida, USA), which is permanently installed on *Polarstern* was intended to be used as a reference for the other systems since it is the most intensively tested and internationally accepted system. Unfortunately the GO/Neill system aboard did not run properly and no data could be recorded during this cruise. The equilibrated air was not sufficiently dried leading to varying water vapour concentrations in the air volume to be analyzed. A dysfunction of the condenser as well as the installed Nafion®-tubes was identified. In addition, the NDIR CO_2 detector (LiCOR 7000) showed some unexpected behaviour every time the routine switched from the measurement of dry standard gases to the measurement of the equilibrated air, which might have been caused by humidity effects as well. Although many repair attempts were undertaken (self-built condenser, additional Nafion®-tubes) the problem could not be solved.

As a point based reference for the tested $p\mathrm{CO}_2$ systems discrete samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were taken about every 6 h for analysis back home at the IFM-GEOMAR in Kiel. The samples were drawn into 500 mL bottles and poisoned with saturated mercuric chloride solution. As a continuous reference for later comparison the $p\mathrm{CO}_2$ data set recorded by J. Kuss during this cruise will be taken into account (see chapter 4.).

The following three different systems were successfully operated throughout the cruise:

Franatech underway system: The Franatech underway system was directly connected to the seawater supply. Within a multistranded-equilibrator consisting of a bundle of equilibrator tubes the seawater is brought to partial pressure equilibrium with a closed air circuit passing the equilibrator tubes in counter flow direction. The CO_2 concentration in the air circuit was continuously analyzed by means of a solid state CO_2 detector. The measurement interval was set to 30 seconds. Since no filter was included before the water reaches the equilibrator, flushing with freshwater from time to time was necessary to prevent clogging and to maintain a constant water flow through the system.

HydroC™/CO_2: Within this submersible sensor a flat silicone membrane acts as an equilibrator between the seawater and the inner gas volume of the sensor. The CO_2 concentration in the air circuit is measured by means of NDIR detection. Two prototypes, equipped with NDIR detectors of different optical path length, ran throughout the entire cruise without difficulties. One was equipped with a total of six additional internal sensors for temperature, relative humidity and pressure. This information about the conditions within the sensor will be carefully analyzed to draw as many conclusions as possible with respect to an optimization of this sensor type. This optimization refers to both engineering and proper data processing as well as correction of the raw detector data. An internal zeroing circuit acting as a regular one point calibration was included into this instrument as well. The lengths of the zeroing and measuring intervals were part of the experiments and hence were varied throughout the cruise. This sensor was calibrated with three different standard gases (ranging from 184 to 740 ppmv) before and after the deployment. The other sensor consisted of a membrane-equilibrator and an NDIR detector with no additional sensors included. It was run to provide a comparable dataset to the HydroC™ sensor. Both sensors provided measurement values every second.

Submersible Autonomous Moored Instrument for CO_2 (SAMI): Like the HydroC™ the SAMI is an autonomous *in-situ* sensor manufactured by Sunburst Systems (Missoula, Montana, USA). In contrast to the two systems described above, which work with a gas circuit, the SAMI is a wet chemical sensor on the basis of a tube shaped membrane and a pH indicator dye solution. Depending on the CO_2 concentration in the water the CO_2 concentration in the solution changes leading to a varying pH value. This effect evokes a change in the colour of the liquid, which is measured photometrically. Measurements are carried out every 15 min.

The instruments were provided with seawater from the ship's seawater supply, which draws water from around 11 m depth via a centrifugal pump and stainless steel tubings. Temperature and salinity were measured directly at the seawater intake by the shipborne thermosalinograph. The Franatech system was connected directly to the tubings, while both the submersible SAMI and the HydroC™s were run in two thermally insulated flow-through boxes. The boxes with a volume of about 78 L each were flushed continuously with about 16 l/min. This principle had proven its functionality during previous cruises. In addition to the $p$$CO_2$ sensors, we submerged an oxygen optode sensor (Aanderaa, Bergen, Norway; measurement interval 30 s;), the HydroC™'s and a GTD Pro gas tension device (Pro Oceanus, Halifax, Canada; measurement interval 30 s) together with the SAMI in the respective flow-through containers. The latter measures the total pressure of all dissolved gases in the seawater. This important parameter will be included in the analysis of the other sensors' data. Especially the measured pressures within the HydroC™ will we analyzed with respect to this reference. The optode measures *in-situ* water temperature along with the dissolved O_2 concentration and can therefore be used to account for the effect of warming of the sample flow between intake and point of measurement. Both, the optode and the GTD successfully operated throughout the whole cruise without any interference.

Expected results

So far, no data can be presented here. The data recorded by the SAMI cannot be read out and processed as long as the sensor is still operated. The values obtained by the Franatech-System, the HydoC™s, the GTD and the Optode will analysed after the end of the cruise. Special emphasis will be put on the development of new processing algorithms for the HydoC™, which takes into account the influences of all the relevant measured parameters on the raw sensor signal.

As stated above the data of the Franatech system, the HydroC™s, the optode and the GTD were successfully recorded throughout the entire trip. During the cruise bloom events and sudden changes in the temperature for example, could be identified in all data sets. Solely due to changes in and tests of newly developed recording software the dataset of the HydroC™ with the additional sensors showed some gaps. The dataset of the other HydroC™ was recorded without any interruption. The samples for the DIC/TA-titration were always taken at times, where all sensors operated properly.

It is intended to derive the sea surface pCO_2 of all the described systems along the cruise track and to compare it to the pCO_2 values, which will be derived from the sample's DIC/TA-titration results, as well as to the pCO_2 results obtained by J. Kuss. The response behaviour (response and decay time), the accuracy and the drift of the used sensors are parameters of interest while looking at and comparing their performance. It will be further investigated, whether similarities exist between the results of the last intercomparison and the data, which was obtained by the new systems during this cruise.

Further analysis will take into account the O_2 concentrations as well as the measured total gas pressures. Both values might help to identify possible problems of the *in-situ* sensors emerging from temporal disequilibria in the gas matrix, which could lead to transient pressure changes and hence changes in the composition of the equilibrated gas phase that do not represent ambient pCO_2. This assumptions as a possible burden for membrane *in-situ* sensors came up during the analysis of the last intercomparison results.

Finally the pCO_2 measurements could be brought into context with the DMS and DMSP concentrations as measured by C. Marandino and C. Zindler (see chapter 5.). Further biological parameters might be considered at that stage as well.

The evaluation of the entire dataset is currently underway at the IFM-GEOMAR. The intercomparison of different pCO_2 systems as well as the optimization of the HydroC™ are ongoing tasks and will be continued during the next cruises with OCEANET participation.

9. COMPOSITION OF THE ATMOSPHERE AND RADIATION BUDGET AT THE ATMOSPHERE/OCEAN INTERACTION (OCEANET-ATMOSPHERE)

Katharina Lengfeld, Timo Hanschmann, Andreas Macke (not on board)
IFM-GEOMAR

Objectives

The net radiation budget at the surface is the driving force for most physical processes in the climate system. It is mainly determined by the complex spatial distribution of humidity, temperature and condensates in the atmosphere.

In the framework of the WGL-PAKT initiative OCEANET the state of the atmosphere and its effect on the net radiation budget at the sea surface are obtained by a combination of full sky imager and pyrano- and pyrgeometer. A further goal is to characterize aerosol column properties, check their consistency with associated measurements of broadband radiative fluxes, and to monitor temporal evolution of aerosol properties in order to explore aerosol-cloud-interaction and to establish meridional gradients of tropospheric aerosols. These observations are performed in the framework of the Marine Aerosol Network of the AERONET project. Finally, the spatial and temporal variability of the solar irradiance at various depths in the ocean is determined together with the sea surface variability.

The present project is also part of the “Meridional Ocean Radiation Experiment” (MORE) which uses Atlantic transfers of various research vessels for the combined measurements of the atmospheric state. The use of *Polarstern* and other research vessels during their Atlantic transects enables the collection of air sea interaction under a variety of different weather and climate conditions.

Work at sea

The downwelling broadband short- and longwave radiation flux at the sea surface were obtained by means of a Kipp & Zonen CM 21 pyranometer and a CG4 pyrgeometer with a temporal resolution of 2 seconds, which enables the detection of cloud induced high frequency fluctuation of the incoming radiation. A full sky imager developed at IFM-GEOMAR monitored the sky appearance every 15 seconds. In addition to the cloud-radiation monitoring, a Microtops sunphotometer was used to measure the aerosol optical thickness (AOT) under clear sky conditions.

In collaboration with the Phyto-Optics Group of AWI and the University of Bremen the fluctuation of the spectral solar radiation at various depths was obtained from a

RAMSES spectroradiometer of the AWI group. To quantify the spatial and temporal characteristics of these light fluctuations the brightness distribution on a white diffuse reflecting plate was filmed at various depths and will be spectrally analyzed later on. From this the characteristic space and time scales of the mostly surface wave induced light fluctuation was obtained as a function of the sea condition and depth. An underwater camera system developed at IFM-GEOMAR, observed the light fluctuations projected on a white board at various depths. In a future step these data will be fed in the Monte-Carlo radiative transfer code to reproduce the observed spatial and temporal light fluctuations in the model.

Preliminary results

For the radiation measurement and the full-sky-imager the conditions have been almost optimal. The instruments worked continuously. Small problems have been encountered due to shadows from the crow's nest and from the smokestack that occasionally disturbed the radiation measurement. The instruments have been mounted on the optimal available position. Fig. 9.1 illustrates the incoming shortwave radiation (top-left panel) over the whole cruise until 16 November. Downwelling longwave radiation is shown in the top right panel and air-temperature in the bottom panel. In all three panels the fluctuations between cloudy and clear sky conditions are obvious. This is especially apparent in the shortwave radiation. An increasing trend in both the downwelling longwave radiation and the temperature is shown. This concurrency is expected because downwelling longwave radiation depends on the temperature of the atmosphere or cloud bottom.

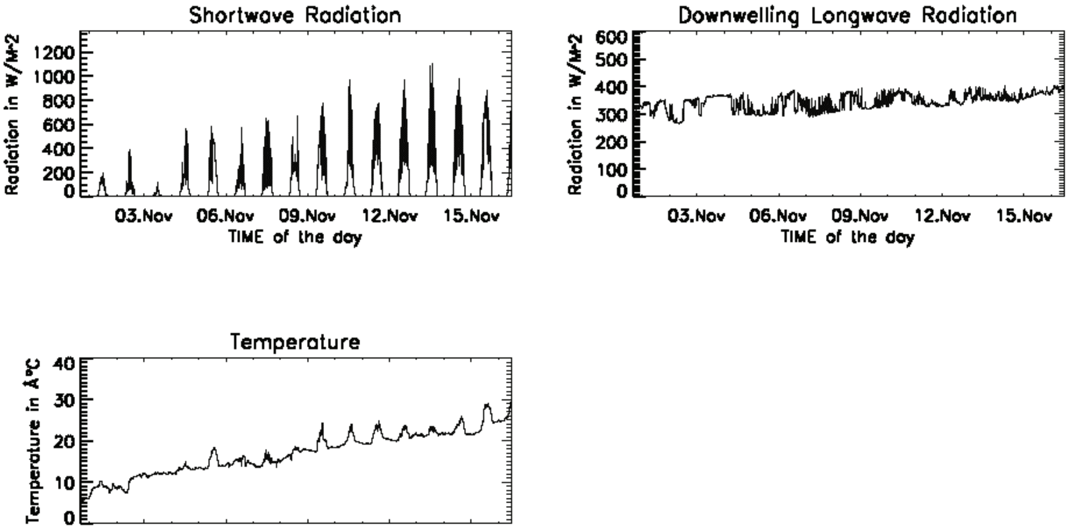

Shortwave Radiation
Downwelling Longwave Radiation
Temperature

Fig. 9.1: Measured radiation during ANT-XXV/1 (preliminary results). Top-left: incoming shortwave radiation. Top-right: downwelling longwave radiation. Bottom: temperature

Several clear sky and broken cloud conditions (Fig. 9.2) were observed. High convective clouds in the inner tropical convergence zone were expected but not observed. During this transect *Polarstern* passed only one tropical rain-event (Fig.

9.2). During the entire cruise track many different types of clouds were observed, which can be used to optimize our parameterizations.

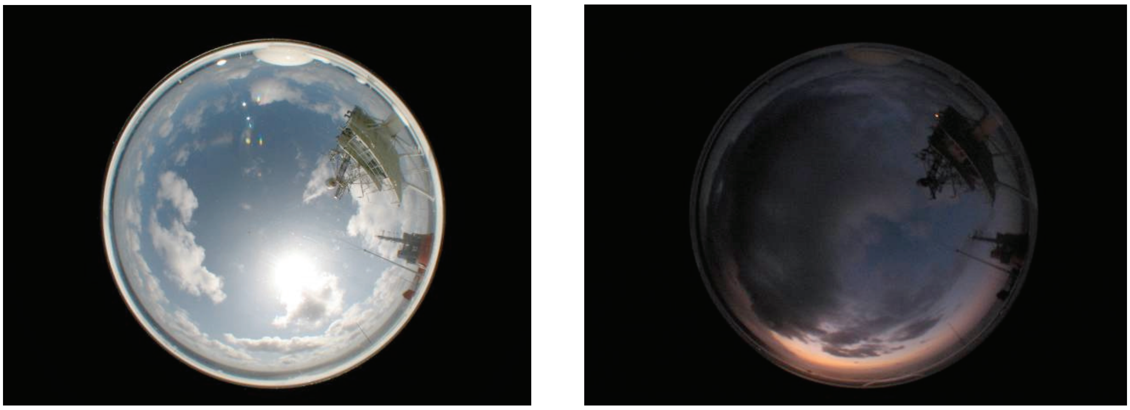


Fig. 9.2: Left: Sky image of a broken cloud case (20.11.2008, 14:31); right: Sky image of a tropical rain event (19.11.2008, 18:58)

A large number of underwater light fluctuation measurements using the Zodiac were performed covering a variety of sea surface roughness states. Back at IFM-GEOMAR a spectrum of the fluctuations and the intensity of the red, green and blue colour parts will be calculated.

The sun-photometer measurements of the AOT were slightly disturbed due to the persistent presence of thin cirrus clouds. A dust-event was not observed on this cruise. South of the equator deep stratiform clouds covered nearly the whole east Atlantic. Only on a few days during noon time and in the afternoon several cloud-free regions were passed and could be used for the AOT measurements.

Fig. 9.3 shows the resulting time series of AOT during the whole cruise with some disturbances mostly due to thin cirrus. Later analysis in combination with the full sky imager data will enable to delete cirrus contaminated “clear sky” AOT measurements.

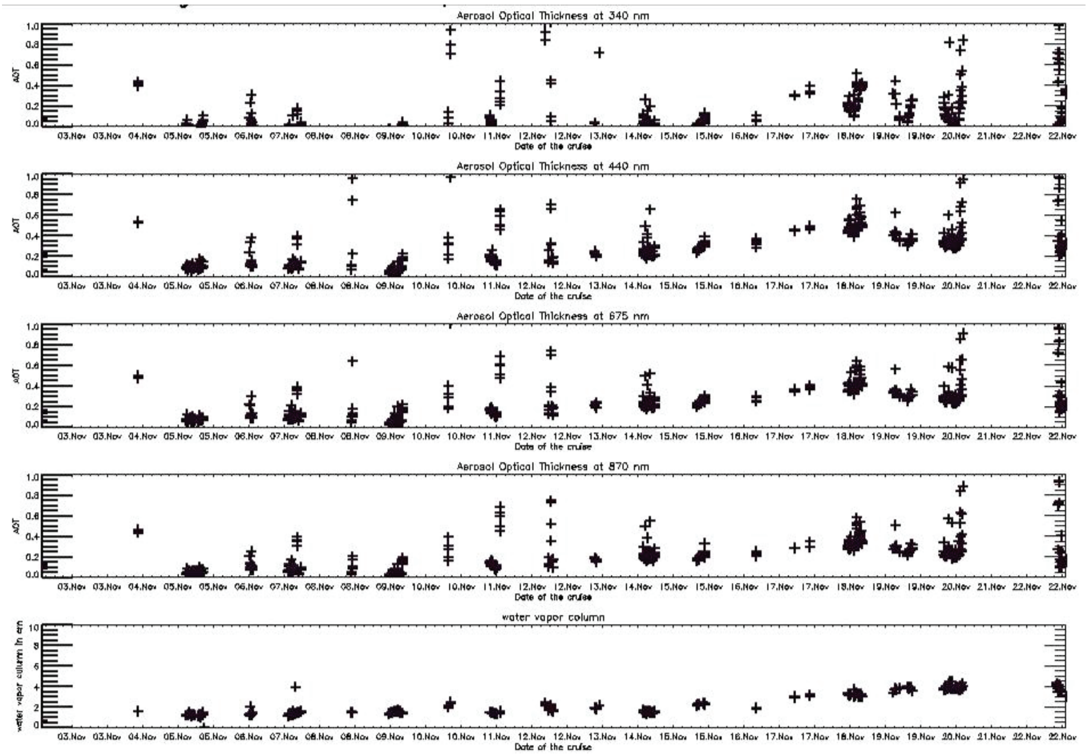


Fig. 9.3: Preliminary results: Panel 1-4: Aerosol optical thickness at 340 nm, 440 nm, 675 nm, 870 nm, respectively. Panel 5: water vapour column in cm

10. SEA TRIAL AND TESTS OF THE NEW UPGRADED UNDER WATER NAVIGATION SYSTEM “POSIDONIA“

Saad El Naggar, Peter Gerchow, Gerd Rohardt (AWI), Johannes Rogenhagen,
Werner Dimmler (Laeisz), Frederic Bellier (IXSEA) (all until Las Palmas)

Objectives

The under-water navigation system POSIDONIA was upgraded during the last shipyard stay of *Polarstern* in Bremerhaven between 20.05.08 and 12.06.08. Newly designed hard and software were installed and tested at the harbour of Bremerhaven. A new acoustic array and window were fix-installed nearby the moon pool in addition to the mobile acoustic array. A complete new electronic cabinet was installed, modified and tested.

Work at sea

The first operational test under real conditions at sea was carried out during the cruise ARK-XXIII/1+2. The final sea trial was carried out during the cruise ANT-XXV/1 on the way to Las Palmas between 31.10.08 and 12.11.08. The mooring and calibration were done on 07.11.08 at 42°51.2’N; 11°38.16’W, at a water depth of 1,822 m.

Unfortunately it was not possible to calibrate the new POSIDONIA system (antenna and electronic cabinet) due to hardware problems detected during initial checks. This system will be replaced by a new one on the next call of *Polarstern* to Bremerhaven in Mai 2009. We performed a calibration test for the old system using the new software to verify the reliability and performance of the old system after modification of the antenna and the electronic cabinet.

A mooring system was prepared for the calibration using the POSIDONIA Transponder RT 861 B Nr. H 204 (Fig. 10.1). The calibration was carried out according to the specification of the producer (IXSEA). The old calibration parameter set was changed to zero, and a new set was measured and determined using the following procedure: The final position of the transponder at the sea floor was measured and used as a reference point for the calibration. The measured water depth was about 1,822 m, and this defined the diameter of the ship track surrounding the transponder (8 calibration circles with a diameter of 0.7 nautical miles, Fig. 10.2). The calibration was carried out with a ship speed of 5 knots. After data processing a new calibration parameter set was calculated and used for the next step of calibration. The first calibration measurement was repeated using the new calibration parameter set (Fig. 10.3). A second calibration parameter set was calculated using the data of the second measurements. Deviations were calculated and the final calibration data set was found. The old POSIDONIA system is again fully operational.

General data and conditions during the test:

Date	07.11.2008
Location	42° 51.2' N; 11° 38.16' W
Water depth	1822 m
Wind speed	6.4 m/s
Wind direction	298°
Air temperature	13.8° C
Water temperature	15.8° C
Sea state	1.5 m
Used Transponder and Releaser	Nr. RT 861 B1S S/N 204
Start of test:	07:00 hour UTC
End of test:	14.30 hour UTC

Old calibration parameter set	Heading:	- 0.79
	Roll:	+ 0.169
	Pitch:	+ 0.41
New calibration parameter set:	Heading:	- 0.43
	Roll:	+ 0.21
	Pitch:	- 2.14

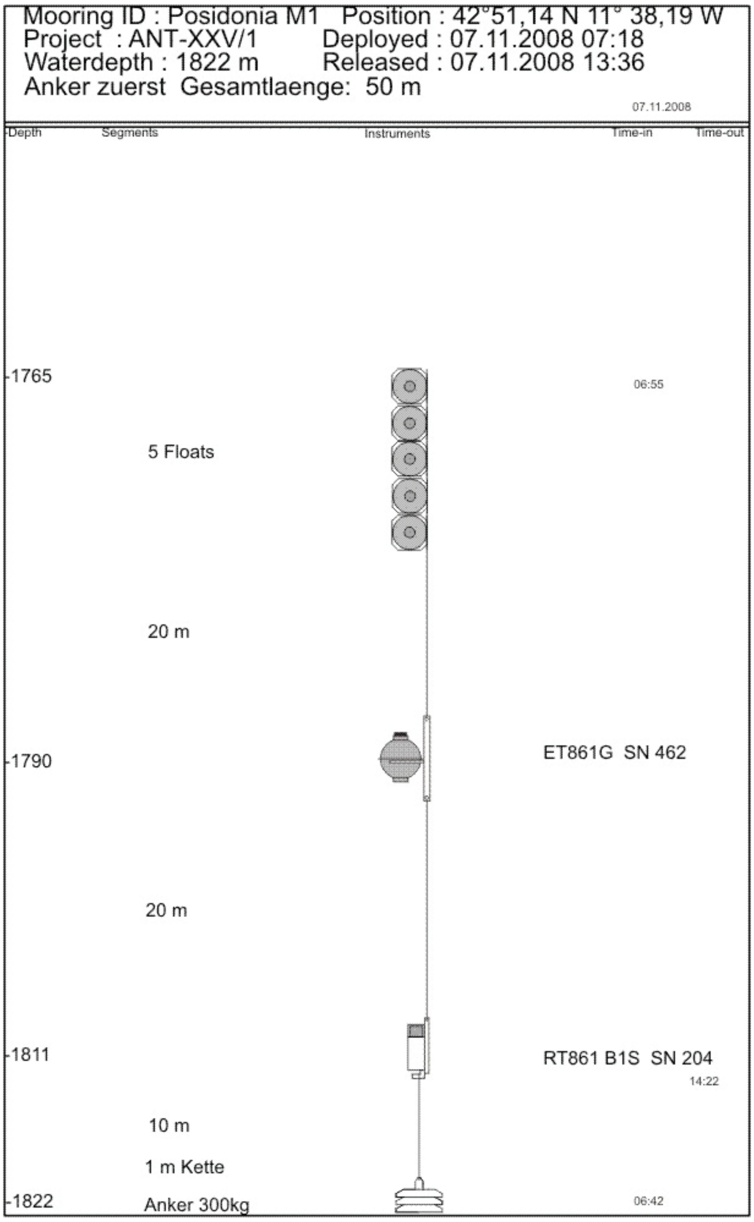
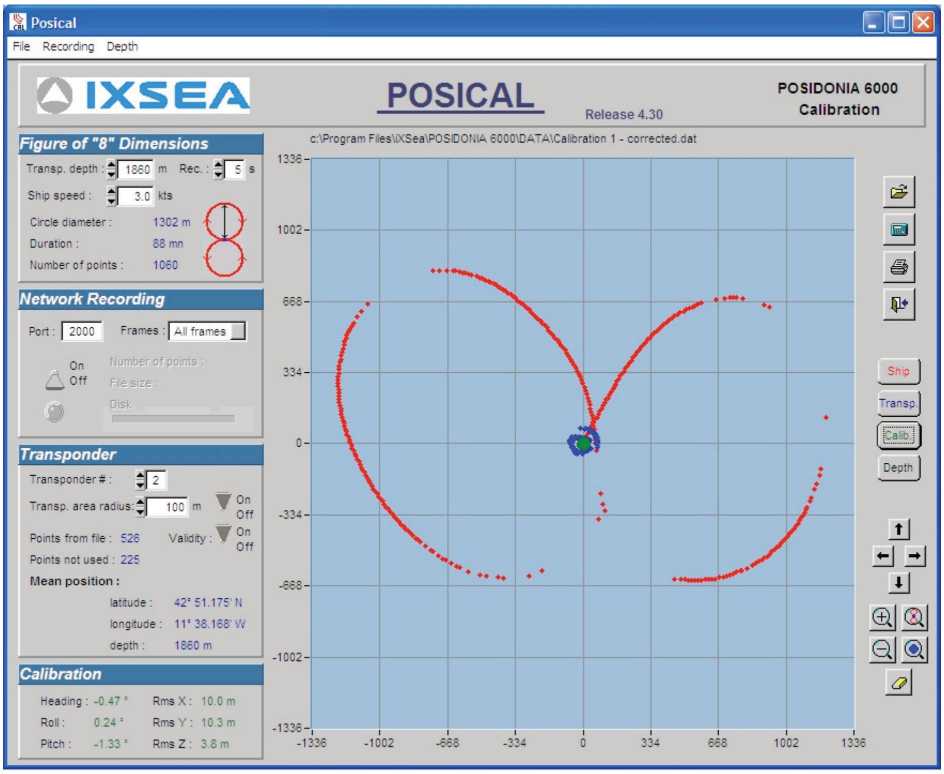


Fig. 10.1: Mooring scheme



c:\Program Files\IXSea\POSIDONIA 6000\DATA\Calibration 1 - corrected.dat

Figure of "8" Dimensions

Transp. depth : 1860 m Rec. : 5 s
Ship speed : 3.0 kts
Circle diameter : 1302 m
Duration : 88 mn
Number of points : 1060

Network Recording

Port : 2000 Frames : All frames
On Off
Number of points :
File size :
Disk

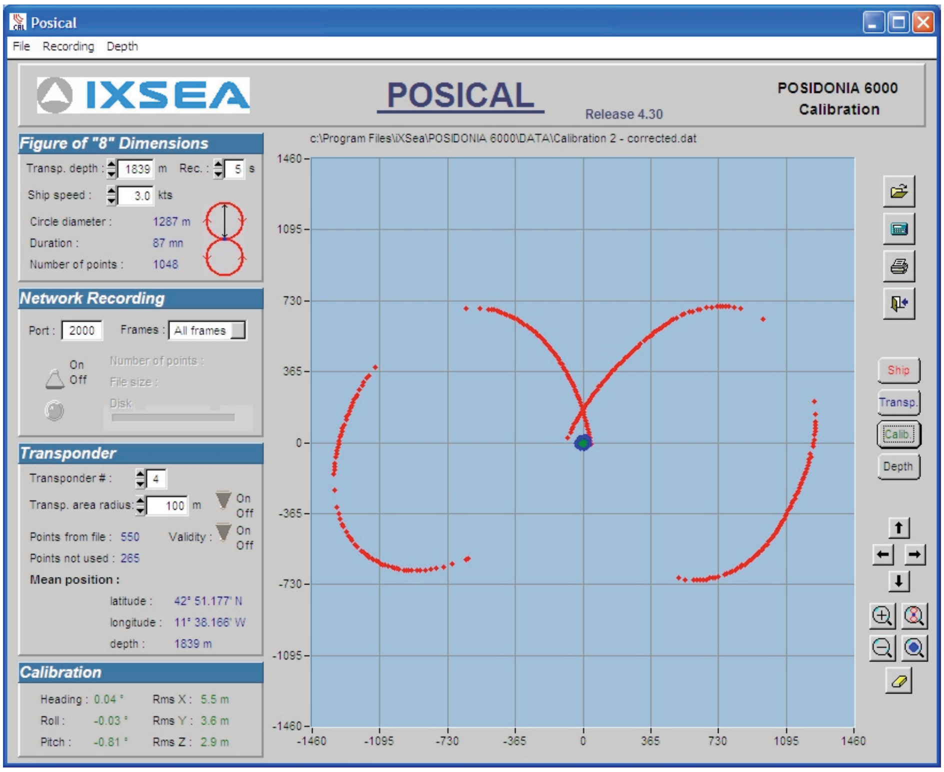
Transponder

Transponder # : 2
Transp. area radius: 100 m On Off
Points from file : 526 Validity : On Off
Points not used : 225
Mean position :
latitude : 42° 51.175' N
longitude : 11° 38.168' W
depth : 1860 m

Calibration

Heading : -0.47 ° Rms X : 10.0 m
Roll : 0.24 ° Rms Y : 10.3 m
Pitch : -1.33 ° Rms Z : 3.8 m

Fig. 10.2: First calibration circle



c:\Program Files\IXSea\POSIDONIA 6000\DATA\Calibration 2 - corrected.dat

Figure of "8" Dimensions

Transp. depth : 1839 m Rec. : 5 s
Ship speed : 3.0 kts
Circle diameter : 1287 m
Duration : 87 mn
Number of points : 1048

Network Recording

Port : 2000 Frames : All frames
On Off
Number of points :
File size :
Disk

Transponder

Transponder # : 4
Transp. area radius: 100 m On Off
Points from file : 550 Validity : On Off
Points not used : 265
Mean position :
latitude : 42° 51.177' N
longitude : 11° 38.166' W
depth : 1839 m

Calibration

Heading : 0.04 ° Rms X : 5.5 m
Roll : -0.03 ° Rms Y : 3.6 m
Pitch : -0.81 ° Rms Z : 2.9 m

Fig. 10.3: Second calibration circle after using the first correction. A minimum of deviations was found

11. SEA TRIAL AND TESTS OF THE NEW UPGRADED DATA ACQUISITION SYSTEM “PODAS” TO “DAVIS-SHIP“

Saad El Naggar, Peter Gerchow (AWI), Johannes Rogenhagen, Lars Rehe (Laeisz), Ralf Löwenberg (WERUM) (all until Las Palmas)

Objectives

The data acquisition system PODAS was upgraded to DAVIS-Ship during the last ship yard stay of *Polarstern* in Bremerhaven between 19.10.08 and 31.10.08. Newly designed software was installed and tested in the harbour of Bremerhaven.

Work at sea

The final sea trial under real conditions was carried out during the cruise from Bremerhaven to Las Palmas in the period between 31.10.08 and 12.11.08. The full functionality and integrity of the complete system were checked and tested. Software and data migration were carried out. 19 computer stations were replaced. The system was operational at the beginning of the cruise in Bremerhaven. Modifications on the data base were carried out during the cruise. Long-term stability tests were performed. The final acceptance test was performed at 06.11.08. The DAVIS-Ship was fully accepted without any claims.

APPENDIX

A.1 PARTICIPATING INSTITUTIONS

A.2 CRUISE PARTICIPANTS

A.3 SHIP'S CREW

A.4 STATION LIST

A.1 TEILNEHMENDE INSTITUTE / PARTICIPATING INSTITUTIONS

	Address
AWI	Stiftung Alfred-Wegener-Institut für Polar- und Meeresforschung in der Helmholtz-Gemeinschaft Postfach 120161 27515 Bremerhaven Germany
DWD	Deutscher Wetterdienst Geschäftsbereich Wettervorhersage Seeschifffahrtsberatung Bernhard Nocht Str. 76 20359 Hamburg Germany
ECNU	East China Normal University The State Key Laboratory of Estuarine and Coastal Research North Zhongshan Rd. 3663 Shanghai 200062 China
EIVA	EIVA Marine Survey Solutions DK-8361 Hasselager Denmark
GKSS	GKSS Research Centre Institute for Coastal Research Department for Environmental Chemistry Max-Planck-Straße 1 D-21502 Geesthacht Germany
HZM	Helmholtz Zentrum München German Research Center for Environmental Health Ingolstädter Landstraße 1 Postfach 1129 D-85758 Neuherberg Germany
IFM-GEOMAR	Leibniz-Institute of Marine Sciences, IFM-GEOMAR West Shore Campus Düsternbrooker Weg 20 D-24105 Kiel Germany

	Address
IOW	Leibniz Institute for Baltic Sea Research Seestr. 15 D-18119 Warnemünde Germany
IXSEA	IXSEA Rue Rivoalon Sainte-Anne du Portzic 29200 Brest France
Laeisz	Reederei F. Laeisz (Bremerhaven) GmbH Brückenstraße 25 27568 Bremerhaven Germany
NIO	National Institute of Oceanography Dona Paula Goa India
UCI	University of California Irvine Urban Water Research Center Department of Civil & Environmental Engineering 254 Social Ecology I Irvine CA 92697-7070 USA
VCU	Virginia Commonwealth University Department of Biology Center for Environmental Studies 1000 W Cary Street Richmond VA 23284 USA
ZMT	Zentrum für Marine Tropenökologie Fahrenheitstr. 6 28359 Bremen Germany

A.2 FAHRTTEILNEHMER / CRUISE PARTICIPANTS

Name/ Last name	Vorname/ First name	Institut/ Institute	Beruf/ Profession
Allhusen	Erika	AWI	Technician
Buldt	Klaus	DWD	Technician
Fietzek	Peer	IFM-Geomar	PhD student, chemistry
Flerus	Ruth	AWI	PhD student, chemistry
Gonsior	Michael	UCI	Chemist
Hanschmann	Timo	IFM-Geomar	Meteorologist
Hertkorn	Norbert	HZM	Chemist
Jenkins	Amy	VCU	Student, biology
Kattner	Gerhard	AWI	Chemist
Koch	Boris	AWI	Chemist
Kubsch	Hildegard	IOW	Technician, chemistry
Kuss	Joachim	IOW	Chemist
Lechtenfeld	Oliver	AWI	PhD student, chemistry
Lengfeld	Katharina	IFM-Geomar	Student, chemistry
Marandino	Christa	IFM-Geomar	Chemist
McCallister	Leigh	VCU	Biologist
Neogi	SucharitBasu	ZMT	Student, biology
Peterke	Dieter	ZMT	Technician
Schmitt-Kopplin	Philippe	HZM	Chemist
Stuart	Anne	VCU	Student, biology
Theis	Anja	AWI	Student, physics
Xie	Zhiyong	GKSS	Chemist
Zhang	Lei	ECNU	Chemist
Zhu	Zhuo-Yi	ECNU	Chemist
Zindler	Cathleen	IFM-Geomar	Biologist
Until Las Palmas, Canary Islands			
Almeida	Anselm	NIO	Physicist
Bellier	Frederic	IXSEA	Engineer
El Naggar	Saad	AWI	Physicist
Gerchow	Peter	AWI	Physicist
Löwenberg	Ralf	WERUM	Engineer
Methar	Anand	NIO	Physicist
Niemeyer	Hauke		Engineer
Rogenhagen	Johannes	Laeisz	Physicist
Rohardt	Gert	AWI	Physicist
Sørensen	Per	EIVA	Engineer
Steinhoff	Tobias	IFM-Geomar	Chemist
Wlost	Klaus-Peter	IOW	Engineer

A.3 SCHIFFSBESATZUNG / SHIP'S CREW

No.	Name	Rank
1.	Pahl, Uwe	Master
2.	Grundmann, Uwe	1. Offc.
3.	Krohn, Günter	Ch. Eng.
4.	Bratz, Herbert	2. Offc.
5.	Hering, Igor	2. Offc.
6.	Janik, Michael	3. Offc.
7.	Uhlig, Holger	Doctor
8.	Koch, Georg	R. Offc.
9.	Kotnik, Herbert	2. Eng.
10.	Schnürch, Helmut	2. Eng.
11.	Westphal, Henning	2. Eng.
12.	Holtz, Hartmut	Elec. Eng.
13.	Dimmler, Werner	ELO
14.	Feiertag, Thomas	ELO
15.	Fröb, Martin	ELO
16.	Rehe, Lars	ELO
17.	Clasen, Burkhard	Boatsw.
18.	Neisner, Winfried	Carpenter
19.	Brück, Sebastian	A.B.
20.	Burzan, Gerd-Ekkehard	A.B.
21.	Hartwig-Lab., Andreas	A.B.
22.	Kreis, Reinhard	A.B.
23.	Kretzschmar, Uwe	A.B.
24.	Moser, Siegfried	A.B.
25.	Pousada Martinez, S.	A.B.
26.	Schröder, Norbert	A.B.
27.	Krösche, Eckard	Storek.
28.	Dinse, Horst	Mot-man
29.	Fritz, Günter	Mot-man
30.	Kliem, Peter	Mot-man
31.	Teichert, Uwe	Mot-man
32.	Watzel, Bernhard	Mot-man
33.	Fischer, Matthias	Cook
34.	Tupy, Mario	Cooksmate
35.	Völske, Thomas	Cooksmate
36.	Dinse, Petra	1. Stwdess
37.	Hölger, Irene	Stwdess/N.
38.	Hischke, Peggy	2. Stwdess
39.	Hu, Guo Yong	2. Steward
40.	Streit, Christina	2. Stwdess
41.	Sun, Yong Sheng	2. Steward
42.	Wartenberg, Irina	2. Stwdess
43.	Yu, Chung Leung	Laundrym.

A.4 STATIONSLISTE / STATION LIST PS 73

Station PS73	Date	Time (start)	Time (end)	Position (Lat.)	Position (Lon.)	Depth (m)	Gear
001-1	03.11.08	7:17	12:53	50° 16.28' N	01° 12.23' W	48.7	Scan-Fish
002-1	03.11.08	13:07	13:25	50° 11.42' N	02° 20.99' W	49.4	CTD/rosette
003-1	03./04.11.08	13:57	12:59	50° 12.05' N	02° 20.33' W	48.4	Scan-Fish
004-1	04.11.08	13:14	13:36	48° 31.33' N	06° 08.91' W	242.2	CTD/rosette
004-2	04.11.08	13:43	13:48	48° 30.93' N	06° 09.05' W	241.8	Radiation-meter
004-3	04.11.08	13:58	14:46	48° 30.76' N	06° 09.09' W	115.0	Scan-Fish
005-1	04./05.11.08	14:54	09:10	48° 30.23' N	06° 08.45' W	114.0	Scan-Fish
006-1	05.11.08	09:14	12:50	46° 20.27' N	07° 50.16' W	4688.6	CTD/rosette
006-2	05.11.08	13:09	13:53	46° 19.96' N	07° 50.71' W	4697.4	Radiation-meter
006-3	05.11.08	14:02	14:24	46° 19.71' N	07° 51.08' W	4689.8	CTD/rosette
006-4	05.11.08	14:34	17:15	46° 19.53' N	07° 51.06' W	4690.4	Scan-Fish
006-5	05.11.08	17:27	17:46	46° 10.64' N	07° 57.73' W	4733.6	Releaser Test
007-1	05./06.11.08	17:48	13:07	46° 10.65' N	07° 57.70' W	4733.2	Scan-Fish
008-1	06.11.08	13:10	13:33	44° 02.82' N	10° 18.02' W	4911.8	CTD/rosette
008-2	06.11.08	13:38	14:02	44° 02.66' N	10° 17.88' W	4911.5	Posidonia
008-3	06.11.08	14:05	14:23	44° 02.61' N	10° 17.82' W	4912.7	Posidonia
008-4	06.11.08	14:25	14:39	44° 02.65' N	10° 17.68' W	4912.2	Posidonia
008-5	06.11.08	14:41	15:51	44° 02.66' N	10° 17.66' W	4912.5	Posidonia
008-6	06.11.08	15:56	19:34	44° 02.70' N	10° 17.68' W	4912.0	Posidonia
008-7	06.11.08	19:42	20:00	44° 02.84' N	10° 17.62' W	4914.5	CTD/rosette
009-1	06./07.11.08	20:05	06:12	44° 02.84' N	10° 17.60' W	4912.9	Iron Fish
010-1	07.11.08	06:42	14:22	42° 51.05' N	11° 38.29' W	1760.2	Mooring
010-2	07.11.08	13:02	13:22	42° 51.10' N	11° 38.32' W	1800.1	CTD/rosette
010-3	07.11.08	15:05	17:14	42° 50.86' N	11° 37.99' W	1813.0	Scan-Fish
012-1	07.08.11.08	17:14	13:04	42° 41.56' N	11° 41.06' W	745.1	Iron Fish
013-1	08.11.08	13:10	13:33	39° 49.58' N	12° 33.87' W	4903.8	CTD/rosette
013-2	08.11.08	13:14	13:26	39° 49.56' N	12° 33.84' W	4904.6	Radiation-meter
014-1	08.09.11.08	13:37	07:57	39° 49.55' N	12° 33.59' W	4906.3	Iron Fish
015-1	09.11.08	08:09	10:44	37° 08.17' N	13° 21.69' W	4029.8	CTD/rosette
015-2	09.11.08	11:44	12:15	37° 07.44' N	13° 21.82' W	4022.5	CTD/rosette
015-3	09.11.08	12:31	13:10	37° 07.32' N	13° 21.86' W	4020.2	Radiation-meter
015-4	09.11.08	13:15	13:30	37° 07.24' N	13° 21.88' W	4018.0	CTD/rosette
016-1	09./10.11.08	13:33	13:46	37° 07.28' N	13° 21.79' W	4020.1	Iron Fish
017-1	10.11.08	11:24	13:24	33° 53.56' N	14° 18.88' W	1713.2	Scan-Fish
017-2	10.11.08	13:46	13:57	33° 41.89' N	14° 25.92' W	467.9	CTD/rosette
017-3	10.11.08	13:48	14:12	33° 41.89' N	14° 25.92' W	472.6	Radiation-meter
017-4	10.11.08	14:19	14:40	33° 41.91' N	14° 25.80' W	427.1	Video camera
017-5	10.11.08	14:55	15:29	33° 41.98' N	14° 25.73' W	340.0	Video camera
018-1	10./11.11.08	16:42	13:00	33° 42.02' N	14° 25.44' W	286.9	Iron Fish
019-1	11.11.08	13:02	13:25	30° 35.95' N	14° 56.88' W	3409.4	CTD/rosette
019-2	11.11.08	13:07	13:46	30° 35.93' N	14° 56.91' W	3407.3	Radiation-meter
020-1	11.11.08	13:49	23:58	30° 35.94' N	14° 56.70' W	3418.5	Iron Fish
021-1	12.11.08	09:39	13:01	27° 53.43' N	15° 15.88' W	669.2	Iron Fish
022-1	12.11.08	13:02	13:28	27° 27.62' N	15° 35.65' W	2388.0	CTD/rosette

Station PS73	Date	Time (start)	Time (end)	Position (Lat.)	Position (Lon.)	Depth (m)	Gear
022-2	12.11.08	13:04	13:43	27° 27.58' N	15° 35.69' W	2390.2	Radiation-meter
023-1	12./13.11.08	13:46	13:02	27° 27.13' N	15° 35.87' W	2333.0	Iron Fish
024-1	13.11.08	13:04	13:26	24° 41.34' N	18° 21.14' W	2769.5	CTD/rosette
024-2	13.11.08	13:05	13:24	24° 41.33' N	18° 21.15' W	2770.0	Radiation-meter
025-1	13./14.11.08	13:30	08:23	24° 41.30' N	18° 21.09' W	2769.2	Iron Fish
026-1	14.11.08	08:24	11:10	22° 29.97' N	20° 30.24' W	4126.5	CTD/rosette
026-2	14.11.08	12:00	12:15	22° 30.04' N	20° 29.90' W	4125.5	CTD/rosette
026-3	14.11.08	12:53	13:21	22° 29.87' N	20° 29.90' W	4123.5	Radiation-meter
026-4	14.11.08	13:05	13:26	22° 29.84' N	20° 29.94' W	4124.5	CTD/rosette
026-5	14.11.08	13:35	13:51	22° 29.77' N	20° 30.09' W	4124.5	Radiation-meter
027-1	14./15.11.08	13:59	08:18	22° 29.58' N	20° 30.03' W	4122.5	Iron Fish
027-2	15.11.08	09:26	13:01	19° 06.05' N	20° 43.33' W	3327.2	Iron Fish
028-1	15.11.08	13:03	13:31	18° 30.09' N	20° 45.49' W	3152.7	CTD/rosette
028-2	15.11.08	13:08	13:40	18° 30.07' N	20° 45.48' W	3153.0	Radiation-meter
029-1	15./16.11.08	13:58	13:02	18° 30.00' N	20° 45.40' W	3152.7	Iron Fish
030-1	16.11.08	13:02	13:23	14° 29.38' N	20° 56.54' W	4253.2	CTD/rosette
030-2	16.11.08	13:05	13:19	14° 29.35' N	20° 56.55' W	4250.2	Radiation-meter
030-3	16.11.08	13:54	14:04	14° 29.05' N	20° 56.71' W	4250.5	CTD/rosette
031-1	16./17.11.08	14:19	12:51	14° 28.96' N	20° 56.70' W	4250.2	Iron Fish
032-1	17.11.08	12:51	13:09	10° 37.55' N	20° 07.92' W	4817.7	CTD/rosette
032-2	17.11.08	12:59	13:16	10° 37.55' N	20° 07.90' W	4817.5	Radiation-meter
032-3	17.11.08	13:22	13:43	10° 37.72' N	20° 07.93' W	4807.2	Radiation-meter
032-4	17.11.08	13:47	16:46	10° 37.89' N	20° 07.96' W	4804.2	CTD/rosette
033-1	17./18.11.08	16:52	13:02	10° 38.18' N	20° 07.73' W	4802.0	Iron Fish
034-1	18.11.08	13:05	13:26	08° 23.24' N	19° 21.18' W	4535.5	CTD/rosette
034-2	18.11.08	13:07	13:40	08° 23.25' N	19° 21.18' W	4536.2	Radiation-meter
035-1	18./19.11.08	13:44	13:01	08° 23.43' N	19° 21.06' W	4542.7	Iron Fish
036-1	19.11.08	13:02	13:23	05° 25.73' N	16° 46.21' W	4955.0	CTD/rosette
036-2	19.11.08	13:05	13:24	05° 25.74' N	16° 46.18' W	4955.0	Radiation-meter
037-1	19./20.11.08	13:28	13:03	05° 25.88' N	16° 45.79' W	4955.0	Iron Fish
038-1	20.11.08	13:05	13:26	02° 27.98' N	14° 09.26' W	4621.7	CTD/rosette
038-2	20.11.08	13:06	13:34	02° 27.99' N	14° 09.26' W	4621.5	Radiation-meter
038-3	20.11.08	13:55	16:51	02° 28.14' N	14° 09.16' W	4621.5	CTD/rosette
038-4	20.11.08	17:34	17:53	02° 28.08' N	14° 08.58' W	4623.7	CTD/rosette
039-1	20./22.11.08	17:56	13:00	02° 28.04' N	14° 08.44' W	4628.5	Iron Fish
040-1	21.11.08	12:49		00° 00.09' N	12° 04.25' W	4157.5	FLOAT
041-1	22.11.08	09:44		03° 00.04' S	09° 32.25' W	3939.2	FLOAT
042-1	22.11.08	13:01	13:23	03° 25.15' S	09° 10.84' W	4307.0	CTD/rosette
042-2	22.11.08	13:05	13:42	03° 25.12' S	09° 10.85' W	4306.7	Radiation-meter
043-1	22./23.11.08	14:11	09:05	03° 26.63' S	09° 09.77' W	4308.0	Iron Fish
044-1	23.11.08	09:07	12:02	05° 55.79' S	07° 03.57' W	4843.5	CTD/rosette
044-2	23.11.08	12:41	12:58	05° 55.69' S	07° 03.76' W	4833.2	CTD/rosette
044-3	23.11.08	13:06	13:30	05° 55.43' S	07° 03.78' W	4844.0	Radiation-meter
044-4	23.11.08	13:26	14:39	05° 55.26' S	07° 03.76' W	4846.0	CTD/rosette
045-1	23./24.11.08	14:43	13:01	05° 54.71' S	07° 03.49' W	4848.0	Iron Fish
046-1	23.11.08	15:26		05° 59.81' S	07° 00.13' W	4732.7	FLOAT
047-1	24.11.08	13:03	13:28	08° 53.18' S	04° 32.49' W	4825.5	CTD/rosette

Station PS73	Date	Time (start)	Time (end)	Position (Lat.)	Position (Lon.)	Depth (m)	Gear
047-2	24.11.08	13:03	13:42	08° 53.18' S	04° 32.49' W	4825.5	Radiation-meter
048-1	24./25.11.08	13:48	13:00	08° 52.76' S	04° 32.48' W	4876.2	Iron Fish
049-1	24.11.08	14:49		09° 00.00' S	04° 26.83' W	4282.7	FLOAT
050-1	25.11.08	12:50		11° 59.98' S	01° 52.43' W	5033.0	FLOAT
051-1	25.11.08	13:04	13:24	12° 00.56' S	01° 51.74' W	4723.0	CTD/rosette
051-2	25.11.08	13:04	13:36	12° 00.56' S	01° 51.74' W	4723.0	Radiation-meter
052-1	25./26.11.08	13:39	13:03	12° 00.45' S	01° 51.75' W	4740.7	Iron Fish
053-1	26.11.08	11:43		15° 00.06' S	00° 43.73' E	5604.5	FLOAT
054-1	26.11.08	13:04	13:28	15° 09.29' S	00° 52.00' E	5178.5	CTD/rosette
054-2	26.11.08	13:04	13:53	15° 09.29' S	00° 52.00' E	5178.5	Radiation-meter
055-1	26./27.11.08	13:53	09:02	15° 09.13' S	00° 51.86' E	5242.7	Iron Fish
056-1	27.11.08	09:06	12:15	17° 43.72' S	03° 07.58' E	5445.0	CTD/rosette
056-2	27.11.08	13:05	13:37	17° 44.39' S	03° 07.70' E	5446.2	Radiation-meter
056-3	27.11.08	13:07	13:29	17° 44.38' S	03° 07.69' E	5445.5	CTD/rosette
056-4	27.11.08	14:11	14:51	17° 44.06' S	03° 07.66' E	5446.2	CTD/rosette
057-1	27./28.11.08	14:53	13:02	17° 43.88' S	03° 07.59' E	5446.0	Iron Fish
058-1	27.11.08	17:02		18° 00.08' S	03° 22.15' E	5437.0	FLOAT
059-1	28.11.08	13:03	13:28	20° 38.71' S	05° 44.05' E	4396.0	CTD/rosette
059-2	28.11.08	13:04	13:44	20° 38.69' S	05° 44.04' E	4396.0	Radiation-meter
060-1	28./29.11.08	13:52	13:05	20° 38.59' S	05° 43.87' E	4395.7	Iron Fish
061-1	28.11.08	16:42		20° 59.98' S	06° 03.14' E	4205.2	FLOAT
062-1	29.11.08	13:05	13:27	23° 42.24' S	08° 31.09' E	4616.7	CTD/rosette
062-2	29.11.08	13:06	13:46	23° 42.24' S	08° 31.09' E	4616.7	Radiation-meter
062-3	29.11.08	14:04	16:45	23° 42.40' S	08° 31.11' E	4616.7	CTD/rosette
062-4	29.11.08	17:25	18:35	23° 42.79' S	08° 31.53' E	4615.2	CTD/rosette
063-1	29./30.11.08	18:37	13:06	23° 42.71' S	08° 31.64' E	4614.0	Iron Fish
064-1	30.11.08	13:09	13:28	26° 04.71' S	10° 43.49' E	4479.2	CTD/rosette

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