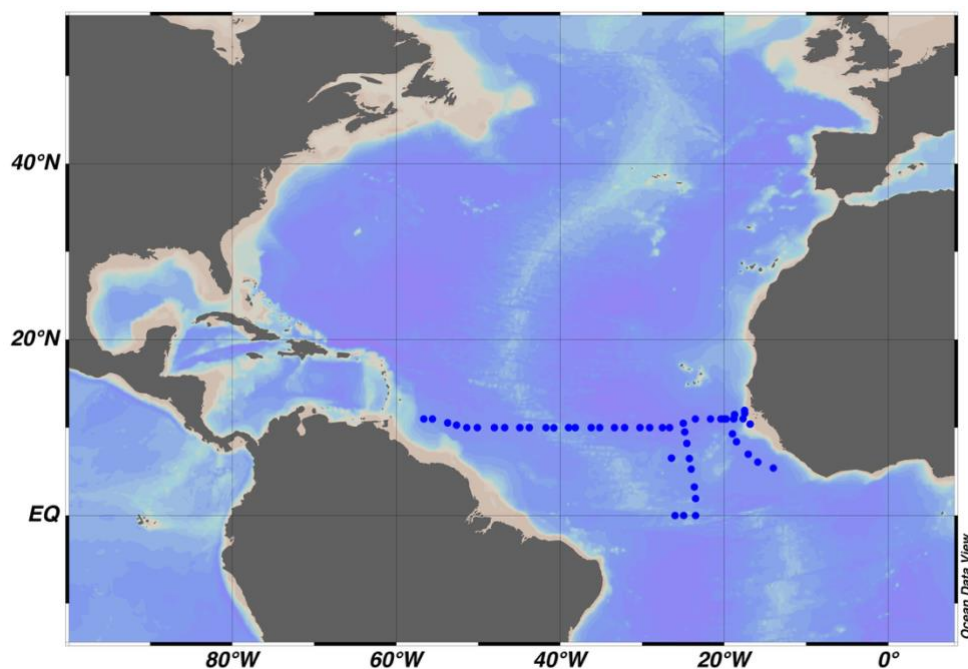


# CRUISE REPORT: SOLAS, Cruise No. 55

Created: September 2025



## Highlights

### Cruise Summary Information

|                                   |   |
|-----------------------------------|---|
| Section Designation               | Meteor 55                               |
| Expedition Designation (ExpoCode) | <b>06MT20021013</b>                     |
| Chief Scientists                  | <b>Douglas Wallace, IfMK</b>            |
| Dates                             | 13 October – 16 November 2002           |
| Ship                              | METEOR                                  |
| Ports of Call                     | Willemstad, Curacao.- Doula, Cameroon   |
| Geographic Boundaries             | 56° 64''W 11° 65''N 14° ''W<br>23° 5''N |
| Stations                          | 51                                      |
| Floats and Drifters Deployed      | 0                                       |
| Moorings Deployed and Recovered   | 1 mooring recovered                     |

### Contact Information:

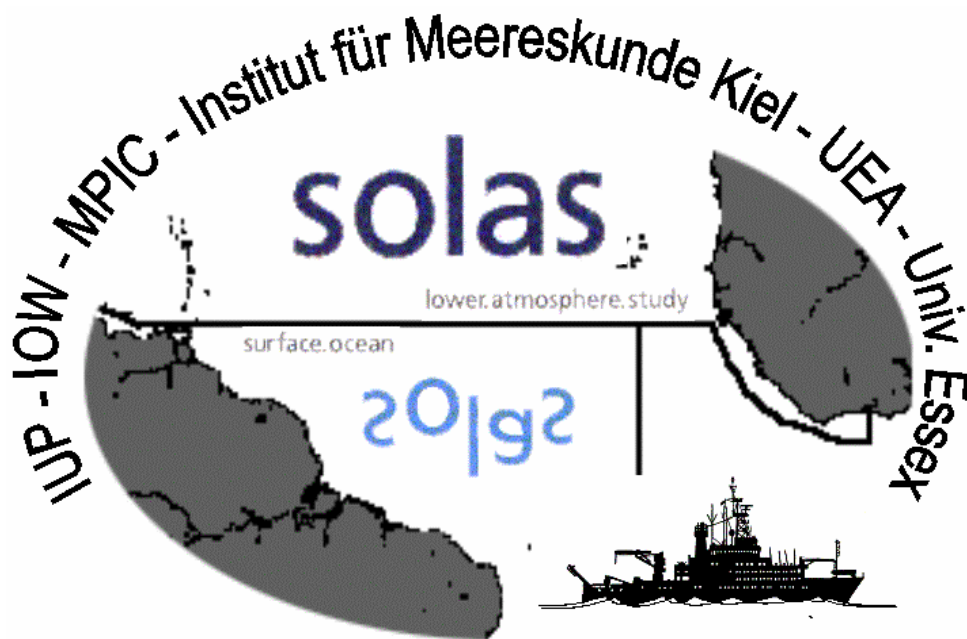
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METEOR-Berichte 06-1

**Surface Ocean Lower Atmosphere Study (SOLAS):  
Tropischer Atlantik 2002**

Cruise No. 55

October 13 to November 16, 2002, Willemstad - Duala



**Meteor 55 – Tropical Atlantic 2002**

Douglas W.R. Wallace

Editorial Assistance:

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Leitstelle METEOR

Institut für Meereskunde der Universität Hamburg

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## Abstract

METEOR cruise M55 departed Willemstad, Curacao on October 12 and ended on November 17, 2002 in Douala, Cameroon following a transect of 51 stations and continuous underway sampling across the tropical Atlantic. The cruise was designed to initiate longer-term research into atmosphere-ocean biogeochemical interactions within tropical regions. As such it was a forerunner to a planned national German SOLAS (Surface Ocean Lower Atmosphere Study) research program. Sampling activities included underway measurements of air, atmospheric particles, rain, and surface seawater, together with mainly shallow (<600 m) CTD casts and biological sampling. Measurements of a wide variety of trace gases, trace metals, nitrogen species and biological parameters were made in both the upper ocean and atmosphere. Experiments were conducted on board to examine the response of carbon and nitrogen fixation to inputs of various nutrients and biological and environmental factors related to trace gas production. The work on the cruise was conducted jointly by atmospheric chemists and physicists together with chemical and biological oceanographers. This report provides a narrative of the cruise, presents the goals of the individual research groups and their preliminary results, documents the stations that were occupied, and provides a listing of the conference presentations, theses, and the 16 papers for peer-reviewed publications that have resulted from the work conducted on board to-date.

## Zusammenfassung

Die Reise M55 des FS METEOR begann am 12. Oktober 2002 in Willemstad (Curacao) und endete am 17. November 2002 in Duala (Kamerun). Entlang eines Transekts wurden 51 Stationen beprobt; hinzu kamen kontinuierliche Messung während der Atlantik-Überquerung. Ziel der Reise war die Initiierung langfristiger Forschung der biogeochemischen Atmosphäre-Ozean-Wechselwirkungen in tropischen Regionen. Damit war die Reise gleichzeitig ein Vorläufer des geplanten nationalen SOLAS (Surface Ocean Lower Atmosphere Study) Forschungsprojektes. Während der Fahrt wurden kontinuierlich Luft-, Partikel-, Regen- und Oberflächenproben genommen. Für weitere Fragestellungen und die biologische Probennahme wurde die CTD/Rosette eingesetzt. Eine Vielzahl von Spurengasen, Spurenmetallen, Stickstoffverbindungen und biologischen Parametern wurde in den oberen Wasserschichten und in der Atmosphäre gemessen. Um den Einfluss der Nährstoffkonzentrationen, biologischer Stellgrößen sowie von Umweltfaktoren, die mit der Produktion von Spurengasen zusammenhängen, auf die Kohlenstoff- und Stickstofffixierung zu untersuchen, wurden diverse Experimente an Bord durchgeführt. An Bord arbeiteten Atmosphärenchemiker und -physiker sowie chemische und biologische Ozeanographen gemeinsam an den Fragestellungen. Dieser Bericht gibt einen Überblick über die Reise, präsentiert die Ziele und vorläufigen Forschungsergebnisse der einzelnen Arbeitsgruppen, dokumentiert die Stationsarbeiten und führt die bis heute erschienenen Konferenzbeiträge und Veröffentlichungen (16 begutachtete Artikel) über die Ergebnisse dieser Reise auf.

## 1. Participants

**Table 1:** Participant List, Scientific Program and Institution.

|     |                             |                                     |        |
|-----|-----------------------------|-------------------------------------|--------|
| 1.  | Wallace, Douglas, Prof. Dr. | Chief Scientist                     | IfMK   |
| 2.  | Baker, Alex, Dr.            | Aerosol and Rainfall chemistry      | UEA    |
| 3.  | Bange, Hermann, Dr.         | N <sub>2</sub> O                    | IfMK   |
| 4.  | Chuck, Adele, Dr.           | Alkyl nitrates                      | UEA    |
| 5.  | Croot, Peter, Dr.           | Trace Metals                        | IfMK   |
| 6.  | Davey, Margaret, Dr.        | Bioassay experiments                | UE     |
| 7.  | Fritsche, Peter             | Nutrients and oxygen                | IfMK   |
| 8.  | Gaul, Wilhelm               | DMSP/DMS                            | IfMK   |
| 9.  | Hansen, Hans Peter, Dr.     | CTD, nutrients, oxygen              | IfMK   |
| 10. | Hoffmann, Linn              | Biology                             | IfMK   |
| 11. | Holzinger, Rupert, Dr.      | Volatile organics                   | MPIC   |
| 12. | Körtzinger, Arne, Prof. Dr. | O <sub>2</sub> and pCO <sub>2</sub> | IfMK   |
| 13. | Laepple, Thomas             | BrO in atmosphere                   | IUP    |
| 14. | Langlois, Rebecca           | N <sub>2</sub> -Fixation            | IfMK   |
| 15. | Lochte, Karin, Prof. Dr.    | Biology                             | IfMK   |
| 16. | Malien, Frank               | Nutrients and oxygen                | IfMK   |
| 17. | Mills, Matthew              | Biology / Bioassay experiments      | IfMK   |
| 18. | Müller, Marius              | DMSP/DMS                            | IfMK   |
| 19. | Peeken, Ilka, Dr.           | Biology                             | IfMK   |
| 20. | Petrick, Gert               | Halocarbons                         | IfMK   |
| 21. | Quack, Birgit, Dr.          | Halocarbons                         | IfMK   |
| 22. | Richter, Uwe                | Halocarbons                         | IfMK   |
| 23. | Ridame, Celine, Dr.         | Bioassay experiments                | IfMK   |
| 24. | Schafstall, Jens            | CTD                                 | IfMK   |
| 25. | Stange, Karen               | Halocarbons                         | GEOMAR |
| 26. | Streu, Peter                | Trace metals                        | IfMK   |
| 27. | Thorsten Truscheit          | Meteorology                         | DWD    |
| 28. | Voß, Maren, Dr.             | N <sub>2</sub> -fixation            | IOW    |
| 29. | Walter, Sylvia              | N <sub>2</sub> O                    | IfMK   |
| 30. | Williams, Jonathan, Dr.     | Volatile organics, air chemistry    | MPIC   |

## **1.1. Participating Institutions**

### **DWD**

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### **GEOMAR\***

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### **IfMK\***

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### **IUP**

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### **MPIC**

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### **NCAR**

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National Center for Atmospheric Research  
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Boulder, Colorado 80305, USA

**UE**

Biological Sciences  
University of Essex  
Colchester CO4 3SQ, United Kingdom

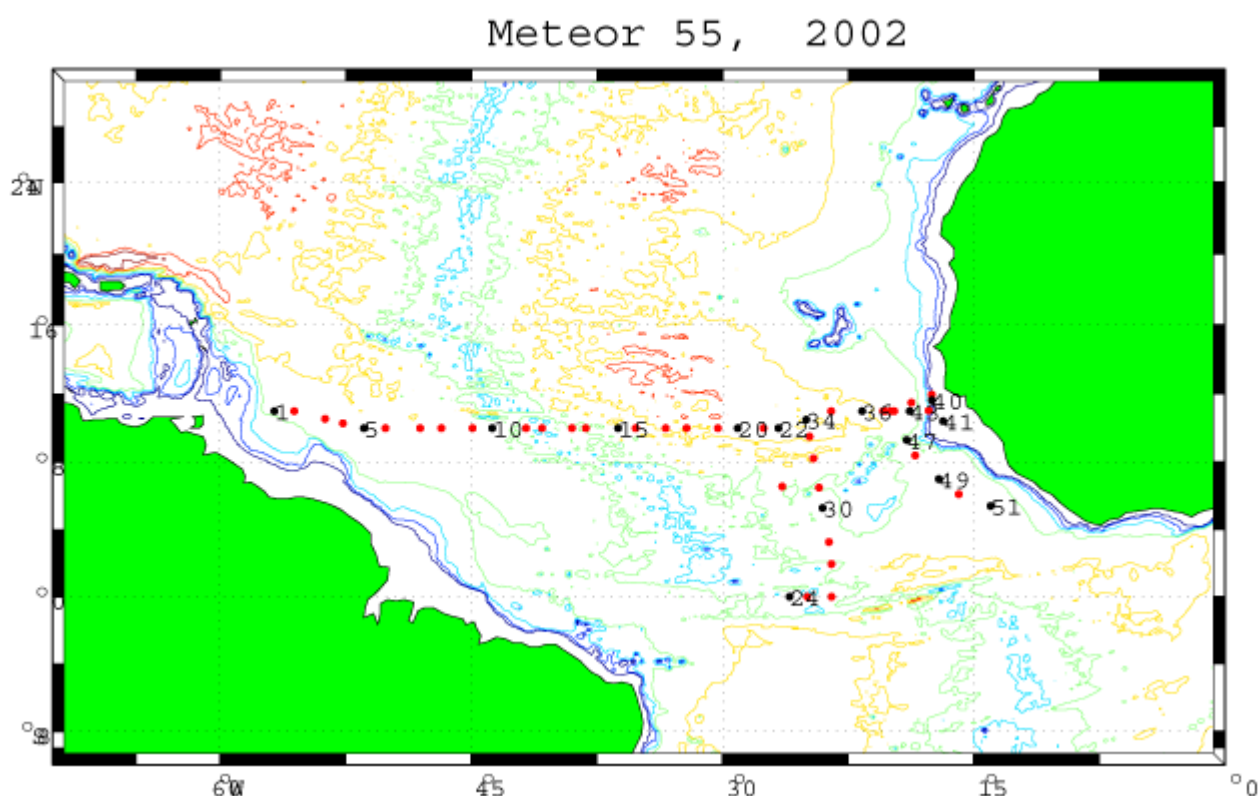
**UEA**

University of East Anglia  
School of Environmental Sciences,  
Norwich, NR4 7TJ, United Kingdom

\*GEOMAR and IFMK merged to IFM-GEOMAR in 2004.

## 2. Research Program (Overview and Activities)

METEOR 55 was a single-leg expedition that comprised a trans-Atlantic section from west to east along 11°N together with a short, mid-ocean North-South transect to the equator (Figure 1).



**Figure 1:** Station locations during cruise M55 of R/V METEOR.

The leg covered a wide range of biogeochemical conditions, including both oligotrophic and high productivity regions, regions with low subsurface oxygen concentrations, and regions subject to significant influence from atmospheric dust input. The cruise was designed to initiate longer-term research into atmosphere-ocean biogeochemical interactions within tropical regions.



As such it is a forerunner to a national German SOLAS (Surface Ocean Lower Atmosphere Study) research program.

Sampling activities included underway measurements of air, atmospheric particles, rain, and surface seawater, together with mainly shallow (<500 m) CTD casts and biological sampling. Measurements of a wide variety of trace gases, trace metals, nitrogen species and biological parameters were made in both the upper ocean and atmosphere. Experiments were conducted on



**Figure 2:** Interior of the Geo Labor during Meteor Cruise M 55.

board to examine the response of phytoplankton to inputs of various nutrients and biological and environmental factors related to trace gas production. The work on the cruise was conducted jointly by atmospheric chemists and physicists together with chemical and biological oceanographers. During the cruise, a long-term sediment trap of the University of Bremen was recovered at the equator.

The overall objective of the cruise was to examine ways in which surface ocean biology and chemistry affect the atmosphere and, how atmospheric chemistry, in particular the deposition of particles, affects surface ocean biology and chemistry. In particular, the west-to-east transit was designed to sample a wide range of continental aerosol inputs. The north-south transect was included to allow sampling of atmospheric conditions at the Inter-Tropical Convergence Zone (including rainfall and wet deposition) and Southern Hemisphere air masses. Along this transect, the following research activities took place:

- Characterization of trace gas distributions and identification of production-degradation pathways within tropical surface waters. ( $\text{N}_2\text{O}$ , sulphur-containing gases, naturally



produced halocarbons and alkyl nitrates, oxygenated organics, CO<sub>2</sub>)

- Determination of the distribution patterns of phytoplankton biomass and species as potential producers of trace gases.
- Characterization of trace gases (including, but not limited to, those in list above) and reactive species (e.g. BrO) distributions in the troposphere. This included an important intercalibration of atmospheric and oceanic measurements, which is necessary for the computation of air-sea fluxes.
- Chemical characterization of atmospheric aerosols and dust particles for their trace metal and nitrogen content. Assessment of the chemical behaviour of such aerosols following deposition to ocean waters.
- Measurement of trace metals (e.g. Fe) and their speciation in surface water and shallow vertical profiles in relation to atmospheric and sub-surface inputs, phytoplankton composition, remineralization, etc..
- Investigation of the surface water nitrogen cycle with an emphasis on nitrogen fixation.
- Assessment of vertical profiles of Fe and nitrogenous nutrients together with estimation of their supply to the euphotic zone via vertical mixing.
- Bioassays and molecular biological studies to determine nutrient and/or trace metal limitation (e.g. N, P, Si, Fe, other metals). Physiological studies of photosynthetic organisms along strong gradients of nutrient limitation.

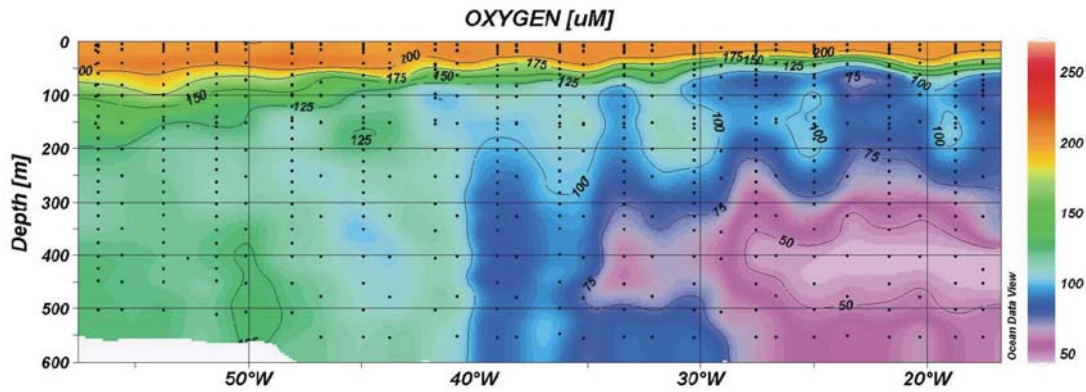
### 3. Cruise Narrative

#### 3.1 Week 1 (12.10.2002-20.10.2002)

Meteor Cruise 55 departed Willemstad, Curacao on Saturday October 12 at 18.15. Just a week prior to departure, the decision was made to shift the end-port for the cruise from Abidjan in the Ivory Coast to Doula, Cameroon. This was required due to continued civil unrest in the Ivory Coast. Arrangements for Doula were still being made as we left. The set-up of the laboratories for this cruise was unusually complex. A large amount of sophisticated analytical equipment was deployed on board, including 7 gas chromatographs within the Universal and Geo Labs alone. Most of these systems were supplied with surface water pumped continuously from the Meteor's 'Moon Pool', as well as by centrally distributed supplies of high-purity nitrogen, ultra-clean air and hydrogen from gas generators.

On a routine basis we occupied 2 stations per day: a morning station with at least 2 CTD casts, a trace-metal hydrocast and net tows and at least one afternoon CTD cast. We made our first station on October 16 about 240 miles due east of Trinidad and Tobago. A very large portion of our measurements however was made on air and pumped surface seawater during steaming.

Based on daily Seawifs images of ocean colour, we altered course to intersect a large region of very high surface chlorophyll that was clearly visible from space at about 10°N, 52°W. The feature reflected Amazon-derived material that had been swept more than 400 miles offshore. Sampling of this plume revealed coastal assemblages of plankton but also, surprisingly for us, many tufts of nitrogen-fixing *Trichodesmium* were seen. Surface salinity and pCO<sub>2</sub> dropped rapidly to <29 and <290 ppm respectively. Later we sailed through a major surface slick of

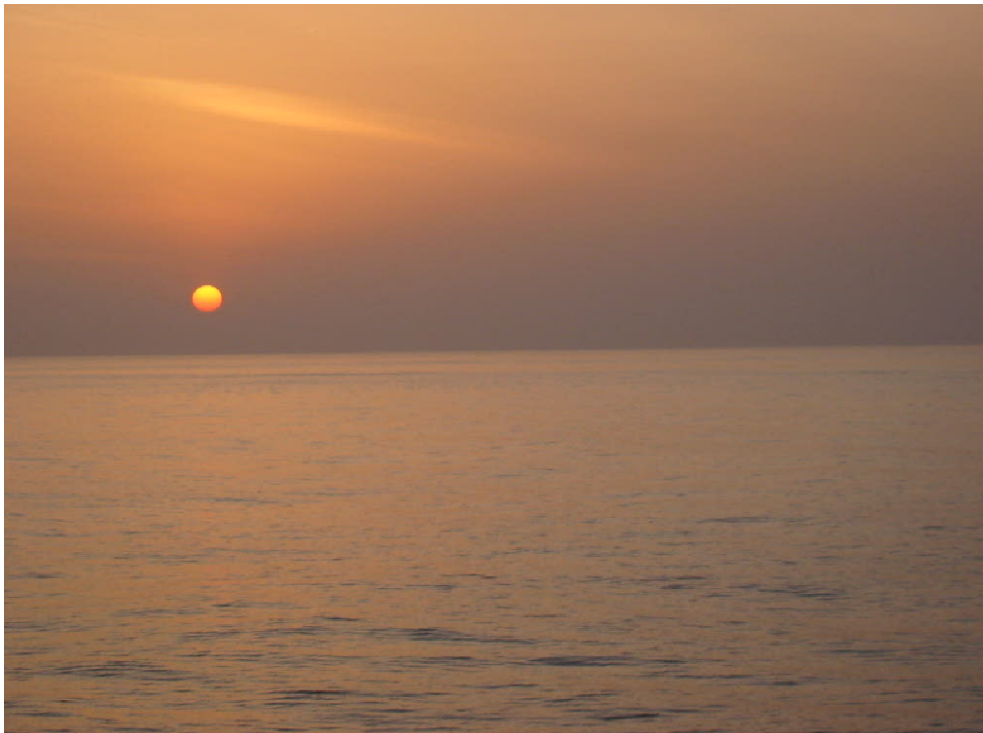


**Figure 3:** Section of Dissolved Oxygen ( $\mu\text{M}$ ) from M 55

blooming *Trichodesmium*. These were growing well above a chlorophyll maximum that was composed of diatoms. This was clearly what Seawifs had detected and without the Seawifs imagery we would have missed this completely. Several experiments were initiated with water collected from within this feature. Most of the remainder of the cruise track continued along  $10^\circ\text{N}$  instead of  $11^\circ\text{N}$  as originally planned.

### 3.2 Week 2 (21.10.2002-27.10.2002)

We continued to occupy two stations per day. The early station, which started at 05.00, was the more extensive with a minimum of 2 separate CTD casts. On most days, we added 1 or 2 additional CTD casts in order to collect large volumes of water for on-board experiments. At this



**Figure 4:** Dusty sunset during M 55.

station we also usually conducted two casts with Go-Flo sampling bottles specially suited for contamination-free sampling of trace metals. Sampling at this station extended to a maximum depth of 600m with a major emphasis on the waters at, and overlying, the chlorophyll maximum. The afternoon station was usually less extensive, with a single CTD cast as well as measurement of light and fluorescence profiles. The afternoon sampling was also usually to 600m but this was, on occasion, replaced by a full-depth CTD cast.

During the 2nd week we steamed steadily east along 10°N. On the evening of the 26th we turned south for a transit to the equator along 26°W. The equator transit was designed to allow air sampling along the steepest gradient of the ITCZ (Intertropical Convergence Zone). On the Saturday evening, just as we started to head south, the staff and crew enjoyed a barbecue on deck accompanied by tropical sunset, warm weather and calm seas. This provided a very welcome break from the constant filtration, experiments, analyses and fighting with complex instrumentation of the previous two weeks.



**Figure 5:** Polarstern approaching.

### **3.3 Week 3 (28.10.2002-3.11.2002)**

The 3rd week started with the transit towards the equator along 26° 30'W. The crossing of the ITCZ was seen very clearly in the atmospheric pCO<sub>2</sub> data (the strong seasonality of northern hemisphere pCO<sub>2</sub> causes northern hemisphere air to have a slightly lower pCO<sub>2</sub> than southern hemisphere air at this time of year). The gradient between the hemispheres was also exceptionally well resolved in several trace gases, with acetone and methanol being higher in the northern hemisphere air and dimethyl sulphide being higher south of the ITCZ. At the time and location of our transit, the gradients were quite sharp, being concentrated into a band between 7°N and 5°N.

The southward transit also allowed us to sample higher surface biomass, visible in Seawifs imagery, lying within 1-degree north and south of the equator. We arrived at the equator early on the morning of 29 October, just in time for the morning productivity station. In total 4 stations were occupied at the equator between 26°W and 23.5°W. At these stations we found significantly deeper mixed layers (up to 80m deep) and, associated with this, higher near-surface bromoform levels and lower methyl iodide concentrations. On the morning of 30 October we arrived at the location of a University of Bremen long-term sediment trap mooring. It took less than 2 hours to release the mooring and get it on deck, which is testimony to the efficiency and great skill of the Meteor's deck crew.

Following the brief stay at the equator we returned northwards along 24°W in order to resume the main west-east transect. Much of this time we lay under a dense swath of cloud and we were able to sample occasionally intense tropical rainstorms.



**Figure 6:** METEOR and POLARSTERN during M 55.

### 3.4 Week 4 (4.11.2002-10.11.2002)

The fourth week was full of incident. Especially memorable was an unexpected meeting with POLARSTERN on the high seas (see below). The week also saw us collect our 2000th water sample, COMPLETE our section across the tropical Atlantic including sampling over the continental shelf of Guinea Bissau, and we also conducted our final 'routine' CTD station. We initiated a series of 'mega-experiments', or on-deck incubations, involving most of the groups on board.

An unusual high-seas meeting of the two major German research vessels, POLARSTERN and METEOR, took place on Friday 8th November. We had learned, mid-way through our cruise, that POLARSTERN was steaming southwards from Vigo to Cape Town. POLARSTERN gave us an ETA at 11°N 20°W of Friday 8th November, 1300 UTC. We were scheduled to finish our last station in the waters of Guinea Bissau at 11°N, 19°W late on Thursday night. Our plan had been to do more stations in the region along 11°N. It was clear that our paths were going to intersect.

Gerhard Kattner of the Alfred-Wegener Institut in Bremerhaven, was chief scientist on board

POLARSTERN and we learned that their science program had some similarities with ours, ranging from measurements of a range of trace atmospheric species including ozone, through to marine chemistry and marine biological investigations. One key goal of their cruise was to collect data (e.g. with an upward-looking FTIR system) in order to calibrate the new European satellite ENVISAT. Following our morning station on Friday the 8th we sailed back to the agreed upon meeting location. Conditions were ideal for the meeting: hot and sunny with calm seas. POLARSTERN manoeuvred into position a few hundred meters away from us and then Gerhard Kattner and the senior scientific staff from the POLARSTERN travelled to METEOR on rubber boats.

After this initial meeting, there was an extensive exchange of scientific staff and crew members between the ships for a period of 3 hours. The rubber boats shuttled back and forth between the two ships while hundreds of photographs were being taken, tours of the ships conducted and souvenirs swapped and purchased. We took the opportunity to transfer frozen samples to Polarstern for safer, cheaper shipment back from Cape Town. The occasion was also used by the atmospheric chemists from POLARSTERN and METEOR to compare their respective programs. Notably, POLARSTERN and METEOR were both equipped with Multiaxial Differential Optical Absorption Spectroscopy systems from the University of Heidelberg.

The meeting was a welcome interlude to our science program. During the 4th week, we crossed the waters of the Guinea Dome and performed several stations over the continental slope and shelf of Guinea Bissau. We completed two east-west transects over the continental margin, including several deep stations. At Station 43 on November 7<sup>th</sup> we celebrated the collection of sample number 2000. During this eastern portion of the transect we sampled an intense oxygen minimum at about 400m as well as a shallow oxygen minimum at less than 100m. Both minima are clearly reflected as maxima in N<sub>2</sub>O concentrations.

### **3.5 Week 5 (11.11.2002-17.11.2002)**

The beginning of the 5<sup>th</sup> week saw us complete our final CTD at station 51 west of Liberia. This was the 110<sup>th</sup> CTD cast of the cruise. This completed a short series of stations that we had made while steaming south-eastwards from 11°N, 20°W at the beginning of our transit to Douala. This short section allowed us some time to do a couple more deep CTD casts in order to resolve the deep N<sub>2</sub>O profiles.

At Station 51 water was collected to initiate a second 'mega-experiment' in which most groups on board once again participated. In these experiments, 48 hour incubation experiments were conducted on-deck using 12-liter bottles. In the first experiment, the incubation bottles had been deliberately manipulated in various ways in order to stimulate either phytoplankton or bacterial growth. The treatments in the 2<sup>nd</sup> experiment were more limited, involving the addition of 'all' nutrients or the addition of dissolved organic carbon (to stimulate bacterial growth), and there were replicate treatments.

After station 51 our work reverted to underway sampling and air analyses along a transit from the last station to Douala of approximately 1400 nautical miles! The halocarbon and alkyl nitrate groups took the opportunity of this long transit to intercompare standards. Other groups spent time working up their data and, of course, writing their sections of the cruise report. An important late evening activity was working on the Meteor guest book. We held a science results

discussion at which the various groups highlighted their initial findings, and outlined their short-term plans for working up samples and analyzing results. In the course of this discussion, additional useful collaborative analyses between groups were identified. It is clear that all groups that were on board have collected excellent data sets and that there are many exciting and new findings to write about. Given the risk associated with taking so many complex analytical systems to sea, several for the first time, it was gratifying to see that all groups had a highly successful cruise.

## **4. Measurement Programs and Preliminary Results**

### **4.1 CTD and Rosette Operation**

H.-P. Hansen and J. Schafstall (IfMK)

The CTD-Rosette used on this cruise was a SEA-BIRD rosette with 24 x 10L GO samplers and a SBE 9+ underwater unit provided by the IfMK's Meerestechnik division. The oxygen sensor installed was a SB43 equipped with a Clark type polarographic membrane electrode. All sensors were mounted in a housing with a pumped seawater flow.

A total of 110 CTD-casts of basically 3 types were made during the cruise.

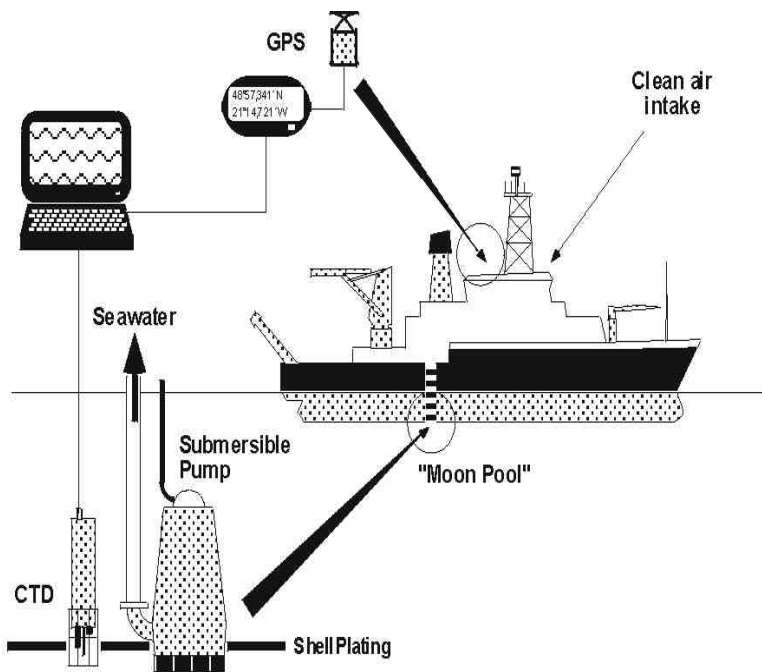
- 10 deep water CTDs (1000 – 5500m)
- 39 upper layer CTDs down to 650 m
- 61 “productivity” CTDs of less than 250 m depth, including surface water sampling (20 to 100 m) for various experiments, where only the “bottle” readings at the sampler depths were noted and no CTD traces were recorded.

About once every day, 2 to 3 salinity samples were collected for later calibration checks of the conductivity sensor. After some initial problems the instrument performed well. Only 10 samplers out of more than 2000 did not close, and, as identified in the data, 4 samplers closed at other than the intended depths. At one station with rather rough sea conditions the rosette hit the ships bottom. Two samplers were severely damaged and another two to a minor extent. (All samplers can be repaired). Because of this accident, and a special sampling requirement during one experiment, a total of 7 samplers were replaced by spare samplers from another rosette. Four of these samplers had to be removed because of significant contamination with trichloroethylene.

Both operators of the CTD had passed a “crash course” for the instrument and the software but lacked practical experience using this particular CTD/software. Unfortunately the SBE 9plus and the sensors had been assembled in a sensor/channel combination that made the CTD inoperable because the pump could not be started. Consequently the sensor readings of the first two profiles were unstable and are not usable. The problem was quickly identified as resulting from the temperature and conductivity sensors being connected to the secondary input channels. The SBE 9plus, however, strictly requires the conductivity sensor to be on the primary channel, because the pump is automatically stopped when the conductivity signal at the primary channel is zero (or close to) indicating “no water” in the pump.

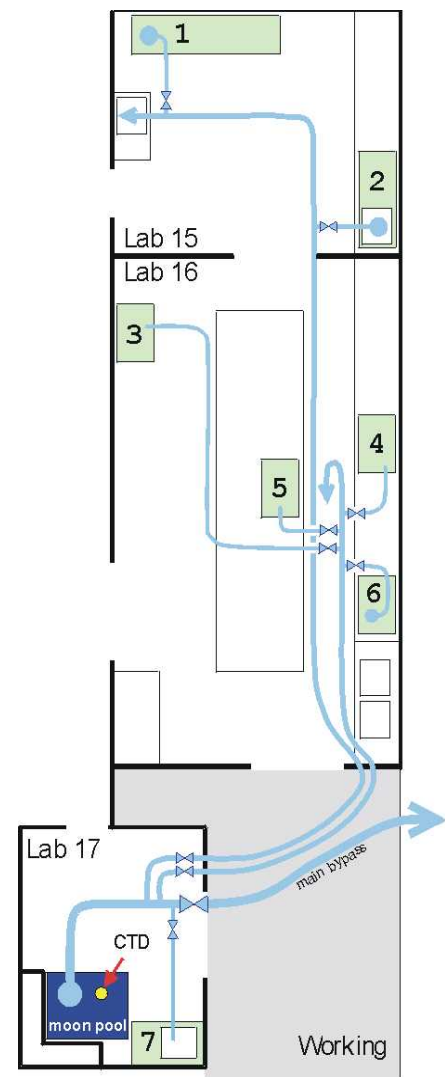
A second problem could not be solved during the cruise. The software-selectable output of the oxygen sensor is either oxygen saturation [%] or concentration [ml/l]. A direct sensor signal (i.e., electrode current or output voltage) is not available. (It may be that the selection is encrypted in the software so that we didn't find it). Consequently the evaluation of calibrated oxygen data





**Figure 7:** The underway seawater sampling system (from Körtzinger et al., 2000).

based on the CTD-sensor requires considerable calculations and calibrations to be done after the cruise (c.f. section below on nutrients and oxygen). The output of the  $O_2$ -sensor of the CTD was software-preset to alternatively oxygen saturation [%] or concentration [ml/l]. Both variables did not match the corresponding Winkler values and could not be calibrated by simple linear corrections. Included in the transformation of the original sensor signal (e.g., sensor current, which was not selectable) into the output variable were temperature and pressure compensation calculations which could not be quantified on the basis of the available documentation. So we decided to store oxygen saturation as the profile value because it has “suffered” less from unspecified computations. The CTD value was only about 77% of the (assumed true) Winkler value and the intercept of the regression were off the origin. The Winkler/CTD relation also appeared to be strongly dependent on the temperature. Compared to many other oceanic transects the Meteor 55 profiles are characterised by an extreme temperature range (2 to 30°C) and very strong vertical gradients. The temperature and depth grouping of oxygen saturations suggest that satisfactory “calibration” required considerable calculation effort, including performing individual profile calibrations. The final calibration is being performed after the cruise in the institute.



**Figure 8:** Schematic diagram of the underway seawater supply during M55 cruise.



## 4.2 Underway pumping system

A. Körtzinger (IfMK)

The underway seawater sampling system used during Meteor cruise 55 is shown in Figure 7. The system consists of a large submersible pump (multivane impeller pump, type CS 3060, ITT Flygt Pumpen GmbH, Langenhagen, Germany) and a CTD probe (type ECO, ME Meerestechnik-Elektronik GmbH, Trappenkamp, Germany) for measuring in situ seawater temperature and salinity at the intake. Both devices were installed in the shell plating at the bottom of the “moon pool”. The system provided a constant high-volume flow (approx. 350 L/min) of uncontaminated and bubble-free seawater. This underway pumping was used by all groups measuring underway samples. Temperature, salinity and navigational data (logged by a GPS receiver) were logged at 1-min intervals throughout the cruise.

Two seawater supply lines were teed-off from the main bypass and run through the geology laboratory (lab 16) and universal laboratory (lab 15) of R/V METEOR (Fig. 8). All underway systems were hooked-up to these supply lines which delivered the required flow of seawater to each system. A sampling station for discrete underway samples was also provided in lab no. 17. Measurements made on this underway pumped seawater:

- CH<sub>3</sub>I (ECD-GC)
- N<sub>2</sub>O (ECD-GC) and CH<sub>4</sub> (FID-GC)
- Volatile oxygenated compounds (PTR-MS)
- Development of miniaturized nutrients autoanalyzer
- Chlorophyll (fluorescence)
- CO<sub>2</sub> partial pressure (NDIR)
- Sampling point for discrete underway samples

## References

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## 4.3 Nutrients and Oxygen:

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A total of 1881 nutrient samples (5 nutrients) and 1444 oxygen samples were collected and analysed. These included 1294 rosette samples and 54 underway samples for oxygen and 134 for nutrients (Figure9). The remaining 60 oxygen and 453 nutrient samples were taken from on-board experiments and some of these exceeded the standard concentration ranges given below.

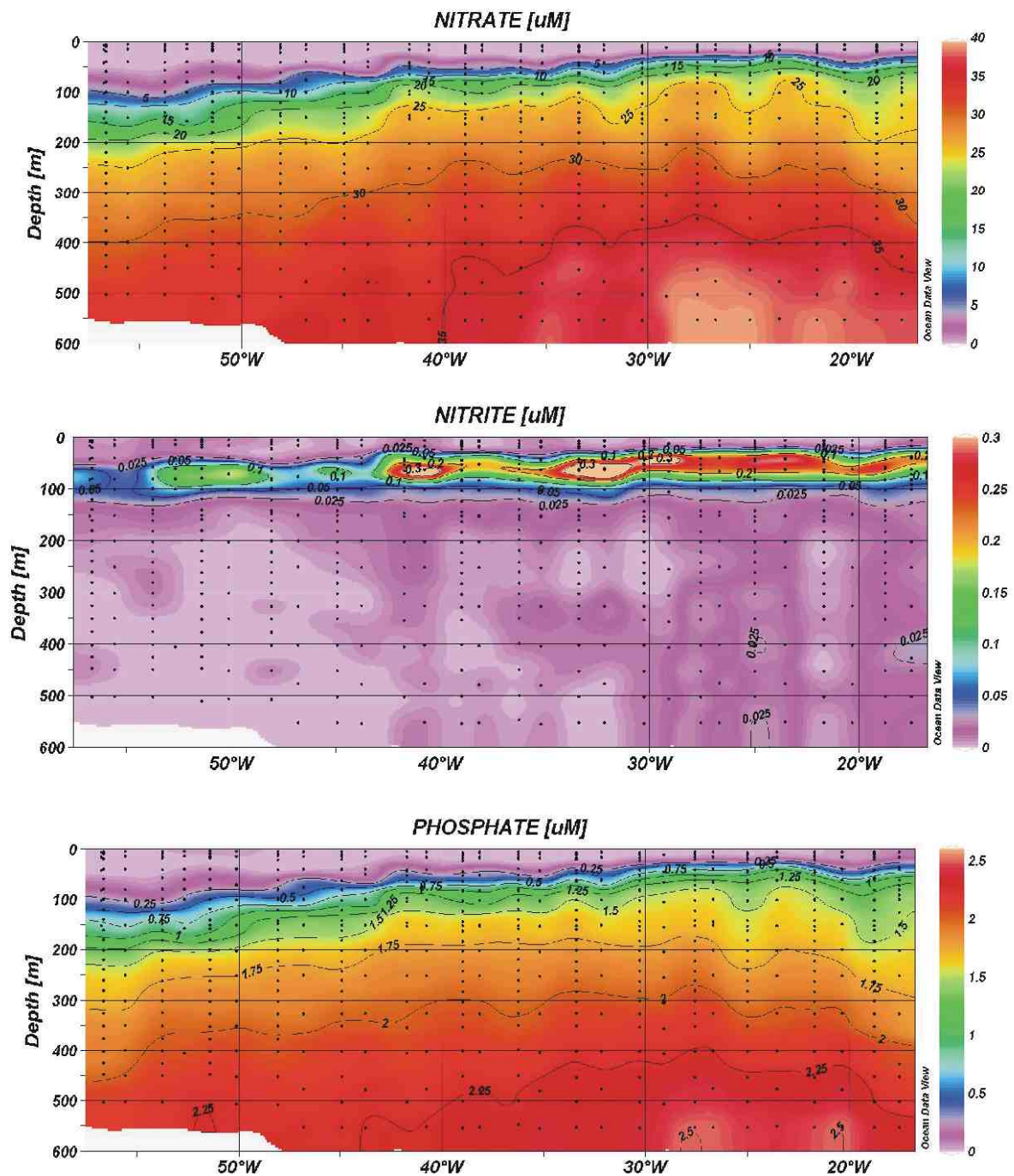
Oxygen samples were collected in 100 ml bottles and titrated in the sampling bottles according to the Winkler method and using a titration set-up as described by Hansen (1999). The nutrients were determined according to Hansen and Koroleff (1999). Ammonia was analysed

manually at 630 nm using 5 cm cuvettes in a Shimadzu UV-1202 spectrophotometer (304 in situ samples and 395 tank experiment samples). The remaining nutrients were analysed in a 4-channel “Kiel-Analyser” (loc cit). Calibration ranges (standard ranges of mixed working standards) and the maximum concentrations found in samples from the natural environment were:

| Para:     | Standard:                                | max. conc.          |
|-----------|--|---------------------|
| Nitrite   | 0 – 0.5 $\mu\text{M}$                    | 0.82 $\mu\text{M}$  |
| Nitrate   | 0- 30.5 $\mu\text{M}$ (nitrite included) | 41.33 $\mu\text{M}$ |
| Phosphate | 0 – 2.5 $\mu\text{M}$                    | 2.63 $\mu\text{M}$  |
| Silicate  | 0 – 50 $\mu\text{M}$                     | 215.6 $\mu\text{M}$ |
| Ammonia   | 0 – 2.0 $\mu\text{M}$                    | 0.39 $\mu\text{M}$  |

The methodical relative standard deviation was less than  $\pm 1\%$  of the high standard concentration.

The extremely high silicate concentrations found in water from the ship’s freshwater tanks caused some severe problems in the preparation of our silicate standards. Silicate, if present in high concentrations, may readily pass through mixed-bed ion-exchange columns without causing a significant rise of conductivity. The silicate is released over time from the inside coverage of the tanks. The resulting silicate concentrations range from 250  $\mu\text{M}$  after 14 days storage of water in the tank to about 70  $\mu\text{M}$  in continuous fill and use mode. The problem was solved with assistance of the Meteor’s Chief Engineer, by connecting the deioniser to the condenser of the freshwater unit following a cooling device. The deionised water thus prepared was free from silicate traces and always at about 0.5  $\mu\text{S}/\text{cm}$ . The lifetimes of deioniser cartridges were thereby considerably extended. As the freshwater tanks of German research vessels are maintained identically, separate fresh water supplies should be available for the nutrient chemistry and other groups that are dependent on good quality deionised water.



**Figure 9:** Nutrient sections from the main M55 W-E transect.

## References

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## 4.4 CO<sub>2</sub> System and Oxygen Sensor Trial

A. Körtzinger (IfMK)

### 4.4.1 Introduction

Due to its anthropogenic perturbation the global carbon cycle remains a major focus of earth system research. As the ocean plays a dominant role in it this is especially true for the marine sciences. So far, much effort has been put into understanding the past and present uptake of anthropogenic CO<sub>2</sub> by the ocean. Converging results from very different, completely independent approaches indicate that our understanding of the present role of the world ocean in the perturbed carbon cycle is fairly robust (albeit not complete). However, more recently the magnitude and causes of natural variability in the oceanic carbon cycle are receiving increased attention. This is due to the recognition of important feedback mechanisms by which a changing physical and biological forcing may act in various ways on the marine carbon cycle and hence the radiative balance of our atmosphere. If we are to come up with reliable and robust predictions of future global change, such feedback mechanisms have to be understood at minimum in a qualitative sense. The mainstay of the CO<sub>2</sub> programme during the M55 cruise was measurements of the CO<sub>2</sub> partial pressure in surface seawater and overlying air. These provide precise quantitative information on the degree of saturation of surface waters with respect to atmospheric CO<sub>2</sub>, which is the basis for calculation of the net exchange flux of CO<sub>2</sub> between ocean and atmosphere.

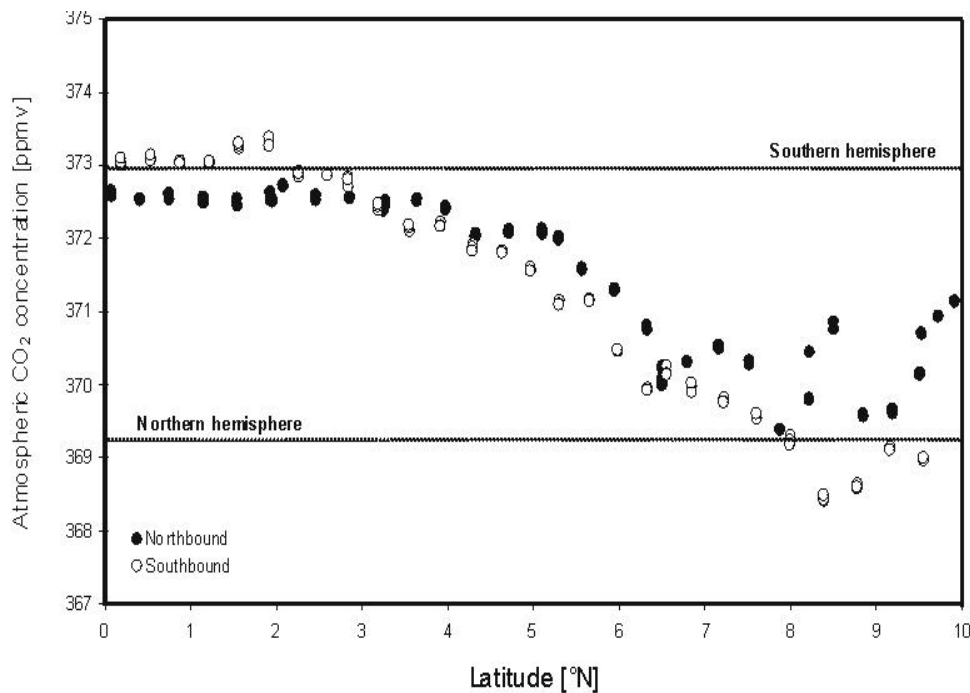
### 4.4.2 Measurements and Sampling

Measurements were carried out with an automated underway *p*CO<sub>2</sub> system based on equilibration of a sample gas stream with a continuous flow of surface seawater and subsequent determination of the sample gas CO<sub>2</sub> mixing ratio by non-dispersive infrared (NDIR) detection (Körtzinger *et al.*, 1996; Körtzinger, 1999).

The continuous flow was provided by the underway pumping system (section 4.2). Ancillary data continuously logged by the underway *p*CO<sub>2</sub> system include seawater temperature and salinity (from CTD located at the seawater intake), barometric pressure, and GPS position. All data were logged throughout the cruise at 1-min intervals. The underway work was further accomplished by discrete samples for determination of DIC, total alkalinity, TOC, and TON taken regularly from the seawater line. The total of 99 samples will be analysed back home.

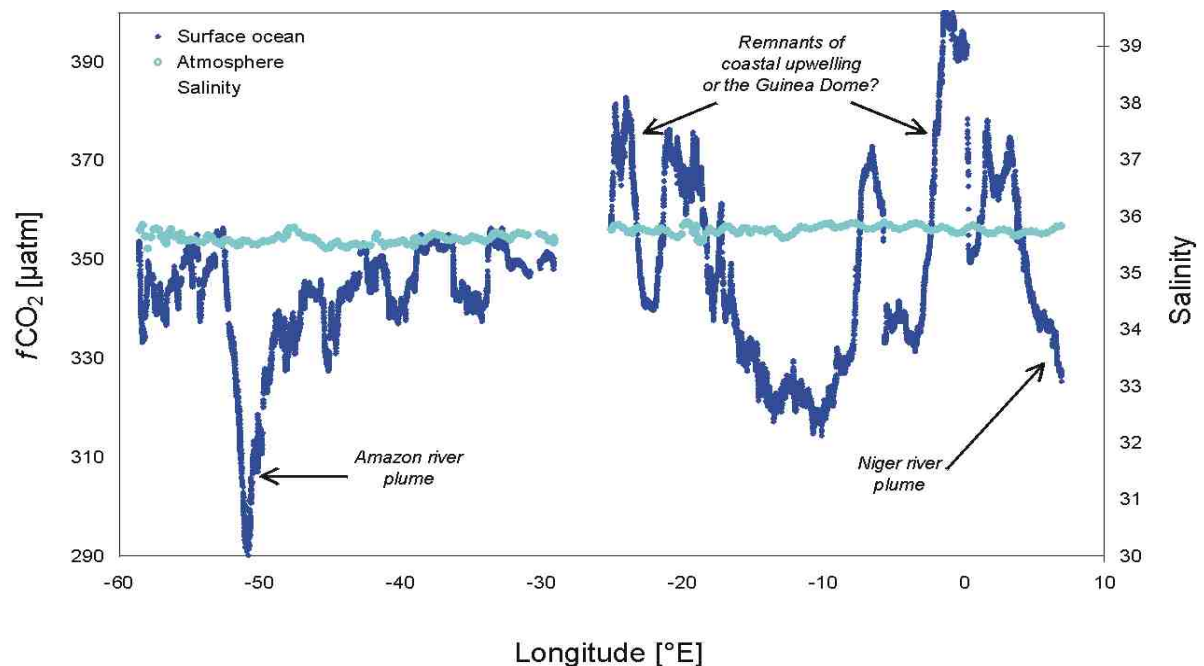
In order to provide some information on the vertical distribution of carbon system species, six hydrocasts (stations number 1, 5, 13, 19, 24, and 36; 82 samples in total) were sampled in the upper 500 m for determination of DIC, total alkalinity, TOC, and TON. These samples will also be analysed ashore.

Atmospheric CO<sub>2</sub> concentrations (in dry air) during the cruise ranged between 368 and 372 ppmv. A clear interhemispheric trend of about 3.5 ppmv was observed twice on meridional transects between 10°N and the equator (Fig. 10) with southern hemisphere concentrations being higher. While annual means of hemispheric CO<sub>2</sub> concentrations show a gradient in the opposite direction, these results are not unexpected as at this time of the year the northern hemisphere is still near its annual minimum and the southern hemisphere near its annual maximum.



**Figure 10:** Atmospheric CO<sub>2</sub> concentration (in dry air) along the two meridional transects between 11°N and the equator.

The  $p\text{CO}_2$  measurements in surface seawater show considerable variability along the transect (Fig. 11). Generally, waters along 10–11°N in the tropical North Atlantic appear to be at or near equilibrium with a typical undersaturation of only 0–15  $\mu\text{atm}$ . Significant stronger deviations from equilibrium were observed where the following special oceanographic conditions prevailed:



**Figure 11:** Surface seawater and atmospheric  $p\text{CO}_2$  as well as sea surface salinity along a zonal transect from 11°N 60°W to 3°N 0°W.

Amazon river plume: A strong Amazon river plume was encountered in the open ocean of the western basin. Surface salinities within the plume dropped to below 30 near 10°N/-58°E indicating the far-reaching influence from Amazon river waters. The plume, a branch of the North Brazil current (NBC) retroflexing into the North Equatorial Counter Current (NECC at ~6°N), exhibited elevated chlorophyll concentrations in contemporary Seawifs images. Surface seawater within the plume was strongly undersaturated by up to 60  $\mu\text{atm}$ . Surface nutrients within the patch were already depleted and no sign of an active bloom was found. The strong undersaturation in  $p\text{CO}_2$  thus likely represents the aftermath of a high biological productivity that had taken place in the most recent history of the present plume.

Equatorial upwelling: Clear indications of recent equatorial upwelling (less obvious in nutrients and chlorophyll data) were found at the equator where seawater was colder by 1-2°C and showed  $p\text{CO}_2$  supersaturation by about 30  $\mu\text{atm}$ . Again, the sluggishness of the air-sea equilibration for  $\text{CO}_2$  implies a rather long (i.e. several months) memory effect of surface seawaters with respect to its more recent biogeochemical and hydrographic history.

Remnants of coastal upwelling (or Guinea Dome) off West Africa: In the region off the coast of Guinea-Bissau as well as during the passage along the northern coast of the Gulf of Guinea two regions of coastal upwelling were passed. Although the two upwelling regions were not touched several patches of moderately to strongly supersaturated (20-40  $\mu\text{atm}$ ) surface water were encountered. Although SST data are inconclusive with respect to the upwelling origin, these features appear to be remnants or filaments of coastal upwelling that have been advected into the open ocean.

Parallel to the  $\text{CO}_2$  measurements programme, an optode-based oxygen sensor (Model 3830, Aanderaa, Bergen/Norway) was tested throughout the cruise. The brand-new sensor is based on the ability of oxygen to act as a dynamic fluorescence quencher. The fluorescent indicator is a special phorphyrin complex embedded in a gas permeable foil that is exposed to the seawater. A black optical isolation coating protects the complex from sunlight and fluorescent particles in the water. The sensing foil is attached to a sapphire window providing optical access for the measuring system. The foil is excited by modulated blue light, and the phase of the returned red fluorescence light is measured.

The sensor was installed in a flow-through bottle of 2 L volume. The seawater flow was drawn from the underway pumping system at a flow rate of 0.5 L/min. The sensor was operated throughout the cruise without any problems and measurements were logged at 1-min intervals. The sensor output was checked frequently against Winkler oxygen titrations. Based on the preliminary data set, this comparison yielded agreement to within 3  $\mu\text{mol/kg}$  and did not reveal a sensor drift during the 5-week exercise. Surface waters encountered along the transect were generally supersaturated by 2-5 %. A diurnal cycle that is, in part, explicable by diurnal temperature variations was also observed.

Based on these and similar results, the new sensor has the potential to be a major breakthrough in oxygen sensor techniques, which have suffered for decades from notorious drift problems of Clark type electrochemical oxygen sensors. We will use this small, low-weight sensor on autonomous platforms such as moorings and profiling floats in the near future.

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## 4.5 Water Column Biology

K. Lochte, I. Peeken, L. Hoffmann, M. Mills, R. Langlois (IfMK)

### 4.5.1 Introduction

The cruise track of M55 crossed several different biogeochemical oceanic provinces which are characterised by different pelagic productivity and standing stock of biogenic material. In the western part of the cruise track the coastal-water influence of the Amazon River plume was encountered. However the transect along  $10^\circ \text{N}$  was, for the most part, a tropical, oligotrophic system although at the equator some influence of upwelling was noted and in the eastern end of the transect some coastal influence was again encountered. Biological activity varies across these gradients and may well be the ultimate source or sink for some of the trace gases observed during the cruise by other groups. However, the pathways of production of the studied trace gases, or their precursors, are in many cases not yet known.

The input of dust enriching the surface water with trace metals and some phosphate is also expected to have an impact on the phytoplankton. In particular, addition of trace amounts of iron may stimulate nitrogen fixation (Falkowski, 1997), influence also other parts of the nitrogen cycle and enhance primary production if other nutrients are not limiting. This dust input increases from west to east.

This first SOLAS cruise attempted to match patterns of distribution of trace gases,  $\text{CO}_2$  and trace metals with biological production and other biological variables in order to obtain information on potential sources for trace gases or impacts on the biology from trace metal supplies. It was the task of our research group to provide basic information on the distribution of biogenic particles and on biological activities in close co-operation with measurements of the chemical species. The emphasis was on mapping of phytoplankton and its activities. A parallel programme will analyse the occurrence of nitrogen fixing organisms with molecular biological methods in order to trace the potential influence of iron inputs on the distribution of organisms capable of nitrogen fixation.



### 4.5.2 Sampling and Measurements

At each station, 6 depths were sampled from CTD casts for biological variables in the upper 150m. The upper and lower two sampling depths were fixed, representing the upper mixed water column (5m and 15m) and the waters below the thermocline (100m and 150m), respectively. Two flexible intermediate sampling depths were chosen for each station to represent the chlorophyll maximum and waters above or below. The location of the chlorophyll maximum was determined from the fluorescence profile of a multi-channel fluorescence probe deployed just prior to the CTD cast. Light measurements with a LiCor 4pi sensor were made at each station to approximately 1% light depth to determine the light climate in the water column. These data were also used to incubate the samples for primary production at the appropriate light conditions.

Samples for the following variables or measurements were collected every morning and evening from CTD casts at 6 depths:

Chlorophyll a, phytoplankton pigments (determination by HPLC), flow cytometry, Utermöhl microscopy, particulate phosphorous, particulate organic carbon (POC) and nitrogen (PON), stable isotope signal of  $^{15}\text{N}$  and  $^{12}\text{C}$  in particulate matter, particulate biogenic silica, carbonate and total seston. (At the evening stations, the last three samples were skipped).

A total of 47 stations were sampled. Chlorophyll a was determined on board. The samples for the other variables were stored frozen (pigments) or dried until analysis in the home laboratory.

Samples for the detection and identification of nitrogen fixing microorganisms were collected in the mornings from a separate CTD, and in the evenings from the same CTD cast as the other biological variables. Samples for the determination of the  $^{15}\text{N}$ -signal in chlorophyll were collected at six stations.

At each morning station (25 stations total), primary production was measured in samples from the same 6 depths. Measurements of bacterial production and alkaline phosphatase activity, determined in parallel samples, were collected from 13 stations. Fractionated primary production and pigment labelling experiments were determined on selected stations.

### 4.5.3 Preliminary Results

Chlorophyll: At all stations a deep chlorophyll a maximum was found. Except for the westernmost stations, this was found at around 40 m to 50 m depth (Fig. 1). It contained 0.6 to 0.8  $\mu\text{g chl a l}^{-1}$ . The surface waters were impoverished, containing only 0.2 to 0.4  $\mu\text{g chl a l}^{-1}$ .

The low concentrations in the surface waters are matched by very low nutrient concentrations (see section 4.3). The depth of the chlorophyll max shallowed from west to east, matching the rise of the nutricline to shallower depths. As is typical for these oligotrophic, tropical waters, lack of nutrients limits phytoplankton growth in the upper water column. Phytoplankton is therefore forced to resort to the deeper part of the water column, where nutrients may diffuse from below the thermocline. However, the deep chlorophyll maximum is not necessarily an indication of a matching higher algal biomass. In low light, phytoplankton produces more photosynthetic pigments in order to harvest the low light intensities most efficiently. Therefore this deep maximum is probably created by a combination of higher cellular chlorophyll a levels and accumulation of biomass. Analysis of the number of cells by flow cytometry and microscopy

as well as bulk analysis of PON and POC will help to determine the characteristics of the deep chlorophyll maximum.

Higher concentrations of chlorophyll a in the equatorial upwelling as seen in satellite images could not be corroborated by chlorophyll measurements. This suggests that the elevated chlorophyll levels observed by the satellite were probably produced “downstream” and had been advected to our position.

In samples taken with a hand net the composition of the plankton <20  $\mu\text{m}$  was briefly observed on board. It was dominated by dinoflagellates, tintinnids, radiolarians and, on a number of stations, by the nitrogen fixing cyanobacterium *Trichodesmium*. Diatoms occurred less frequently. They were found in the western part influenced by the Amazon plume with some coastal species present and in the eastern part close to the coast of Guinea Bissau. Utermöhl microscopy and flow cytometry will be done in the home laboratory for a more detailed description and quantification of the plankton community.

**Primary production:** Primary production was determined by uptake of  $^{14}\text{C}$ -bicarbonate in 250 ml samples incubated at simulated light intensities in deck incubators. The samples were incubated for 24 h in order to determine the net primary production. The incubators were cooled by a flow of surface water. Five different neutral screen shades were used to simulate the light intensities at the depths of sampling (Table 2). The profile of light in the water column was determined at each station by a LiCor 4pi light sensor. It did not change very much along the transect.

**Table 2:** Light intensities used for the incubations of samples from 6 depths.

| Sampling depth<br>(m) | Light intensity<br>(% of surface illumination) |
|-----------------------|--|
| 5                     | 50%  |
| 15                    | 20%  |
| Variable              | 6%   |
| Variable              | 1%   |
| 100                   | 0.3%   |
| 150                   | 0.3%   |

Primary production was, as expected, highest at the surface due to the higher light intensities. The chlorophyll maximum did not show up as a subsurface peak. Highest values are around  $80 \text{ mg C m}^{-3} \text{ d}^{-1}$ , while average surface water production ranges around  $30 \text{ mg C m}^{-3} \text{ d}^{-1}$ . In many cases light inhibition was observed in the top samples.

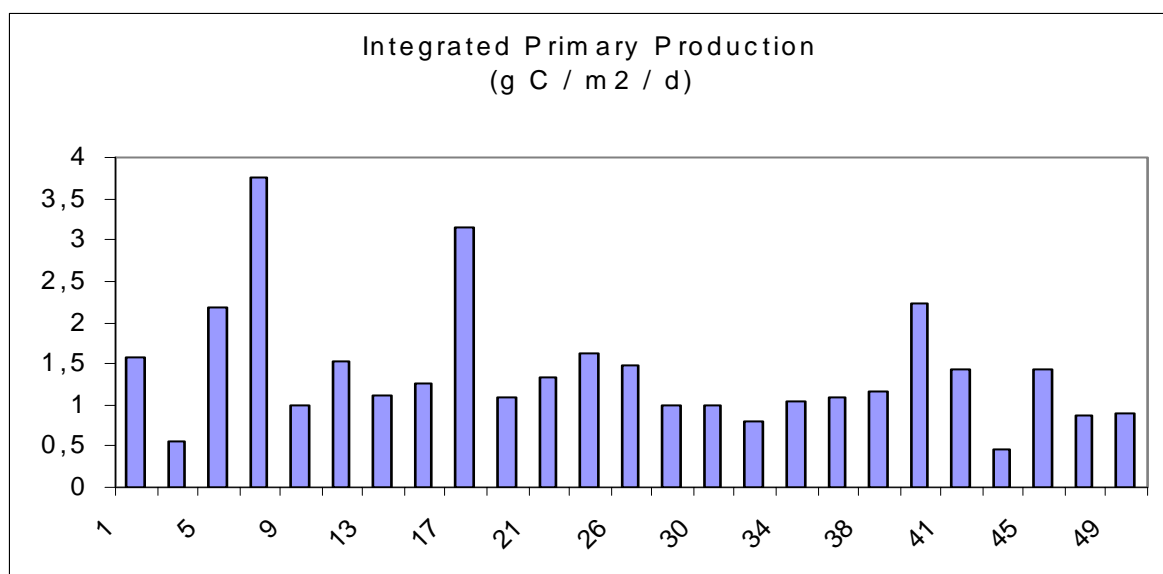
When integrating the data over the upper 150 m changes in regional productivity become more obvious (Fig. 12). On average integrated primary production was around  $1 \text{ g C m}^{-2} \text{ d}^{-1}$ , but some stations clearly deviated from this value. Stations 5-9 were influenced by the plume of the Amazon and were the most productive; stations 26 and 28 were located in the equatorial upwelling but had only slightly elevated productivity; the stations from 41 onwards were sampled waters along the African coast and were more variable. An exception was station

17 at 33°W which had very high surface water productivity. The reasons for this peak are still unclear.

Fractionated primary production and pigment labelling: Fractionated primary production was determined by uptake of  $^{14}\text{C}$ -bicarbonate in 230 ml for surface (5, 15m) and chlorophyll maximum samples incubated at simulated light intensities in deck incubators (details see above). The samples were incubated for 24 h and filtered through 0.2; 0.8; 2.0 and 5.0  $\mu\text{m}$  polycarbonate filters and analysed on board.

Highest primary production occurred at the shallowest depth (5m). A slight increase in total production from west to the east was observed. On average 75% of primary production was associated with small phytoplankton ( $<2\ \mu\text{m}$ ). We noted that within this small size class, the fraction 0.8 – 2  $\mu\text{m}$  became more important in the eastern stations while the smallest size class (0.2 – 0.8  $\mu\text{m}$ ) dominated at the western stations. Phytoplankton  $>5\ \mu\text{m}$  are negligible within the chlorophyll maximum. No change of this group was observed along the transect, while the size fraction 2 – 5  $\mu\text{m}$  increased from west to east. Further investigations using flow cytometry will help to determine which groups of phytoplankton occur in the different size classes.

The growth rate of different phytoplankton groups was determined by pigment labelling. These experiments were performed 6 times on samples collected from the evening casts. Two replicates of 2,3 l of seawater were sampled from the 5 and 15m depths.  $\text{H}^{14}\text{CO}_3^-$  was added to the bottles, which were incubated for 24 hours on-deck at simulated 50%, 20 % and ambient light levels. In order to determine  $^{14}\text{C}$  incorporation into Chl a and taxon specific carotenoids, samples were filtered on GF/F-filters at the end of the incubation and frozen at  $-80^\circ\text{C}$  for later analysis. Phytoplankton growth rates will be determined from the specific  $^{14}\text{C}$ -activity of Chl a or the taxon-specific carotenoids using functions which relate pigment specific activity to growth rates. Such estimates of phytoplankton growth rate are unaffected by the possible recycling of carbon in the incubation bottles (e.g. via algal respiration or zooplankton grazing) because

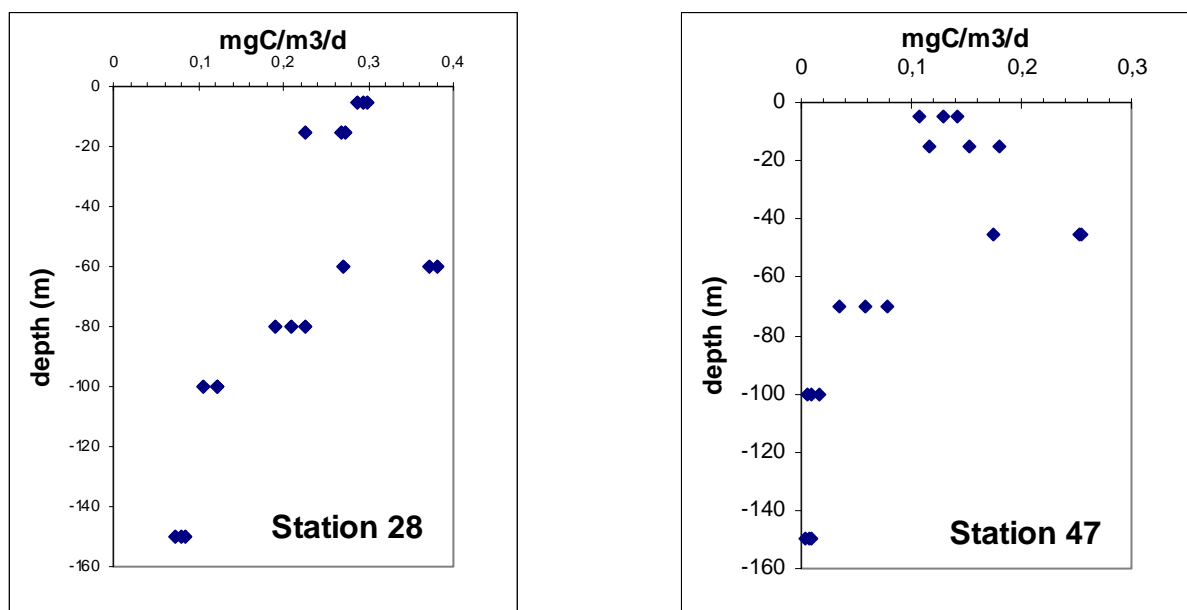


**Figure 12:** Integrated primary production in the upper 150m as a function of station number.

specific  $^{14}\text{C}$ -activity of a pigment is not affected when zooplankton remove and destroy pigments over the course of an incubation. The isolation of Chl a and the marker carotenoids will be performed according to Goericke and Welschmeyer (1993; 1993) in the isotope lab at the IfM in Kiel.

Due to a lack of nutrients, phytoplankton accumulates in the deeper part of the water column at very low light intensities forming the deep chlorophyll maximum. Some experiments were carried out on board to investigate the capacity of this deep phytoplankton community for biomass production. Phytoplankton from the deep chlorophyll maximum was subjected to higher light intensities (50%) and plankton from surface layers was transferred to deepwater conditions. Further experiments considered the effect of the higher nutrient supply in the deep chlorophyll maximum by adding nutrient rich ambient deep water. The experiments were run for 12, 24 and 48 h. Primary production, fast repetition fluorometry, and changes in the composition of the plankton community by flow cytometry, pigment composition (via HPLC) and microscopy are determined during the experiments.

**Bacterial production and phosphatase activity:** Bacterial production was determined by incorporation of  $^3\text{H}$ -thymidine into DNA. The samples were incubated for 4 h in the dark in water baths at in situ temperatures. Conversion of thymidine incorporation to biomass production assumes a production of  $1.1 \times 10^{18}$  cells per mol thymidine, an average cell size of  $0.03 \mu\text{m}^3$  per bacterial cell, and a carbon conversion factor of  $0.25 \times 10^{-6} \mu\text{g C per } \mu\text{m}^3$  of bacterial cell volume. On the basis of these assumed conversion factors bacterial biomass production was always less than  $1 \text{ mg C m}^{-3} \text{ d}^{-1}$ . In many cases at the deep chlorophyll maximum bacterial production was highest as shown in Fig. 13. Obviously bacterial degradation of organic matter is intense in this layer. Alkaline phosphatase is a hydrolytic enzyme for the degradation of organic phosphorus compounds. It is produced by bacteria and phytoplankton especially when phosphate supply is low. Considering that nitrogen fixation may alleviate nitrogen limitation, the



**Figure 13:** Bacterial production at Stations 28 (1°57'N 23° 30'W) and 47 ( 9° 18.5'N 19°0.3' W). showing elevated productivity at the deep chlorophyll maximum.

phosphatase activity may help to detect areas with particularly high phosphate turnover. The activity of this enzyme was determined with the fluorogenic substrate MUF-phosphate. In most cases phosphatase activity was highest in the surface water and only occasionally a small peak was found at the chlorophyll maximum. This pattern does not match the bacterial production in the water column (Fig 13) and indicates a high capacity for organic phosphate hydrolysis in the upper water column. This may be related to the high primary production and perhaps nitrogen fixation in the surface layer.

Detection of nitrogen fixing organisms: A total of 255 samples were collected for molecular analysis of nitrogen fixing organisms. Of these, 210 samples were taken from CTD casts. The chlorophyll maximum and 5 meter depths were sampled from 47 stations and samples from a depth just below the euphotic zone were collected at 11 stations. One DNA and one RNA sample of 1.5 to 1 l volume were filtered from each depth onto 25mm x 0.22µm filters and frozen at -80°C. Large *Trichodesmium* colonies, when noted, were on filters from the shallowest CTD sample (5 m depth). In addition 40 DNA samples were collected from the Bioassay experiments (see Section 4.9). All treatments plus an initial sample were filtered from experiments 05, 06, and 07. Selected samples were taken from experiment 04.

Attempts were made to culture N-fixers. The attempts were not successful, however the water remaining from these attempts was filtered for analysis back in Kiel. Two samples of *Trichodesmium* colonies were collected using the hand plankton tow net. One was collected from Station 6, and the other from station 42. Real-Time Polymerase Chain Reaction (RT-PCR) for the *nif*-genes involved in nitrogen fixation will be run on the samples in Kiel.

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## 4.6 Nitrous oxide (N<sub>2</sub>O) measurements

S. Walter and H.W. Bange (IfMK)

### 4.6.1 Introduction

Nitrous oxide is an important atmospheric trace gas, which received increased attention in recent years because of its relevance for the Earth's climate and stratospheric chemistry. Like CO<sub>2</sub>, N<sub>2</sub>O is a radiatively active atmospheric trace gas, however, its global warming potential is, on a 100 years time horizon, about 300 times higher than that of CO<sub>2</sub>. Due to its relatively long atmospheric lifetime of 120 years, N<sub>2</sub>O is mixed into the stratosphere where it is photochemi-

cally decomposed forming nitric oxide radicals which are involved in one of the major catalytic ozone reaction cycles.  $\text{N}_2\text{O}$  is produced during microbial processes such as nitrification and denitrification in considerable amounts in the subsurface layer of the ocean. Thus, oceanic emissions of  $\text{N}_2\text{O}$  play a major role for its atmospheric budget. Measurements of  $\text{N}_2\text{O}$  in the tropical Atlantic are sparse. Recent improvements to the coupling of gas chromatography with isotope-ratio mass spectrometry have facilitated acquisition of dual-isotope composition ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ) of  $\text{N}_2\text{O}$ . Based on dual-isotope data from the subtropical Pacific Ocean, it was suggested that nitrification is the dominant  $\text{N}_2\text{O}$  production pathway in surface waters of the ocean. However, dual-isotope data from the Atlantic Ocean are not available yet. Moreover, the responsible organisms involved in formation of oceanic  $\text{N}_2\text{O}$  are largely unknown.

#### 4.6.2 Measurements and sampling

$\text{N}_2\text{O}$  concentrations were made on water samples from selected 'shallow' CTD/rosette profiles (<650m) as well as a limited number of full-depth profiles interspersed along the cruise track. Samples for the isotopic analysis of  $\text{N}_2\text{O}$  were collected at the deep profiles. Finally samples from selected stations were filtered on board for later DNA analysis.

**Table 3:**  $\text{N}_2\text{O}$  Profile statistics.

| Station no. | Date, m/d/y | Long [°E] | Lat [°N] | Depth range, m | No. of depths sampled for               |                       |                      |
|-------------|-------------|-----------|----------|----------------|---|-----------------------|----------------------|
|             |             |           |          |                | $\text{N}_2\text{O}$ conc. <sup>a</sup> | Isotopes <sup>a</sup> | Filters <sup>b</sup> |
| #04         | 10/17/2002  | -52.66    | 10.29    | 0 - 5000       | 20                                      | 12                    | 12                   |
| #05         | 10/18/2002  | -51.41    | 10.00    | 0 - 150        | 6                                       |                       |                      |
| #07         | 10/19/2002  | -48.06    | 10.00    | 0 - 500        | 12                                      |                       |                      |
| #11         | 10/21/2002  | -41.73    | 10.00    | 0 - 3700       | 24                                      | 12                    | 12                   |
| #17         | 10/24/2002  | -33.40    | 10.00    | 0 - 625        | 12                                      |                       |                      |
| #20         | 10/25/2002  | -29.10    | 10.01    | 0 - 5400       | 24                                      | 12                    | 12                   |
| #22         | 10/26/2002  | -26.67    | 10.00    | 0 - 625        | 13                                      |                       | 12                   |
| #24         | 10/29/2002  | -26.00    | 0.00     | 0 - 625        | 12                                      |                       |                      |
| #25         | 10/29/2002  | -24.94    | 0.00     | 0 - 625        | 13                                      |                       |                      |
| #26         | 10/30/2002  | -23.50    | 0.00     | 0 - 625        | 12                                      |                       |                      |
| #27         | 10/30/2002  | -23.50    | 0.00     | 0 - 3800       | 24                                      | 12                    | 12                   |
| #31         | 11/01/2002  | -24.25    | 6.50     | 0 - 4200       | 24                                      | 12                    | 12                   |
| #35         | 11/03/2002  | -23.52    | 11.00    | 0 - 625        | 13 <sup>c</sup>                         |                       |                      |
| #36         | 11/04/2002  | -21.67    | 11.00    | 0 - 625        | 24                                      |                       |                      |
| #40         | 11/05/2002  | -17.50    | 11.65    | 0 - 1000       | 18                                      | 12                    | 12                   |
| #41         | 11/06/2002  | -16.83    | 10.42    | 0 - 190        | 15                                      |                       |                      |
| #42         | 11/06/2002  | -17.70    | 11.03    | 0 - 2900       | 24                                      | 12                    | 12                   |
| #44         | 11/07/2002  | -19.75    | 11.00    | 0 - 4800       | 24                                      | 12                    | 12                   |
| #47         | 11/09/2002  | -19.00    | 9.31     | 0-4100         | 24                                      | 12                    | 12                   |
| #49         | 11/10/2002  | -17.08    | 7.00     | 0 - 625        | 24                                      |                       | 12                   |
| #50         | 11/10/2002  | -15.90    | 6.10     | 0 - 2500       | 18                                      |                       |                      |

<sup>a</sup> Triplicates per depth.

<sup>b</sup> Filters were taken at same depths as isotopes samples

<sup>c</sup> A double set of samples was taken in order to evaluate the long-term stability of the samples. Samples will be measured in Kiel.

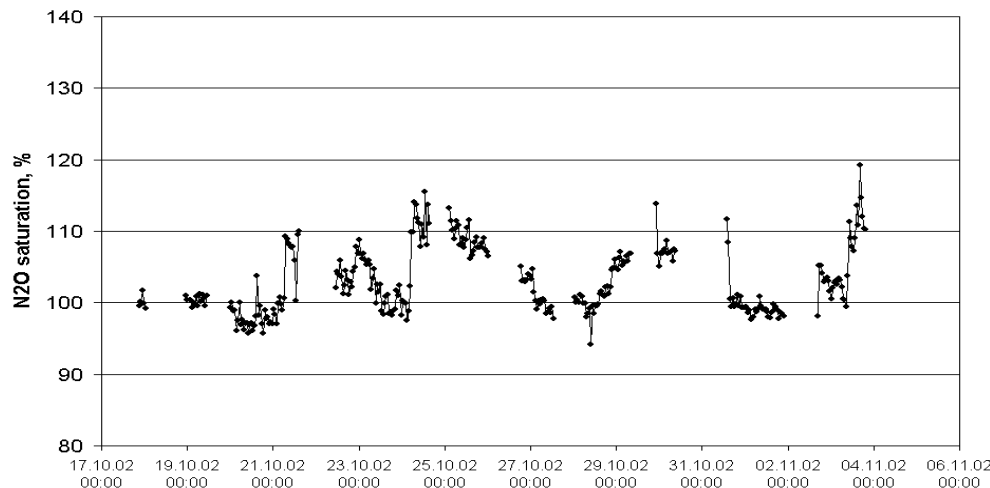
Sampling locations and numbers of samples are presented in the attached table. In addition, approximately 1000 measurements of  $\text{N}_2\text{O}$  were made on continuously pumped air and surface water from the atmospheric boundary layer and ocean surface layer, respectively. About 25 surface water samples for the isotopic analysis of  $\text{N}_2\text{O}$  were also collected (in triplicate) from the continuous pumped surface water supply.

#### 4.6.3 Preliminary results

Shipboard data quality was judged to be very good with the precision of atmospheric measurements being about 0.9% and the mean relative error for  $\text{N}_2\text{O}$  concentrations measured in the water samples being about 2%. The continuous measurements revealed  $\text{N}_2\text{O}$  surface saturations close to the equilibrium value (98-110%) indicating that oligotrophic tropical Atlantic is a weak source of atmospheric  $\text{N}_2\text{O}$ . Saturations up to 120% were observed in the coastal waters off Guinea-Bissau (see Figure 14).

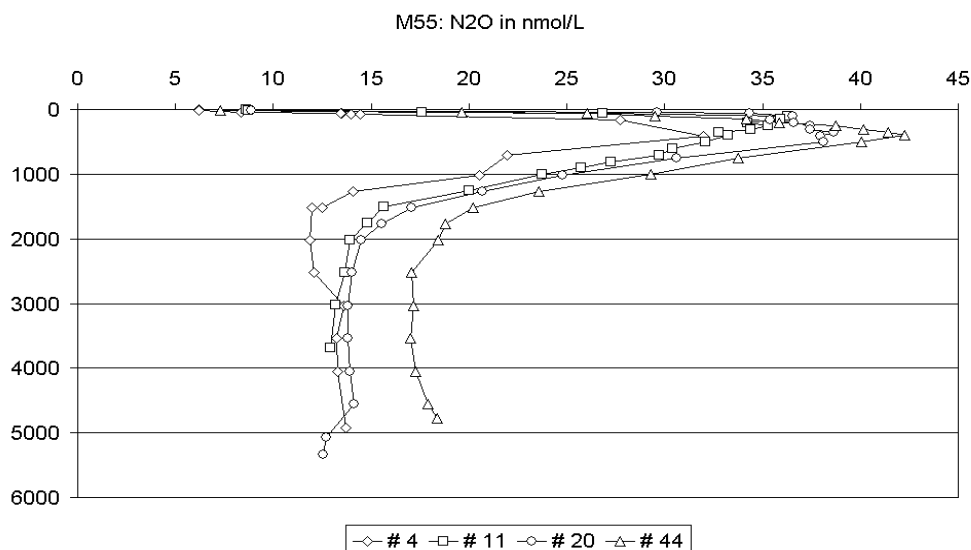
Three general features were visible from the depth profiles (see Figure 15):

- $\text{N}_2\text{O}$  is supersaturated throughout the water column.
- There is a considerable accumulation of  $\text{N}_2\text{O}$  below the euphotic zone with maximum values (up to 43 nmol/l) at about 400m water depth.
- There is an increasing trend in the maximum  $\text{N}_2\text{O}$  concentrations from the western to the eastern Atlantic basin. This seems to be inversely related to decreasing dissolved oxygen values in the oxygen minimum zone.



**Figure 14:**  $\text{N}_2\text{O}$  saturation along the M55 cruise track.





**Figure 15:** N<sub>2</sub>O depth profiles at selected stations in the tropical Atlantic.

## 4.7 Biogenic Halocarbons and Light Alkyl Nitrates.

B. Quack, U. Richter, G. Petrick, K. Stange, D. Wallace (IfMK), A. Chuck (UEA)

### 4.7.1 Introduction

The ocean plays a significant role in determining the trace gas composition of the atmosphere, via sea-to-air emissions, which are controlled by biotic and abiotic production and consumption processes occurring within the water column. Both the halogenated hydrocarbons (halocarbons) and alkyl nitrates affect the 'oxidising capacity' of the atmosphere, primarily as a result of their influence on ozone concentration. Halocarbons have been shown to be produced biogenically by various species of microalgae in laboratory studies. However, the production processes and their fluxes in the open ocean remain poorly characterised. The Meteor 55 oceanic trace gas program focussed on three main issues: methyl iodide, bromoform and alkyl nitrates.

Methyl iodide (CH<sub>3</sub>I) is an organic trace gas that received increasing attention in recent years. It is a major carrier of iodine to the atmosphere and takes part in many atmospheric reactions. Of special interest is its potential to destroy ozone. Due to its short atmospheric lifetime, methyl iodide is restricted to the troposphere unless it can be transported to the stratosphere very fast by strong upwinds, e.g. in tropical clouds. Methyl iodide is a natural compound and the ocean is a major source for the atmosphere. In previous studies it has been shown that some algae and plankton species produce methyl iodide, however the quantities are too small to explain the measured concentrations. One study showed results indicating a photochemical production in the ocean water.

Bromoform (CHBr<sub>3</sub>) has its principal source in the oceans and is the major organic source for atmospheric reactive bromine. Besides a large macroalgal source in coastal regions,

oversaturation in the worlds open oceans contributes significantly to the global emissions, suggesting an (unknown) open ocean source. Investigations of phytoplankton species have revealed production of bromoform by some species of cold water diatoms. Other diatoms and marine organisms are likely to produce significant bromoform and abiotic sources may also exist. Atmospheric studies in the equatorial Pacific and Atlantic have revealed a meridional maximum in atmospheric bromoform in tropical and equatorial regions, however the specific cause of this is unknown. In these tropical regions, despite bromoform's short lifetime due to photolysis, oceanic emissions may be transported to great heights due to tropical convection and thus influence lower-stratosphere chemistry. Destruction of the compound occurs mainly via photolysis in the atmosphere and most likely halogen-exchange reactions in the water column. To elucidate source and sink terms, which are important for the global bromine budget and for atmospheric chemistry, measurements of bromoform as well as other brominated and chlorinated trace gases were performed in both the lower atmosphere and surface ocean during the cruise.

Alkyl nitrates ( $\text{RONO}_2$ ) are a significant component of the odd nitrogen reservoir ( $\text{NO}_y$ ) and, along with the other chemically labile components of  $\text{NO}_y$ , such as peroxyacetyl nitrate (PAN,  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ ), play an important rôle in regulating the levels of tropospheric ozone in remote marine regions where the typically low levels of  $\text{NO}_x$  lead to a close balance between the formation and destruction of tropospheric ozone. Since the discovery of the light alkyl nitrates in the atmosphere, the source of these compounds has been assumed to be exclusively anthropogenic, via primary emissions from combustion and chemical processes and secondary formation from atmospheric photooxidation of organic compounds in the presence of  $\text{NO}_x$ . However, observations of a strong positive correlation between ethyl and propyl nitrate and the marine biogenically produced halocarbon, bromoform, in the marine boundary layer over the equatorial Pacific Ocean led Atlas *et al.* (1993) to propose an oceanic source for alkyl nitrates to the atmosphere. Measurements of methyl and ethyl nitrate in surface seawater and air along two north-south Atlantic Ocean transects provided direct evidence for an oceanic source of these compounds (Chuck *et al.*, 2002), particularly in the tropical and equatorial waters. The objectives for this cruise were to better characterise the distribution and sea-to-air flux of the light alkyl nitrates in the tropical Atlantic, and to investigate the processes responsible for the production of these compounds.

#### 4.7.2 Sampling and Measurements

Bromoform and other halocarbons: Water-column profiles of halocarbons (especially bromoform, dibromochloromethane, dichlorobromomethane, dibromomethane and trichloromethane) were measured using purge-and-trap gas chromatography with mass spectrometry. The group from IfMK performed these measurements on board. A total of 250 samples that had been collected from the CTD/Rosette were measured, together with 90 surface water samples collected from the underway pumping system. An additional 40 measurements of atmospheric concentrations were made on samples provided either through an online „Dekabon“ air inlet or from canisters collected at the bow of the ship

The GC-MS system, which was constructed with all glass-transfer lines, was used for the first time on a ship. It performed well for the aquatic samples after some modifications to the system

were made. The modifications were necessary due to the high environmental temperatures and, especially, the high humidity. The set-up of the analytical system for measuring air samples took two weeks and the number of air samples that could be measured was also restricted by the limited number of GC-runs that could be processed per day. Several different systems for sampling were tested (Dekabon sample line, Teflon line and canisters). The Dekabon was found to emit large quantities of phthalates, which did not appear to interfere with the halocarbon analyses, however.

In addition to the on-board measurements, samples of boundary layer air were collected in stainless steel canisters for two research groups in the US (Elliot Atlas, NCAR, Boulder, CO and Jim Butler, CMDL, Boulder, CO). These canisters will also be analysed for halocarbons and other atmospheric species by gas chromatography and mass spectrometry. A total of 140 canisters were collected for Elliot Atlas and an additional 27 for Jim Butler.

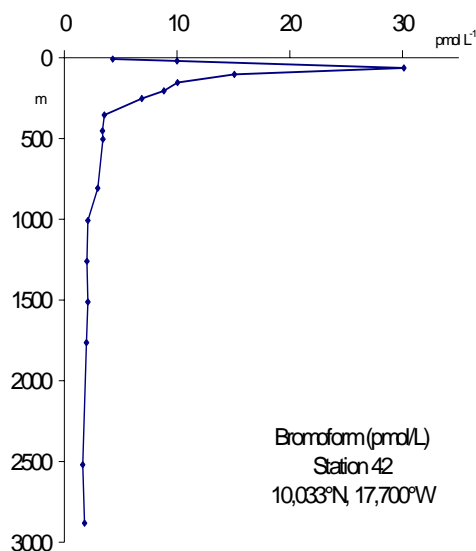
Methyl Iodide: Two separate measurement systems for CH<sub>3</sub>I were used on board. The IFMK made measurements of air and on surface water from the pumped seawater supply using a shower-type equilibrator that was interfaced to a 2-dimensional gas chromatograph (GC) system (Fisons 8160/8180) equipped with an electron capture detector. The same system was also used for measuring samples from incubation experiments designed to study the factors responsible for CH<sub>3</sub>I production. A total of 300 air and surface water samples were analysed with this system and analyses were also made on a total of 7 separate incubation experiments (see below).

Analytes from air samples, equilibrated air or purged water samples were initially trapped on an open tubular capillary trap (20cm x 0.5mm i.d. of Ultimetall uncoated tubing from Chrompack) at liquid nitrogen temperatures. After trapping, the trap was removed from the coolant, and the analytes backflushed onto GC column #1. Tests with standard injections showed recovery to be 98%. A heartcut of compounds eluting close to CH<sub>3</sub>I was made from column 1. Standardization was made using injections of gas-phase standards that had been gravimetrically prepared according to procedures described by Happell and Wallace (1997). The P5 standard had a CH<sub>3</sub>I mixing ratio of 171.2 nmol mol<sup>-1</sup> and was injected via a septum into the 'gas mouse' (Figure 1b) using a gas-tight 100 µL syringe. Precision of replicate standard injections was 8.3%.

Alkyl nitrates: A separate purge-and-trap gas chromatography system was used for vertical profile measurements of alkyl nitrates and some iodocarbons. Water samples were collected in 100 ml glass syringes from the pumped underway supply and from the Niskin bottles on the CTD rosette. All samples were analysed on board within 12 hours of collection. In addition to methyl nitrate and i-propyl nitrate measurements, the chromatographic conditions enabled measurements of the biogenic halocarbons methyl iodide and chloroiodomethane. Unfortunately, poor resolution of ethyl nitrate from carbon tetrachloride meant that ethyl nitrate could not be measured during this cruise.

In total, 26 depth profiles were measured, with samples being taken from 12 depths between the surface and 400 metres. In addition, one deep cast was sampled down to 4000m. Air samples were collected in a 1 L aluminium canister from the bow of the ship using a metal bellows pump supplied by Elliot Atlas (NCAR). The sampling frequency was one air sample per day.

Measurements of these trace gases were also made during two incubation experiments carried out during the cruise. The aim of these experiments was to investigate the effect of several enrichment treatments on the biology and trace gas production. Samples for the methyl nitrate and methyl iodide were taken at the beginning of the experiments, after 24 hours and after 48 hours. Towards the end of the cruise, several large rain events enabled sufficient water to be collected to analyse for the presence of the trace gases. Four separate rain water samples, collected using the equipment of Alex Baker (UEA), were analysed.



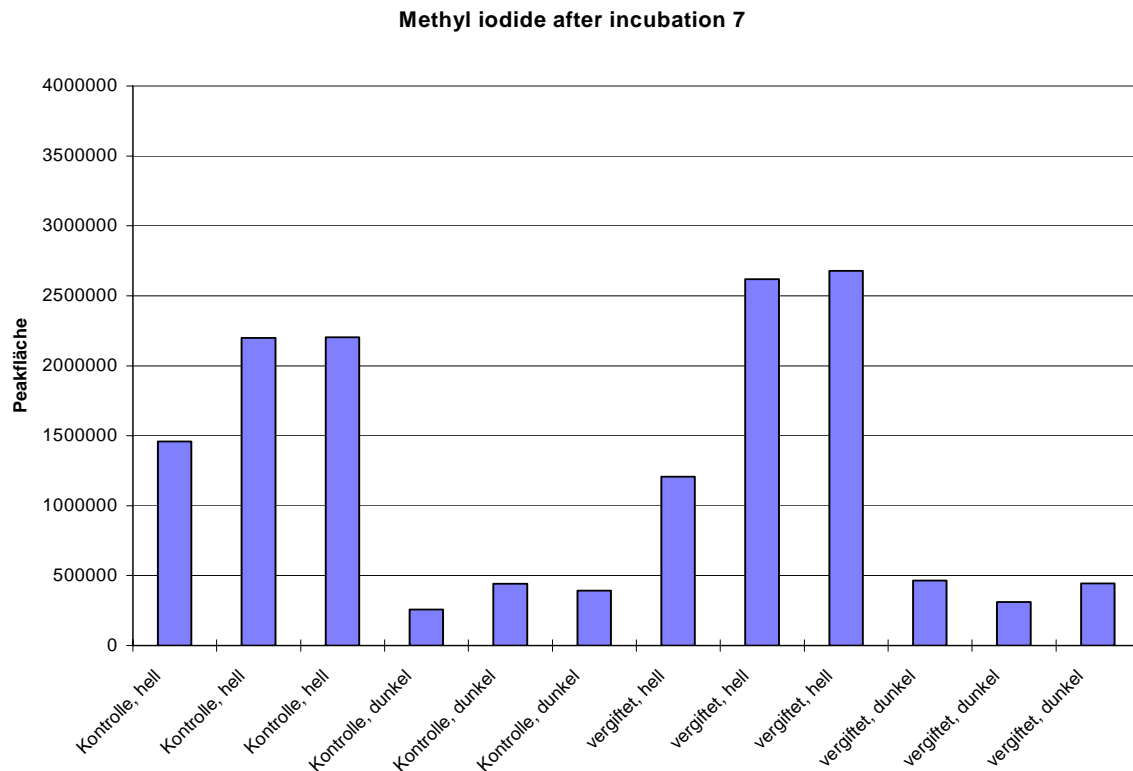
#### 4.7.3 Preliminary results

**Bromoform:** Bromoform was found throughout the water column. Background concentrations were in the range of 2 to 4 pmol/L in surface and deep water. Concentrations increase to 10 to 30 pmol/L with depth and the maximum seems to be correlated at the chlorophyll maximum at 40 to 70 m depth. A typical depth profile of bromoform is shown in Fig. 16. Surface waters reached a maximum of 8 to 14 pmol/L at the equator whereas background concentrations were around 4 pmol /L. Air concentrations seemed to be generally below 1 ppt, which makes the tropical oceanic surface waters a source of bromoform for the atmosphere.

Extremely high concentrations of up to 8 nmol/ L of bromoform as well as high levels of other haloforms (dibromochloromethane, dichlorobromo-methane and chloroform) were detected in the Amazon plume at the interface of the river plume with the oceanic waters at about 40 m depth. The ratio of dibromochloromethane and dichlorobromomethane to bromoform increased in deep waters. This may be due to halogen – exchange reactions of chloride with bromoform.

**Methyl iodide:** During the cruise two main questions relating to  $\text{CH}_3\text{I}$  were studied: First, methyl iodide concentrations in surface water and in the atmosphere were measured to calculate the flux between ocean and atmosphere. All showed very high supersaturations of the seawater with respect to the atmosphere. This may be partly due to the low wind speeds encountered during most of the cruise. Secondly, incubations with surface seawater and water from 200 m, well underneath the euphotic zone, were performed under different conditions to evaluate the contribution of different pathways to the methyl iodide production. The incubations were conducted in 100 mL quartz glass bottles kept on deck in a bath of flowing seawater for 24 hours. In total 7 experiments were conducted with sets of 12 bottles each. In all experiments the incubations kept in the light showed increased production compared to dark incubations, even after sterile filtration with 0.1  $\mu\text{m}$  filters or poisoning with mercury chloride. On the other hand all incubations kept in the dark showed very low production. The results implied a photochemical pathway without direct contribution by photosynthesis.

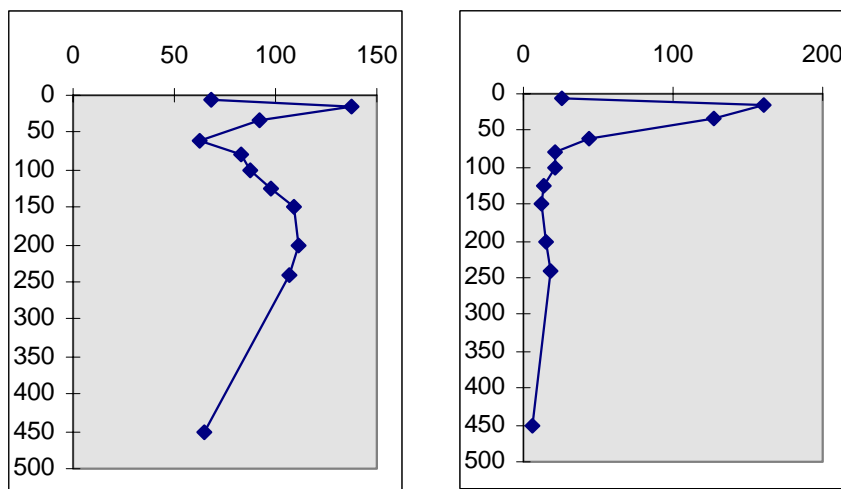
**Figure 16:** Bromoform profile at station 42 with surface maximum.



**Figure 17:** Methyl iodide content after incubation (plain sea water [Kontrolle] vs. poisoned sea water (vergiftet), dunkel = kept in the dark, hell = kept in ambient light).

Alkyl Nitrates: A thorough work-up of the data, including the calibration of the data, will be carried out back at the home laboratory. Preliminary results of the raw data are presented here in peak areas.

Depth profiles: An example of a depth profile (station 40) of methyl nitrate is shown in Figure 18a. The general trend was of a maximum in the surface waters, possibly associated with the chlorophyll maximum, decreasing with depth down to 100m, followed by elevated concentrations in waters between 150 and 300 metres. For methyl iodide, all stations exhibited a



**Figure 18:** Vertical profiles from Station 40 of (a) methyl nitrate; (b) methyl iodide. Both profiles are shown as relative concentrations based on chromatographic peak area.

surface or shallow sub-surface maximum between 15 to 20 metres, with decreasing concentrations with depth. Figure 18 shows the methyl iodide profile from station 40.

Surface underway measurements: 65 underway samples were measured. The most notable feature was the elevated concentrations of methyl nitrate between 1N and the equator.

Calculations of the percent saturation in seawater will be performed using the measured air concentrations to investigate whether the tropical ocean is a source of this compound.

## References.

E. Atlas, W. Pollock, J. Greenberg, L. Heidt, Journal of Geophysical Research 98, 16933-16947 (1993).

A. Chuck, S. Turner, P. Liss. Science 297. 1151-1154 (2002).

## 4.8 Production and Microbial Turnover of DMS and DMSP

W. Gaul, M. Mueller (IfMK)

Dimethylsulfoniopropionate (DMSP) is generated in large amounts by phytoplankton and is a precursor of dimethyl sulfide (DMS), it is the major biogenic source of volatile reactive sulphur emitted from the ocean.

Measurements were made using a purge and trap gas chromatography system with flame photometric detection. A total of 8 *in situ* simulated incubation experiments were conducted along the west-east transect to estimate the production and turnover of dissolved and cellular DMSP and its response to enrichments of the main dissolved organic and inorganic nutrients. *In situ* simulated experiments were conducted on deck in large volume incubation containers attached to a special rolling device that was submerged in a tank with flowing surface water. Furthermore we conducted 4 incubation-experiments with < 2µm fractionated plankton to determine the variability of the bacterial degradation of dissolved DMSP due to selective nutrient enrichments. We found high responses of the DMSP degradation to enrichment with dissolved organic nutrients but relatively low responses to enrichment with dissolved inorganic nutrients in the equatorial upwelling as well as in the oligotrophic waters.

The vertical distribution of the DMS and the cell-particulate DMSP concentration was determined down to a depth of 150m at 26 hydrographical stations along the east-west transect. A total of 156 replicate DMS and cell-particulate DMSP measurements were carried out.

Experimental collaboration had been planned with the ORSUM group from the MPI-CH Mainz to determine the biological or physical production and consumption of VOC's. Therefore a special large-volume incubation device with a closed sampling system and a large-volume purge and trap equipment was developed to enable measurements of trace VOC's in seawater samples with the PTNMR system. However the modified system was extensively used for high frequency underway measurements of surface water concentrations, therefore the experimental collaboration turned out to be extremely difficult and was confined to a total of 8 measurements in two highly simplified incubation experiments.

We wish to say special thanks to Ch. Electron. Ronald Heygen, Helmut Schlinsog and Fitter Volker Blohm for rapidly and professionally improvising a propulsion system for defective incubation apparatus.

## **4.9 Nutrient addition bioassays**

C. Ridame, M. Mills, R. Langlois (IfMK), M. Davey (University of Essex, UK)

### **4.9.1 Introduction**

Low nutrient concentrations in the surface waters of the Tropical Atlantic are thought to be limit phytoplankton biomass and productivity found in the region.. The nutrient abundance and availability affects phytoplankton productivity in two fundamental ways i.e. the abundance and the growth rate. The fluxes of inorganic nutrients into, and organic nutrients out of, the euphotic zone may be responsible for limiting phytoplankton abundance, whereas the concentration of inorganic nutrients could constrain the growth rate (Dugdale & Wilkerson 1992). Resolving the different types of limitation described here has important implications for the understanding of oceanic productivity (Graziano et al 1996).

The Tropical Atlantic is strongly influenced by the atmospheric inputs of Saharan dust with an increasing concentration gradient along the cruise track. The Saharan dust inputs govern the cycle of oceanic iron as these particles represent the main source of dissolved iron for the open Ocean and can also represent a significant source of dissolved phosphate to the water column. Consequently, the study of the impact of a Saharan dust input on the biological production is particularly relevant for this oligotrophic area. The availability of iron, essential for the synthesis of the nitrogenase enzyme (playing a main role in nitrogen fixation), and/or phosphorus, suspected to limit the N<sub>2</sub> fixation, suggests that Saharan inputs might significantly stimulate fixation of atmospheric dinitrogen that in return may enhance new production in the surface layer.

Nutrient bioassay experiments were conducted during M55 to investigate the N, P and/or Fe limitation of carbon and nitrogen fixation rates. Examination of phytoplankton nutrient limitation using bioassay techniques is not simple and the interpretation of results is subject to some controversy. For example the absence of accumulation of biomass following enrichment is not necessarily a result of growth rate limitation, but may be due to more complex interactions of grazing and nutrient recycling (Cullen et al 1992). The measurements of bulk parameters such as [chl *a*] and cell numbers reveals little about the physiological status and responses of the population. Responses of different groups and taxa within an assemblage are also difficult to determine from these basic measurements.

### **4.9.2 Experimental programme**

Bioassay experiments were carried out in 1.0 L polycarbonate bottles, cleaned and filled under trace metal clean conditions where possible. Water was collected after dark from 1-3m depth using a trace metal clean diaphragm pump (FISH) in order to avoid iron contamination. Water was then siphoned into bottles to reduce cell damage due to turbulence. Bottles were filled and nutrients (N,P, and Fe) added within 4h of sampling. Additionally, a Saharan soil, considered a

proxy for Saharan aerosols, was exposed to the oligotrophic surface seawater in two particulate concentrations: 0.5 and 2 mg/L (Dust 1 and Dust 2). Each treatment was made in triplicate and the bottles were separated into three parameter sets for each experiment as follows:

- Biological and chemical parameters: [chl *a*], AFC, FRRF, Total dissolved iron, [PO<sub>4</sub>] by the MAGIC procedure, nutrients, DNA.
- <sup>15</sup>N<sub>2</sub> fixation <sup>13</sup>CO<sub>2</sub> measurements, POC and PON
- <sup>14</sup>CO<sub>2</sub> fixation and fractionation

The number of experiments and range of treatments is summarized in Table 1. Each set of bottles was incubated in on-deck acrylic incubators cooled by a continuous flow of surface seawater supplied from the ship's pumps. Light entering the incubators was filtered with blue acrylic filters ("Lagoon Blue") which removed red and far-red wavelengths. The acrylic material of the incubators effectively removed UV.

**Table 4:** Bioassay experiments and treatments for nitrogen and carbon fixation using the stable isotopes <sup>15</sup>N and <sup>13</sup>C.

| Bioassay 1 | Bioassay 2       | Bioassay 3       | Bioassay 4       | Bioassay 5       | Bioassay 6       | Bioassay 7       |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Initial    | Initial          | Initial          | Initial          | Initial          | Initial          | Initial          |
| Control    | Control          | Control          | Control          | Control          | Control          | Control          |
| P          | N                | N                | N                | N                | N                | N                |
| Fe         | P                | P                | P                | P                | P                | P                |
| Dust 2*    | Fe               | Fe               | Fe               | Fe               | Fe               | Fe               |
|            | NPF <sub>e</sub> | NP               | NP               | NP               | NP               | NP               |
|            | Dust 2*          | Nf <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  |
|            |                  | Pf <sub>e</sub>  | PF <sub>e</sub>  | PF <sub>e</sub>  | PF <sub>e</sub>  | PF <sub>e</sub>  |
|            |                  | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> |
|            |                  | CDust 1*         | CDust 1*         | CDust 1*         | CDust 2*         | CDust 2*         |
|            |                  | CDust 2 *        | CDust 2*         | CDust 2*         |                  |                  |
|            |                  |                  | ADust 3**        |                  |                  |                  |
|            |                  |                  | ADust +N 4**     |                  |                  |                  |

\* Dust samples provided by Dr. C. Ridame, IFM Univ. of Kiel, Germany, Dust 1 = 0.5 mg L<sup>-1</sup>, Dust 2 = 2 mg L<sup>-1</sup>

\*\* Dust samples provided by Dr. A. Baker, UEA, United Kingdom, Dust 3 = 0.5 mg L<sup>-1</sup>, Dust 4 = 0.5 mg L<sup>-1</sup> + 1 μM of NO<sub>3</sub><sup>-</sup>

Measurements of [chl *a*], cells, FRRF, iron, MAGIC phosphate and nutrients were made on the seawater collected at the start of the 48h incubation. <sup>14</sup>CO<sub>2</sub> and <sup>15</sup>N<sub>2</sub> fixation rates, [chl *a*],



cells and FRRF were measured on sets of untreated bottles over the first 24h to determine "initial" production rates and examine any possible "bottle effects" of the incubation. The nutrient treatment bottles for  $^{15}\text{N}_2$  /  $^{13}\text{CO}_2$  and  $^{14}\text{CO}_2$  fixation were "spiked" with isotope, pre-dawn, after the first 24h of incubation and then terminated 24h later by filtration. Investigation of the impact of grazing and nutrient limitation upon grazing was carried out by dilution experiment. A 1:10 dilution of seawater with filtered seawater was prepared, biological parameters and  $^{14}\text{CO}_2$  fixation rates were measured.

In several experiments, extra parameters were sampled: bacterial production in the dust treatments, phosphatase enzyme activity (considered an indicator of the degree of the phosphorus limitation), and the production of methanol. There were 7 experiments in total. The sample breakdown was:

**Table 5:** Sampling procedure for bioassay experiments.

| Analysis (parameter)                                    | Number of Samples<br>(approx) | Analysis complete |
|---|-------------------------------|-------------------|
| $^{15}\text{N}_2$ and $^{13}\text{CO}_2$ fixation rates | 250                           | 0                 |
| $^{14}\text{CO}_2$ fixation rates                       | 255                           | 255               |
| $^{14}\text{C}$ fractionation                           | 255                           | 255               |
| [Chl a]   | 255                           | 255               |
| AFC   | 500                           | 0                 |
| FRRF  | 255                           | 255               |
| [Fe]  | 150                           | 0                 |
| [PO <sub>4</sub> ], Magic procedure                     | 150                           | 0                 |
| Nutrients   | 200                           | 200               |
| DNA   | 28                            | 0                 |
| POC / PON   | 250                           | 0                 |
| TDN   | 200                           | 42                |
| Bacterial production                                    | 30                            | 30                |
| Phosphatase   | 41                            | 41                |
| X-ray micro analysis                                    | 20                            | 0                 |
| [Acetone] & [Methanol]                                  | 36                            | 0                 |

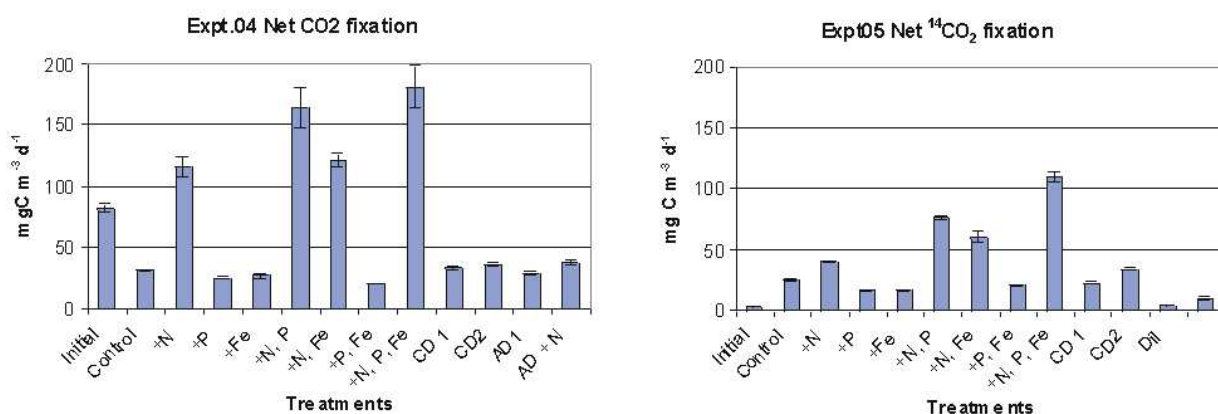
Problems with signal-to-noise ratios in the FRRF measurements made it necessary to use a modified approach to sampling. Samples which would ordinarily be measured in 13ml cuvettes had to be filtered onto GF/F filters and the filters held at 45° angle to both the excitation and detection windows of the light chamber of the FasTracka™ instrument. Samples were dark adapted for 2-4h then analysed within 5 min of filtering. Due to this modification of the technique the analysis of the data collected could not be done during the cruise as planned.

Additional calibration of the instrument has been done during the cruise with further planned on return to the lab.

The first measurements of TDN (total dissolved nitrogen) have shown contamination coming most probably from the potassium persulfate used for the oxidation step. By consequence, the samples were frozen after filtration, and will be analyzed in Kiel.

#### 4.9.3 Preliminary findings

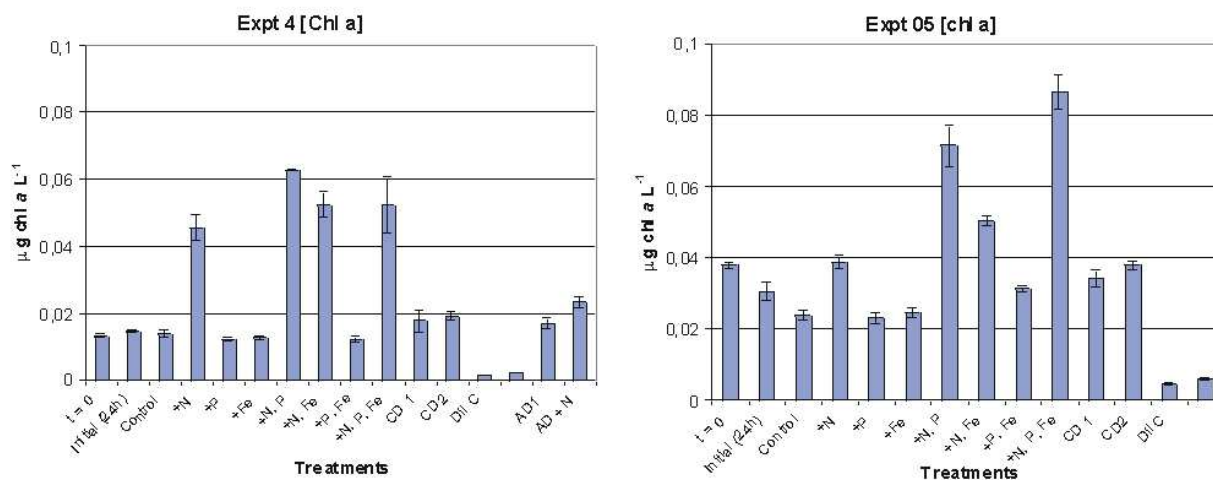
The measurements of [chl a] and  $^{14}\text{CO}_2$  fixation rates indicated a consistent pattern of phytoplankton responses throughout the cruise track. In all but the first experiment the greatest



**Figure 19:** Primary production measured in each treatment during the last 24 h of a 48 h incubation (first 24 h for initial treatment) for experiments 4 and 5. CD 1, CD 2, AD1, and AD + N correspond to additions of different amounts and types of dust.

response of the phytoplankton populations has been to the addition of inorganic nitrogen. The data from experiments 4 and 5 are presented Figure 19 and 20.

Whilst similar, there were some interesting details revealed by these experiments. The



**Figure 20:** Chl a concentration, expressed in µg/L, measured in each treatment, after an incubation time of 48 h (24 h for initial treatment) for experiments 4 and 5.

insignificant differences between the responses to N & P and N, P & Fe additions in Expt. 04 indicated relatively high background iron concentrations in the seawater, yet to be confirmed by [Fe] analysis. The significant differences in the responses between these treatments in Expt. 05 suggests that background iron in the area this water was collected was substantially lower. An additional feature of Expt. 04 was the comparison of production stimulated by approx.  $1\mu\text{M}$   $\text{NH}_4\text{NO}_3$  addition, compared to  $1\mu\text{M}$   $\text{NO}_3$  addition which was made to dust treatment AD (Saharan aerosols provided by A Baker UEA). Whilst the addition of inorganic N to the dust treatment appeared to stimulate  $^{14}\text{CO}_2$  fixation in this treatment compared to the dust alone, it was clear that the presence of ammonium in the inorganic N supplied stimulated greater fixation. The data from the AFC samples for this experiment may reveal interesting differential responses to the two inorganic N sources from the sub-populations of phytoplankton present.

The preliminary results of the dilution or grazing experiments indicate stimulation of  $^{14}\text{CO}_2$  uptake by the added nutrients. This suggests that both growth rates and biomass yield are constrained by nutrient availability.

The biological response in the dust treatments, in terms of chl a concentration and primary production, seems higher in the western Tropical Atlantic waters (Exp. 1) compared to that in the eastern waters. For experiment 4 there was an increase in the chl a concentration of about 30-40% in the dust treatments (CD1 and CD2) and a lower increase of the primary production is recorded, about 15%. A very similar biological response is observed between the two types of mineral dust. Saharan aerosols supplied by A. Baker (treatment AD) and Saharan soil representative of the Saharan aerosols supplied by C. Ridame (treatment CD). In experiment 5, the phytoplankton response is more significant with an increase of 40 to 60 % of the algal biomass (treatments CD1 and CD2) and a primary production increased approximately 40 % (treatment CD2). These preliminary results seem to suggest a stimulation of the phytoplankton activity after an addition of Saharan dust for the oligotrophic tropical Atlantic waters.

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## 4.10 Nitrogen Fixation

Matthew Mills (IfMK) and Maren Voß (IOW)

### 4.10.1 Introduction

Marine nitrogen fixation and the import of deep water nitrate are the two most important sources of new nitrogen for large parts of the otherwise nitrogen-limited tropical oceans. The evaluation of both processes is very different. While the input from below the thermocline can be estimated from temperature, density, and nutrient profiles, the estimate of nitrogen fixation is more time

consuming and, therefore, far fewer data are available. New measurements suggest higher fixation rates than described roughly two decades ago (Carpenter and Romans 1991, Capone et al. 1998) and a strong dependence on trace metal inputs from the continents has been hypothesised (Falkowski 1997). Other limiting factors like low phosphorous concentrations have also been proposed however (Samudo-Wilhelmy et al. 2001). Dinitrogen might also be fixed by picocyanobacteria in the deeper part of the euphotic zone, as suggested by data on the genetic variability of the *nifH* genes plus fixation rate measurements (Zehr et al. 2001). The *nifH* gene encodes the enzyme that reduces dinitrogen in the cells as is found in the tropical and subtropical oceans (Zehr et al. 1998). These small cells might have been missed in some earlier rate measurements that focussed on colonies of *Trichodesmium*.

These findings and hypotheses call for new experimental and field investigations to quantify nitrogen fixation in the tropical ocean. A combination of experiments with natural phytoplankton assemblages and bioassays as well as natural nitrogen isotope abundance measurements in particulate and dissolved compounds was therefore applied during the cruise.

Stable nitrogen isotopes occur in two forms: one of which is abundant  $^{14}\text{N}$  (99,96%) while  $^{15}\text{N}$  only exists in trace amounts of 0,4%. The isotope ratio of  $^{14}\text{N}/^{15}\text{N}$ , measured as  $\delta^{15}\text{N}$ , varies in natural systems and among compounds in predictable ways. Nitrate from the deep oceans has a  $\delta^{15}\text{N}$  value between 4,5 to 6 ‰ (Liu and Kaplan 1989, Sigman et al. 1997) nitrogen in air or in water has 0‰, while nitrate from surface waters or from anoxic waters can have much higher values due to the uptake by phytoplankton or denitrification by bacteria. Nitrogen fixation, however, does not change the isotope signature of the dinitrogen that the cyanobacteria use and the algae are reported to show values between -1 und 0‰ (Carpenter et al. 1997). The low  $\delta^{15}\text{N}$  values are mirrored in the nitrate generated through bacterial breakdown of the biomass and are thus significantly lower than deep water nitrate. Below the mixed layer down to roughly 500m depth lower  $\delta^{15}\text{N}$  values in nitrate can be expected if nitrogen fixers are abundant and have largely contributed to the nitrate pool (Montoya, unpubl. data). The low  $\delta^{15}\text{N}$  values from N-fixation can potentially be picked up by organisms higher in the food chain and than indicate the role that the new nitrogen plays for feeding higher trophic levels.

#### 4.10.2 Measurement and Experimental Program

$^{15}\text{N}$  natural abundance and non-amended  $\text{N}_2$  fixation incubations: Along the transect between 56°W and 20°W altogether 28 station were sampled for  $\delta^{15}\text{N} - \text{NO}_3$ , and  $\delta^{15}\text{N} - \text{PON}$  through the upper 400m with a spatial resolution of up to 10 depth. Five deep casts were sampled together with H. Bange for the same variables. Filters were dried immediately after sampling and nitrate samples were preserved with HCl. Nitrate was only collected where concentrations were above 5  $\mu\text{Mol}$ .

At 20 stations net tows with the zooplankton net were performed and fractionated into 3 size classes (>1000 $\mu\text{m}$ , 500-1000 $\mu\text{m}$ , 200-500 $\mu\text{m}$ ). Samples were immediately frozen.

Nitrogen fixation was measured under simulated in situ conditions at 9 stations. Therefore, septum bottles were filled from Niskins with unenriched water from the productivity cast in the morning and incubated in parallel to the primary production. For better comparison with the  $^{14}\text{C}$  method  $\delta^{13}\text{C}$  bicarbonate was added in the nitrogen fixation bottles as an additional marker for carbon uptake. Incubation times were always 6 hours to be sure that no isotope dilution effect

could occur. During longer incubation times tracer might be released from the nitrogen fixers and be taken up by other organisms such as other phytoplankton and microzooplankton.

In six experiments the fraction larger than 20µm was enriched either with a net tow or through sieving the water from several Niskin bottles and adding the concentrate in a large volume from which the incubations were filled. Hopefully the amount of small grazers thus added to the bottles do not interfere with the fixation measurements. Two daily cycle experiments were done with 6 incubations starting every 4 hours over 24 hour. Dark/daylight fixation rates might be deduced from these.

On two occasions, water from the deep chlorophyll maximum was incubated over 12 and 24 hours to check for the activity of picocyanobacteria that are supposed to fix nitrogen at night.

All together, over 250 samples from 19 Experiments were collected. From the CTD casts 280 filters and 192 nitrate samples were collected. 20 net tows were caught through the upper 200m and each was size fractionated in 3 size classes, adding 60 more samples. All stable isotope analyses will be made on stored samples at the IOW in Warnemünde or at the IFM-Kiel. At this time there are no preliminary results regarding the  $^{15}\text{N}$  or  $^{13}\text{C}$  samples.

**N<sub>2</sub>-Fixation in Nutrient Bioassay Experiments:** Nutrient bioassay experiments were conducted to investigate the P and/or Fe limitation of N<sub>2</sub> fixation rates (Table 6). Likewise, inorganic N additions were conducted to assess the inhibitory effect of inorganic nitrogen on N<sub>2</sub> fixation. Initially, a 60 L carboy was filled with trace metal clean surface seawater, and then siphoned into

**Table 6:** Bioassay treatments analyzed for nitrogen and carbon fixation using the stable isotopes  $^{15}\text{N}$  and  $^{13}\text{C}$ .

| Bioassay 1 | Bioassay 2       | Bioassay 3       | Bioassay 4       | Bioassay 5       | Bioassay 6       | Bioassay 7       |
|------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Initial    | Initial          | Initial          | Initial          | Initial          | Initial          | Initial          |
| Control    | Control          | Control          | Control          | Control          | Control          | Control          |
| P          | N                | N                | N                | N                | N                | N                |
| Fe         | P                | P                | P                | P                | P                | P                |
| Dust 2*    | Fe               | Fe               | Fe               | Fe               | Fe               | Fe               |
|            | NPF <sub>e</sub> | NP               | NP               | NP               | NP               | NP               |
|            | Dust 2*          | NF <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  | NF <sub>e</sub>  |
|            |                  | PFe              | PFe              | PFe              | PFe              | PFe              |
|            |                  | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> | NPF <sub>e</sub> |
|            |                  | Dust 1*          | Dust 1*          | Dust 1*          | Dust 2*          | Dust 2*          |
|            |                  | Dust 2*          | Dust 2*          | Dust 2*          |                  |                  |
|            |                  |                  | Dust 3**         |                  |                  |                  |
|            |                  |                  | Dust 4**         |                  |                  |                  |

\* Dust samples provided by Dr. C. Ridame, IFM-Kiel, Germany, Dust 1 = 0.5 mg L<sup>-1</sup>, Dust 2 = 10 mg L<sup>-1</sup>

\*\* Dust samples provided by Dr. A. Baker, UEA, United Kingdom, Dust 3 = 0.5 mg L<sup>-1</sup>, Dust 4 = 0.5 mg L<sup>-1</sup> + NO<sub>3</sub><sup>-</sup>

1 L incubation bottles. The nutrients were then added alone and in combinations, and the bottles were incubated for 48 hours. Parameters measured were, POC/PON, nutrient concentrations, nitrogen and carbon fixation rates at initial and final time points. Fixation rates were assessed in all treatments using the stable isotopes  $^{15}\text{N}$  and  $^{13}\text{C}$  (bicarbonate) during the first (initial) and final 24 h of the incubations. Additionally, the effects of Saharan dust on nitrogen and carbon fixation were investigated. Dust was added to the incubation bottles in two concentrations (0.5 and 2 mg L<sup>-1</sup>) and the above parameters were measured.

In total 7 separate experiments were conducted producing approximately 250 samples for  $^{13}\text{C}$  and  $^{15}\text{N}$  analysis.

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## 4.11 Reactive Organics: Ocean-Air Chemistry

J. Williams, R. Holzinger (MPI Mainz)

### 4.11.1 Introduction

The aim of the Organic Reactive Species Understanding and Measurement (ORSUM) group from the Max Planck Institute for Chemistry was to investigate the role of organics within the tropical atmosphere-ocean interface region. A wide variety of instrumentation was used to make quantitative measurements of organic species in the air and in the ocean. While the importance

of reactive organics in the atmosphere is already established, the oceanic role remains largely unexplored. The extent of coupling between ocean and atmospheric chemical systems will be investigated.

Particular attention was given to the organics in clean background conditions and dust-laden air. The potential effects of dust stimulating biological activity in the ocean surface layer through the addition of iron have been investigated. Water and air samples will be compared to assess whether such iron fertilisations (and other experimental treatments) can lead to enhanced emission of organics in the water and then to the atmosphere. Any organic emissions from the ocean in this region are important, as the proximity of the ITCZ means that such species can be convected rapidly to the upper troposphere, a region of critical importance to the Earth's radiative and oxidative budget.

#### 4.11.2 Sampling and Measurement

1) 100 canisters were filled at the bow in collaboration with Kiel, UEA, NCAR and NOAA. These electropolished stainless steel 2.4 L canisters were pressurised to 2.5 Bar (35 psig). The canisters are being shipped back to Mainz where they will be analysed for ca. 40 volatile organic species including alkanes, HCFCs, CFCs and organohalogens.

2) 100 cartridges were also taken at the bow of the ship. These ¼ inch wide, 10 cm long cartridges are packed with Tenax and Carbosorb. As air is drawn through them at 100 ml per minute and semivolatile organic substances from C6-C14 are retained on the sorbents in the cartridge. The cartridges have been taken 4 times per day for most of the cruise. The cartridges will be shipped back to Mainz for analysis on a two dimensional gas chromatograph. It is not known which species will be measured with this technique in this region, but the instrument is calibrated for several hundred components.

3) Proton transfer reaction mass spectrometer (PTR-MS).

a) One instrument was sited in the Luftchemie Labor. This on-line analysis method measured species such as methanol, acetonitrile, acetone, DMS, isoprene, benzene and toluene. A measurement was taken approximately every 2 minutes.

b) A second instrument located in the Geolabor was used to measure the same components in seawater after purging with helium. In normal mode, surface samples were taken every 2 hours. Four depth profiles (details given in table below) were made as well as circa 250 surface ocean measurements and one rainwater sample. The instrument was also used in on-board experiments in which seawater was treated with various additions (see experimental report).

**Table 7:** Depth Profiles for Volatile Organics

| Profile | Laufnummer                                     | Date     | Comment      |
|---------|--|----------|--------------|
| 1       | 100847, 100856, 100855, 100858, 100866         | 25.10.02 | Morning cast |
| 2       | 101046, 101050, 101055, 101058, 101066, 101069 | 29.10.02 | Morning cast |
| 3       | 101453, 101454, 101455, 101474, 101475         | 02.11.02 | Morning cast |
| 4       | 101861, 101863, 101864, 101865, 101880, 101860 | 06.11.02 | Morning cast |

4) Ozone (with a GPS, relative humidity and light sensor) was measured using a UV photometric detector, (Thermoenvironmental USA). Measurements were made every 30 seconds.

5) CO was measured using a reduction gas analyzer (Traceanalytical, USA). It is essentially a mini GC coupled to a HgO bed followed by a mercury detector. Measurements were made every 3 minutes.

6) 200 (30 ml) seawater samples were taken from the surface and from various incubation experiments. The samples will be analysed by HPLC for various organic species in collaboration with the University of Freiburg. Samples were collected 4 times a day and additional samples were taken from experiments conducted on board.

7) Model Predictions. In addition to experimental data we arranged for model output to be generated for the cruise in collaboration with Mark Lawrence (MPI-Mainz) and Phil Rasch (NCAR). These models give 3D global chemical ( $O_3$ , CO, acetone and methanol) and aerosol distributions. Atlantic dust deposition plots have also been designed and generated for comparison with the oceanographic data.

#### 4.11.3 Preliminary Results

In surface seawater we saw a range of organics. The most abundant was in all cases DMS, although many other reactive species could be measured including acetonitrile, acetone and isoprene. In contrast a single rainwater sample showed little DMS but enhanced acetone and acetaldehyde. The seawater samples showed the same latitudinal gradients as the air samples. Depth profiles, (e.g. Figure 21) indicate that most organic compound concentrations strongly

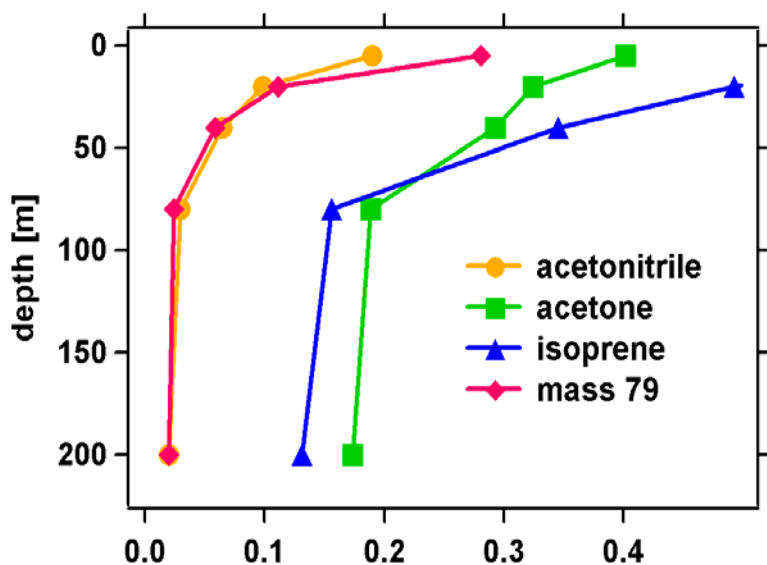


Figure 21: Depth profiles of selected organics.

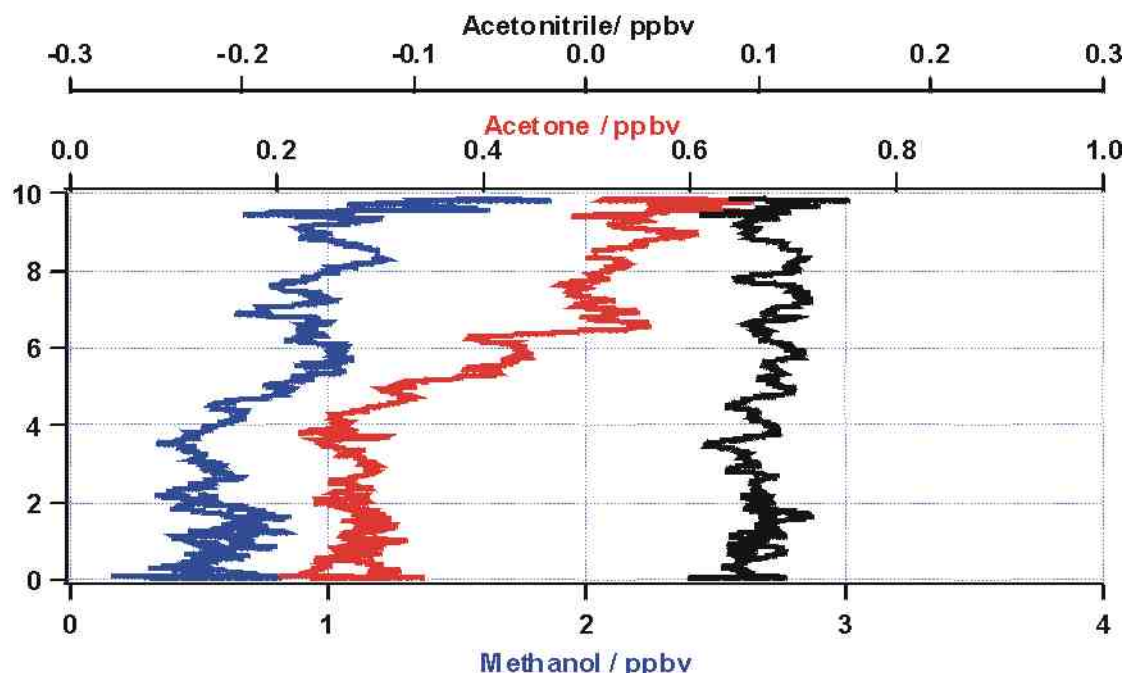
decrease in the upper 50m and do not show indications of being produced at depth. In the atmosphere clear latitudinal gradients were seen when crossing the ITCZ (See Figure 22). Acetone, methanol and acetonitrile decreased while, because of weak upwelling, DMS increased in the region of the equator. Clear longitudinal gradients were seen in  $O_3$  and CO.

In the on-board experiments, strong DMS production was observed on addition of DOC in the form of starch. Dust was encountered

periodically throughout the cruise, increasing in concentration and frequency as we approached Africa. It was discovered that the visibility sensor is an excellent means of separating dust and



rain events. The dust deposition model showed that the whole of the tropical Atlantic has been impacted with dust.



**Figure 22:** Changes in mixing ratios of selected organics when crossing the ITCZ from NH to SH.

On board comparisons of trace gas species with model predictions showed reasonable agreement. The expected high biomass burning signatures in the Southern Hemisphere were not encountered. The model relies on a climatological average biomass burning emission and this year may have been different.

We gratefully acknowledge the assistance from IfM-Kiel in this undertaking. In particular for the co-ordination of D. Wallace, the organisation of H. Bange, advice of W. Gaul and A. Körtzinger, and canister assistance of B. Quack. For the considerable help in preparation of instruments we thank D. Scharffe, F. Helleis and T. Klüpfel. For the friendly, professional assistance of the Meteor crew we are equally grateful.

## 4.12 Halogen Oxide Studies in the Boundary Layer by MAX-DOAS

T. Laepple, G. Hönninger and U. Platt (University of Heidelberg)

### 4.12.1 Introduction

The importance of reactive halogen oxides in the troposphere is due to their strong effect on tropospheric ozone levels, which has first been discovered in the polar boundary layer during surface ozone depletion episodes. The effect of halogen oxides on the tropospheric chemistry in the mid-latitudes is still unclear however. In these latitudes organic bromine precursors such as methyl bromide and bromoform produced by phytoplankton and macroalgae could play a major role. Model simulations for the remote marine boundary layer indicate that, even at BrO

levels below 1 ppt, reactive halogen chemistry can account for 5-40% of total ozone loss, depending on aerosol surface and speciation.

#### **4.12.2 Measurements**

The Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) system measures scattered sunlight in different telescope elevation angles and different sun zenith angles. By analysing the spectra, and comparing the results of the different viewing angles, height profiles of different trace gases can be measured. DOAS is very sensitive for halogen oxides, as well as for a large number of other molecules that exhibit strong and highly structured absorption cross sections in the UV and visible spectral regions.

On Meteor, a USB2000 spectrometer by Ocean Optics was set up on the port-side deck immediately outside the Luftchemie Labor. The wavelength region of the detector was set to 320nm - 450nm to include major parts of the cross sections of IO and BRO. The measurements started the morning of October 14, 2002 and were continuously performed on the cruise during daytime. About 11000 Spectra were taken, each spectra consisting of 1000 Scans of the CCD-Line.

One complete run with four spectra on each of the telescope angles 5° 10° 20° 40° 90° took about twenty minutes, depending on the light intensity. Every night, dark current and offset measurements took place, and each week a wavelength calibration measurement was processed. On October 7, during the unscheduled meeting with FS-Polarstern, inter-comparison measurements with a similar MAX-DOAS system that was installed on the Polarstern took place.

#### **4.12.3 Preliminary Results**

Due to the very low concentrations of IO and BrO which are close to the measurement's detection limit (about 1ppt), the spectra have to be re-analyzed very carefully in Heidelberg. The results will then be compared with the organic halogene compound measurements and the biological data.

### **4.13 Trace Metals**

P. Croot and P. Streu (IfMK)

#### **4.13.1 Introduction**

In many open ocean regions iron has been shown to be a key limiting nutrient for phytoplankton growth. This phenomena is mostly derived from the chemistry of iron in seawater, where the thermodynamically favoured species in oxygenated seawater, Fe(III), is only sparingly soluble and rapidly forms larger particles that can sink from the photic zone. Phytoplankton has thus evolved numerous mechanisms by which they can efficiently utilise the iron that is present in ambient seawater. One of these mechanisms probably involves the production of iron binding complexes, known as siderophores, to increase the overall solubility of the iron. Recent studies

have shown that most dissolved iron species in seawater are bound by these organic ligands and these ligands control the concentration and reactivity of the iron in the seawater.

The Tropical Atlantic is a unique study area with regard to oceanic iron biogeochemistry as it sits directly in the deposition area of the dust plume originating from the Sahara. The episodic pulses of iron rich dust arrive throughout the year and dissolve, mix and sink through the near surface waters potentially creating strong gradients in iron species. The goal of the iron work during the SOLAS cruise, Meteor 55, was to study several of the key processes affecting the biogeochemistry of iron in near surface seawater and in particular to examine the influence of the Saharan dust plume on the Equatorial Atlantic along a longitudinal transect.

#### 4.13.2 Sampling and Measurement

Samples for trace metal analysis were obtained from trace metal clean GO-FLO bottles suspended from the plastic coated Kevlar line on the Meteor. Underway samples for trace metals were obtained by means of a towed fish, deployed from the aft starboard crane, in conjunction with a Teflon diaphragm pump. Samples for  $\text{H}_2\text{O}_2$  were obtained either from the Niskin bottles on the CTD casts or from the GO-FLO bottles.

Onboard analysis was performed for both iron and  $\text{H}_2\text{O}_2$  in a HEPA (Class 100) filtered, positive pressure, clean container located on the working deck. Dissolved ( $0.2\ \mu\text{m}$  filter) and total (unfiltered) iron analysis was performed using flow-injection analysis (FIA) with a chemiluminescence detection system. Samples were acidified to  $\text{pH} < 2$  with quartz distilled HCl for at least 24 hours and then buffered to  $\text{pH} 5.5$  with ultra clean ammonium acetate. A reducing agent, sodium sulfite, was added and the Fe(III) in the sample was reduced to Fe(II). The Fe(II) in the sample was pre-concentrated prior to analysis by means of a small column containing a oxine derivative chemically bound to a resin material (Dierssen et al., 2001). The Fe(II) was then eluted from the column with a HCl carrier stream and detected by measuring the chemiluminescence produced when reacted with luminol at  $\text{pH} 10.1$  (Bowie et al., 1998; Powell et al., 1995).

Iron speciation measurements were performed on selected samples throughout M55 by using a competing ligand exchange - cathodic stripping voltammetry method (Croot and Johansson, 2000) on a Voltammetric system in the clean container. Equilibrium speciation measurements were made as well as several studies into the kinetics of iron uptake by the natural ligands present in the seawater. Measurements of  $\text{H}_2\text{O}_2$  were made using a FIA chemiluminescence method with reagent injection also utilising luminol (Yuan and Shiller, 1999). Samples were kept in the dark until analysis, typically within 1-2 hours of collection, to avoid  $\text{H}_2\text{O}_2$  production from laboratory lighting. A limited set of experiments on the production rate and decay rate of  $\text{H}_2\text{O}_2$  in natural seawater were also performed during M55. Samples for later analysis back in Kiel were also collected from the trace metal hydrocasts. These samples will be analysed in the home laboratory for other indicators of Saharan dust input, notably Al, Mn and Ti. Samples will also be analysed for Cu, Cd, Zn and Co where possible.

During the course of M55, we occupied 14 stations where trace metal casts were made; they are collated in Table 8. Over 1200 analyses for iron were made during the course of this work and over 250 samples bottles were collected for later analysis in the laboratory in Kiel.

Samples were analysed for dissolved iron ( $0.2\ \mu\text{m}$  filter) and total iron at all stations. While at

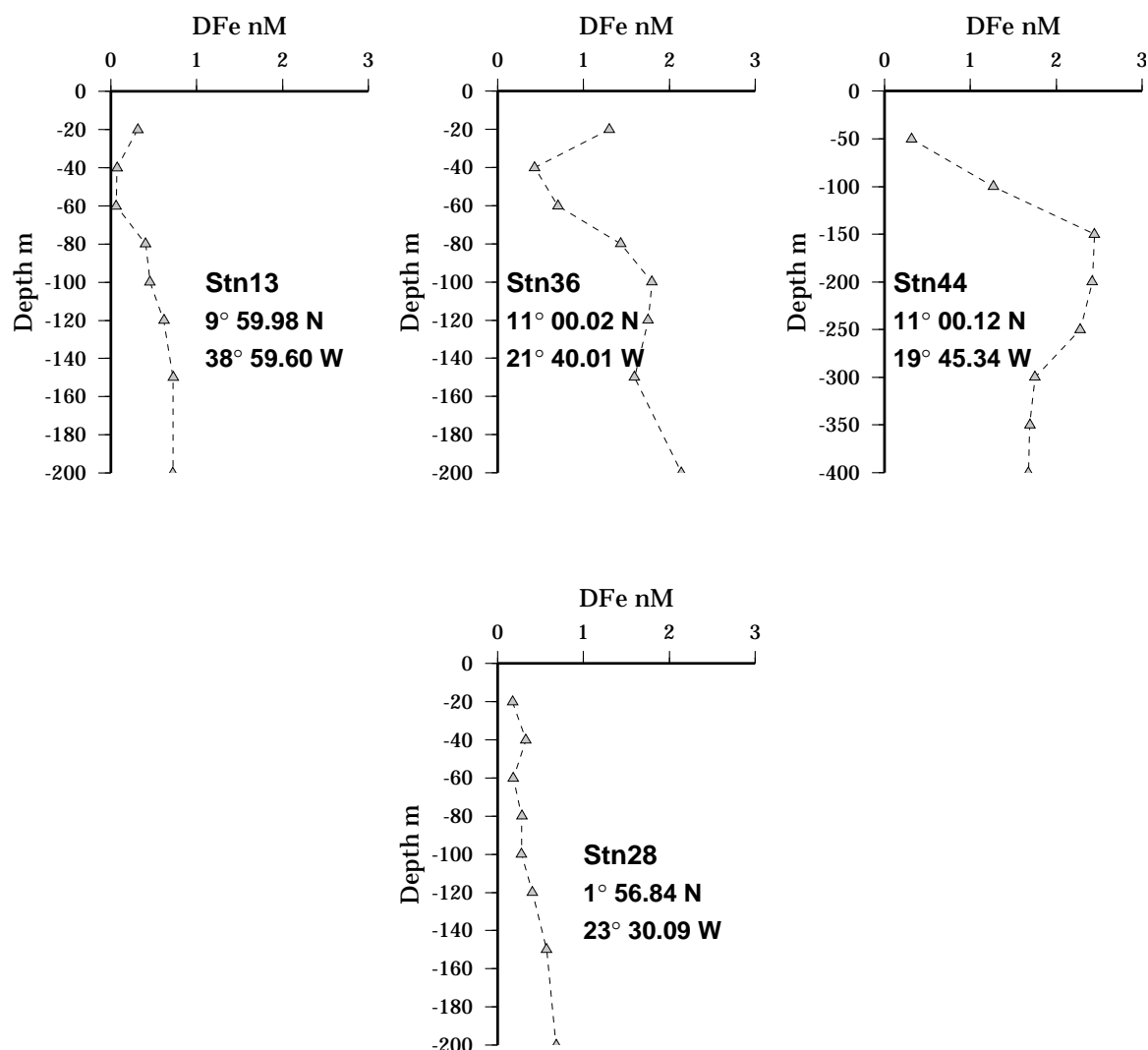
several stations, samples were also analysed for truly dissolved iron (that which passes through a 0.02  $\mu\text{m}$  filter) and iron solubility (iron added to sample and then filtered through 0.02  $\mu\text{m}$  filter). Ligand titrations were performed on 20 samples along the cruise track and a further 7 samples were examined for iron complex formation and dissociation kinetics. Underway surface samples for dissolved iron and Fe(II) were also collected and analysed onboard from a transect across the continental shelf in the waters of Guinea-Bissau.

**Table 8:** Station Locations – Samples for Trace Metals. Note: All stations to 200m depth unless noted. Standard bottle depths used were as follows: 20, 40, 60, 80, 100, 120, 150 and 200 m. All samples taken using Teflon coated GO-FLO sampling bottles deployed on the plastic coated Kevlar line onboard the Meteor.

| Station # | Latitude     | Longitude    | Notes:                            |
|-----------|--------------|--------------|-----------------------------------|
| 3         | 10° 33.09' N | 53° 43.85' W | 17.10.2002                        |
| 5         | 10° 00.01' N | 51° 24.68' W | 18.10.2002                        |
| 7         | 9° 59.98' N  | 48° 03.37' W | 19.10.2002                        |
| 11        | 9° 59.99' N  | 41° 43.76' W | 21.10.2002                        |
| 13        | 9° 59.98' N  | 38° 59.60' W | 22.10.2002                        |
| 15        | 10° 00.02' N | 36° 13.66' W | 23.10.2002                        |
| 19        | 9° 59.97' N  | 30° 17.01' W | 25.10.2002                        |
| 21        | 10° 00.09' N | 27° 33.36' W | 26.10.2002                        |
| 24        | 00° 00.01' S | 26° 00.00' W | 29.10.2002                        |
| 28        | 01° 56.84' N | 23° 30.09' W | 31.10.2002                        |
| 30        | 05° 17.38' N | 24° 01.59' W | 1.11.2002                         |
| 36        | 11° 00.02' N | 21° 40.01' W | 4.11.2002                         |
| 42        | 11° 02.13' N | 17° 41.94' W | 6.11.2002                         |
| 44        | 11° 00.12' N | 19° 45.34' W | 7.11.2002 – Station to 400m depth |

#### 4.13.3 Preliminary Findings

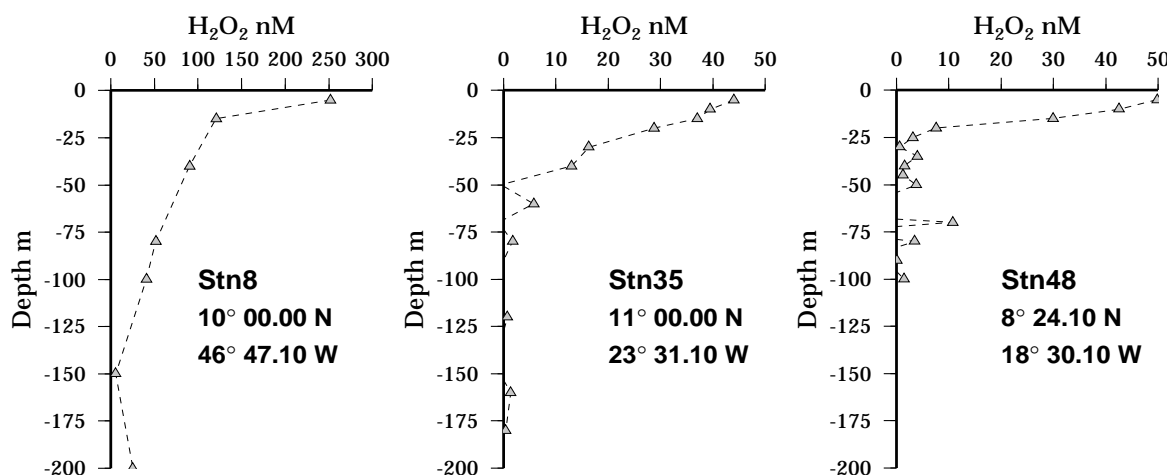
Iron concentrations in the surface waters were found to increase dramatically with distance from the West African coast and the source regions of the Saharan dust. Typical dissolved iron concentrations found during this cruise are shown in Figure 23. The Amazon plume waters also had elevated iron levels, while the surface waters of the Equatorial Upwelling were strongly depleted relative to the region to the north. At most stations there was often a slight enrichment for dissolved iron in the upper 20-40 m, a minimum in the vicinity of the chlorophyll maximum and then a gradual increase with depth. Measurements of total iron showed similar profiles to those for dissolved iron, but concentrations were significantly higher ranging from 1 nM in the west to a dramatic 12 nM at one station in the east.



**Figure 23:** Selected vertical profiles of dissolved (0.2 mm) iron concentrations determined onboard using FIA-chemiluminescence during M55.

H<sub>2</sub>O<sub>2</sub> vertical profiles were measured at 22 stations during M55, sampling normally occurred at the station occupied in the late afternoon when H<sub>2</sub>O<sub>2</sub> concentrations were at their highest values. Highest values were found in the DOC rich Amazon plume waters and all stations showed the characteristic exponential decay from the surface (Figure 24).

Several rain samples were also analysed for H<sub>2</sub>O<sub>2</sub> and all showed the high values expected in tropical rain ([H<sub>2</sub>O<sub>2</sub>] > 1 µM). Comparison of the surface H<sub>2</sub>O<sub>2</sub> values with measurements of TOC, the preceding PAR flux and rainfall obtained during this cruise will allow more insight into the potential sources of H<sub>2</sub>O<sub>2</sub> in this region. The H<sub>2</sub>O<sub>2</sub> profiles will be used to estimate the mixing rate of the surface waters, when combined with the light profiles also obtained during this cruise. The data gathered here can also be used with O<sub>2</sub> data to estimate the half-life of Fe(II) in these waters and this information can provide clues to the kinetics of other processes affecting iron speciation.



**Figure 24:** Preliminary  $\text{H}_2\text{O}_2$  data obtained during M55. Note the five-fold higher concentrations in the water from the Amazon Plume (Stn 8).

We appreciate the help of Chief Scientist D. Wallace and for providing the opportunity for us to participate in this cruise. Many thanks to H. Bange who was instrumental in providing the necessary logistic support in making this cruise a reality. Thanks also to U. Schüßler and W. Balzer at the University of Bremen for the loan of their clean container. Finally an extra special thanks to the officers and crew of Meteor, whose dedication and skill helped this work be completed.

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## 4.14 Aerosol and Rain Collection

A. Baker (University of East Anglia, Norwich, UK)

### 4.14.1 Introduction

Marine aerosols provide an important pathway for exchange of material between the oceans and land. In the case of the marine trace nutrient iron, the major process is the transportation of terrestrial dust to the remote, iron-poor, ocean (Jickels and Spokes 2001). For iodine, which is emitted from iodine-rich seawater in volatile organic compounds, aerosol provides a route for the removal of an element with ozone-destroying potential (Solomon et al. 1994) from the atmosphere, and facilitates its transportation from the oceans to land.

The Sahara / Sahel desert accounts for approximately one third of the global dust deposition flux to the oceans, and is easily the dominant source of dust to the tropical North Atlantic Ocean. Much of this dust is deposited directly to the oligotrophic gyre where it is believed to have a significant impact on the nutrient balance of the region. Iron associated with the dust is thought to stimulate nitrogen-fixing organisms (nitrogen fixers have a high iron requirement (Bergman-Frank et al. 2001) and the solubility of iron in seawater is extremely low (Liu and Millero 2002)). Dust inputs may therefore help to alleviate nitrogen limitation of phytoplankton growth. A crucial factor in determining the iron supply to the plankton is the solubility of the dust-borne iron. This is a key area of uncertainty in our understanding of iron biogeochemistry, although solubility is believed to be very low (of the order of 1% (Jickels and Spokes 2001)) and probably increases due to the effects of cloudwater processing of the dust particles while they are in the atmosphere (Jickels and Spokes 2001). Recent results from our laboratory suggest that the air masses that transport Saharan dust also carry nitrate and other macronutrients, which co-deposit with the dust (Capone 2001). The potential effects of this co-deposition of nutrients on the nitrogen-fixing plankton population are unclear, although it is recognised that nitrogen fixation does not occur if a source of fixed nitrogen is present in the water column (Vogt 1999).

The chemical speciation of iodine in aerosol appears to be a crucial factor in controlling its removal from the atmosphere. Iodate ( $\text{IO}_3^-$ ) is believed to be refractory in aerosol and this species is therefore removed from atmospheric processing reactions once formed. Iodide ( $\text{I}^-$ ) can be returned to the gas phase (and to ozone-destroying cycles) via reactions with hypohalous acids<sup>7</sup>. In addition to these two species, we have recently found evidence for the presence of soluble organic iodine and insoluble iodine in aerosol (Baker et al. 2000). Current knowledge of the speciation of iodine in aerosol and rain is extremely limited (e.g. almost all reported data is for iodide / iodate speciation in the UK, see (Baker et al. 2001), but it appears that the proportion of iodate present increases as aerosol age (Baker et al. 2001). This data coverage is clearly insufficient to constrain the removal terms of models of the complex and important atmospheric chemistry of iodine. The goals of the aerosol and rain collection program are to examine:

- Expected gradients in iron solubility due to variations in cloud processing time of dust particles.
- Atmospheric deposition of nutrients (i.e. Fe, N, P & Si) to surface seawater.
- Expected gradients in iodine speciation (including the first systematic study of soluble organic iodine concentrations in aerosol) due to variations in atmospheric processing time.

In addition, samples of Saharan dust that had previously been subjected to simulated cloud processing in the laboratory were brought on board for use in experiments.

#### 4.14.2 Measurement and Experimental Program

Two aerosol collectors equipped with cascade impactor sampling heads were employed throughout the cruise. One of the collectors (with acid-washed filters) was used to sample for analysis of Fe and other trace metals. Samples from the other collector will be analysed for their major ion ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) and organic nitrogen content, as well as iodine speciation ( $\text{I}^-$ ,  $\text{IO}_3^-$ , organic iodine). The filters in these collectors were changed once each day, and the samplers operated continuously, except for brief periods when it was occasionally necessary to stop collection because of the risk of contamination from the ship's stack smoke. Up to three rain collection funnels were deployed manually during rain events. As with aerosol collection, separate funnels were used for trace metal and major ion sampling. Occasionally a third (trace metal clean) funnel was also deployed, in order to collect large volume samples for analysis of Fe complexation in rainwater. Sample collection for aerosol and rain started on the morning of 13<sup>th</sup> September and continued until the morning of 14<sup>th</sup> November. A total of 32 pairs of aerosol samples ( $\sim 78000 \text{ m}^3$  of air filtered, Table 10) and 17 rain samples ( $\sim 13 \text{ L}$  of rain, Table 11) were collected during this time. Whenever possible rain samples have been provided to other interested groups during the cruise. These were:

**Table 9:** Rain samples and their use.

| <u>Sample</u>          | <u>Analysis</u>               | <u>Participant</u>                      |
|------------------------|-------------------------------|---|
| 5, 6, 11, 15 – 17      | Fe                            | P. Croot, IfM                           |
| 3, 6, 7, 9, 11, 13, 14 | $\text{H}_2\text{O}_2$        | P. Streu, IfM                           |
| 14 – 17                | methyl nitrate                | A. Chuck, UEA                           |
| 14                     | volatile organics             | R. Holzinger and J. Williams, MPI Mainz |
| 15, 16                 | nitrate $\delta^{15}\text{N}$ | M. Voss, IOW                            |

Laboratory-processed Saharan dust samples were provided for use in the following experiments:

- bioassay experiments to assess nutrient limitation and nitrogen fixation (carried out by M. Davy, M. Mills and C. Ridame).
- kinetics of Fe release from Saharan dust in near-surface equatorial seawater (carried out by P. Croot)
- mega-incubation experiment to examine marine trace gas sources (M.Voss, W.Gaul, et al.)

#### 4.14.3 Preliminary findings

Although no chemical analysis of the aerosol samples collected was carried out on board, it was possible to make a qualitative assessment of the loading of Saharan dust on the filters using their



colour. When dust was present, the larger particle size fractions of the aerosol had a distinctive brown / orange colour. Based on the intensity of this colouration, the highest loadings of Saharan dust were present in samples 11, 20 - 23, 25 and 26.

I would like to thank the officers and crew for all the help they have given me during the cruise. The duty officers' efforts to warn me of approaching rain, particularly Peter Vogel's cheerful enthusiasm when waking me up in the middle of the night, are much appreciated. Thanks to the Chief Scientist, Doug Wallace, for inviting me to participate and for coordinating a thoroughly enjoyable and interesting cruise. Thanks also to everyone on board for tolerating my happiness in the rain - I was smiling because I had a sample, not because you just got soaked.

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**Table 10:** Aerosol sample collection start dates and ranges. (Samples 1, 2 and 32 were blanks).

| Sample | Start Date | Start Position | End Position   | Dust Present? |
|--------|------------|----------------|----------------|---------------|
| 3      | 15/10/02   | 11.0°N, 58.7°W | 10.6°N, 53.7°W | Yes           |
| 4      | 17/10/02   | 10.6°N, 53.7°W | 10.0°N, 51.4°W | Yes           |
| 5      | 18/10/02   | 10.0°N, 51.4°W | 10.0°N, 48.1°W | No            |
| 6      | 19/10/02   | 10.0°N, 48.0°W | 10.0°N, 44.9°W | Yes           |
| 7      | 20/10/02   | 10.0°N, 44.8°W | 10.0°N, 41.7°W | Yes           |
| 8      | 21/10/02   | 10.0°N, 41.6°W | 10.0°N, 39.0°W | Yes           |
| 9      | 22/10/02   | 10.0°N, 39.0°W | 10.0°N, 36.2°W | Yes           |
| 10     | 23/10/02   | 10.0°N, 36.2°W | 10.0°N, 33.4°W | Yes           |
| 11     | 24/10/02   | 10.0°N, 33.3°W | 10.0°N, 30.3°W | Yes           |
| 12     | 25/10/02   | 10.0°N, 30.3°W | 10.0°N, 27.6°W | Yes           |
| 13     | 26/10/02   | 10.0°N, 27.4°W | 7.0°N, 26.5°W  | Yes           |
| 14     | 27/10/02   | 6.9°N, 26.5°W  | 3.2°N, 26.2°W  | No            |
| 15     | 28/10/02   | 3.1°N, 26.2°W  | 0.0°, 26.0°W   | No            |
| 16     | 29/10/02   | 0.0°, 26.0°W   | 0.0°, 23.5°W   | No            |
| 17     | 30/10/02   | 0.1°N, 23.5°W  | 2.0°N, 23.5°W  | No            |
| 18     | 31/10/02   | 2.0°N, 23.5°W  | 2.7°N, 23.5°W  | No            |
| 19     | 01/11/02   | 6.1°N, 24.2°W  | 8.2°N, 24.6°W  | Yes           |
| 20     | 02/11/02   | 8.4°N, 24.6°W  | 10.6°N, 24.8°W | Yes           |
| 21     | 03/11/02   | 10.6°N, 24.7°W | 11.0°N, 21.7°W | Yes           |
| 22     | 04/11/02   | 11.0°N, 21.7°W | 11.5°N, 18.7°W | Yes           |
| 23     | 05/11/02   | 11.6°N, 18.6°W | 10.5°N, 17.0°W | Yes           |
| 24     | 06/11/02   | 10.9°N, 17.1°W | 11.0°N, 18.9°W | Yes           |
| 25     | 07/11/02   | 11.0°N, 19.0°W | 11.0°N, 20.4°W | Yes           |
| 26     | 08/11/02   | 11.0°N, 20.4°W | 9.3°N, 19.0°W  | Yes           |
| 27     | 09/11/02   | 9.3°N, 19.0°W  | 7.0°N, 17.1°W  | Yes           |
| 28     | 10/11/02   | 6.9°N, 17.0°W  | 5.4°N, 13.8°W  | No            |
| 29     | 11/11/02   | 5.3°N, 13.7°W  | 4.1°N, 10.2°W  | No            |
| 30     | 12/11/02   | 4.0°N, 10.0°W  | 3.5°N, 5.9°W   | No            |
| 31     | 13/11/02   | 3.5°N, 5.8°W   | 3.6°N, 1.6°W   | No            |

**Table 11:** Approximate positions and volumes (major ion funnel only) of rain samples collected during M55.

| Sample | Date     | Position       | Volume/mL |
|--------|----------|----------------|-----------|
| 1      | 15/10/02 | 11.0°N, 60.6°W | 250       |
| 2      | 20/10/02 | 10.0°N, 43.8°W | 60        |
| 3      | 20/10/02 | 10.0°N, 43.3°W | 170       |
| 4      | 20/10/02 | 10.0°N, 43.0°W | 10        |
| 5      | 21/10/02 | 10.0°N, 41.1°W | 150       |
| 6      | 21/10/02 | 10.0°N, 40.8°W | 350       |
| 7      | 22/10/02 | 10.0°N, 38.2°W | 380       |
| 8      | 27/10/02 | 6.0°N, 26.4°W  | 120       |
| 9      | 27/10/02 | 4.6°N, 26.3°W  | 310       |
| 10     | 28/10/02 | 2.8°N, 26.2°W  | 125       |
| 11     | 01/11/02 | 6.5°N, 24.3°W  | 260       |
| 12     | 01/11/02 | 6.5°N, 24.3°W  | 31.5      |
| 13     | 09/11/02 | 8.3°N, 18.4°W  | 170       |
| 14     | 10/11/02 | 6.1°N, 15.9°W  | 870       |
| 15     | 11/11/02 | 5.6°N, 14.6°W  | 1200      |
| 16     | 12/11/02 | 4.5°N, 11.3°W  | 1100      |
| 17     | 12/11/02 | 3.8°N, 9.5°W   | 500       |

#### 4.15 Joint Meteor 55 Experiments

W. Gaul (IfMK) and M. Voß (IOW)

During the cruise biological and chemical working groups collected an extensive data set of partly new variables such as volatile organic hydrocarbons (VOC) such as acetonitrile, acetone, isoprene, and DMS which were measured using a PTR-MS system and GC systems. Biologists provided information on biological variables and rate measurements. All gases mentioned play an important role in atmospheric chemistry, however, little is known about potential oceanic sources or sinks. The participation in this experiment was an excellent opportunity to study biological influence on VOC concentrations. Together with measurements of VOC concentrations in air and surface water; which was the main task of the cruise; the outcome of this study will be important information to identify marine VOC sources or sinks. Evaluation and data processing is work in progress.

The processes responsible for the production of the light alkyl nitrates in the ocean are as well unknown. In the atmosphere production involves a radical reaction between NO and CH<sub>3</sub>OO radicals, and it is thought that this reaction could occur in the water column, mediated either by

biotic (e.g. phytoplankton production) or abiotic (e.g. photochemical) processes. The rationale behind the incubation experiments was to test whether stimulating the biological system via various addition treatments would result in an increase in methyl nitrate production. From the depth profiles collected during this cruise and on a previous Atlantic Ocean transect, it had been seen that the alkyl nitrate concentrations were often elevated below the mixed layer, with high concentrations being seen as deep as 250 metres. This suggested that it could be bacterial processes responsible for the production of the alkyl nitrates, and so it was hypothesised that increases in methyl nitrate would be seen in one treatment, where DOC was enriched.

To investigate the relationship between biological production or degradation and the generation and of certain compounds/gases was the aim of a joint experiment (Table 12). It was designed very simply: Six large incubation bottles were filled with surface water and amended with different compounds to either foster phytoplankton growth by nutrient addition, or bacterial growth by starch addition. One bottle was kept dark to exclude sunlight and thus primary production, and the water for another setup was filtered through 0,2µm to remove most bacteria. The cyanobacterium *Trichodesmium* was enriched in one bottle to test its role in buildup and destruction of compounds. A control bottle was incubated as well. Not all treatments were successful and in some growth of bacteria happened although not planned. We therefore started a second experiment right after the first one ended with just 2 treatments plus a control and incubated in duplicates.

**Table 12:** Variables measured in the two Meteor 55 Joint Experiments.

|   | 1 Exp | 2 Exp |
|---|-------|-------|
| Volatile organic hydrocarbon (VOC)                                  | yes   | yes   |
| Alkyl nitrates  | yes   | yes   |
| Halocarbons   | yes   | No    |
| N <sub>2</sub> O  | yes   | No    |
| DMS, dissolved & cellular DMSP                                      | yes   | yes   |
| N <sub>2</sub> fixation rate (in the beginning and in the end only) | yes   | yes   |
| Primary production  | yes   | yes   |
| Bacterial production  | yes   | yes   |
| Phytoplankton pigment composition                                   | yes   | yes   |
| Phosphatase activity  | yes   | yes   |
| Inorganic nutrients and ammonia                                     | yes   | yes   |

In detail: The first joint experiment started Friday, November 8. in the morning 05:30 at 21°W in fairly oligotrophic though probably not iron-limited waters. Water from 10m depth was sampled and distributed in six 12l incubation bottles. Six 12-liter bottles with different experimental treatments were incubated on deck in a basin at surface water temperature and

slowly rotated. Samples were taken at the start of the experiment and after 48h. A limited number of small volumes was taken after 6h, 12h and 24h incubation which was constrained to a total volume of 2 dm<sup>3</sup> for each bottle. The chosen experimental treatments were:

- Full supplemented of inorganic nutrients (10μM NO<sub>3</sub>, 1μM NH<sub>4</sub>, 1 μM PO<sub>4</sub> , 5μM Si(OH)<sub>4</sub>,) plus Saharan-dust
- Dissolved organic carbon enriched ( 100μM amylo-pectin )
- Trichodesmium enriched – roughly by a factor of 10
- Sterile filtered ( < 0.2 μm )
- Dark incubated
- Control: unenriched water sample

Primary production was determined by uptake of <sup>14</sup>C-bicarbonate during an incubation time of 48 hours in a deck incubator. The samples were shaded by a neutral light screen allowing 78 % of the light to penetrate. Bacterial production was determined by incorporation of <sup>3</sup>H-Thymidine into DNA. The samples were incubated for 4 hours in the dark in the same deck incubator as the primary production samples. For further explanations of the methods see section “Water column biology”. N<sub>2</sub> fixation rates were determined in the beginning and the end of the experiment with <sup>15</sup>N<sub>2</sub> addition and incubation for 24 hours under the same screening used for the experiment bottles.

### Experiment I

Almost no changes in the nutrient concentration were observed, even in the enriched treatment no new production took place but probably high regenerated production has happened (Table 13). The increase in ammonia concentration was very obvious and indicated strong heterotrophic processes.

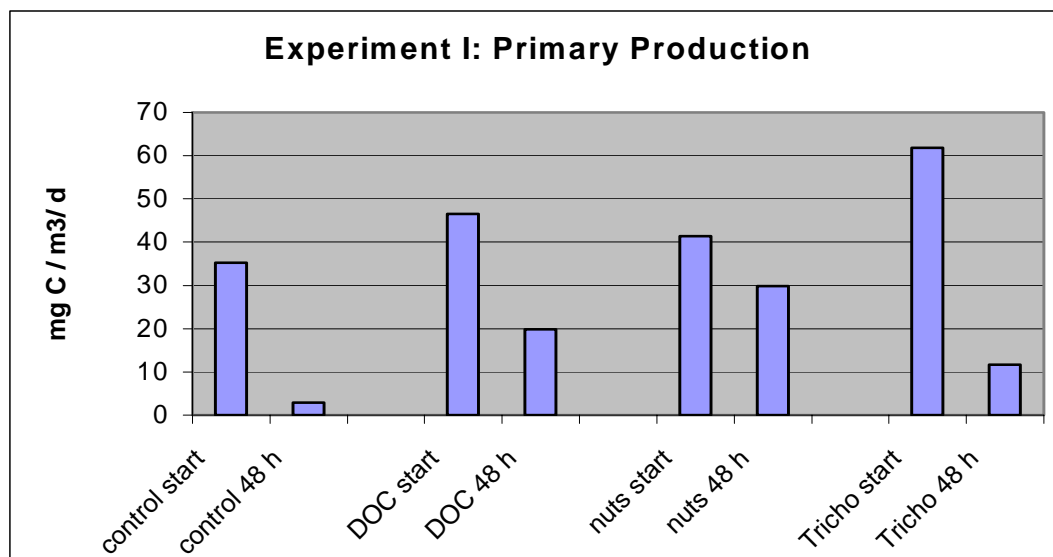
**Table 13:** Nutrient data from the 1st Meteor 55 Joint Experiment.

| Date       | treatment | time point    | hour | NO3 [μM] | NO2 [μM] | mean NH4 [μM] | PO4 [μM] | SiO4 [μM] |
|------------|-----------|---------------|------|----------|----------|---------------|----------|-----------|
| 08.11.2002 | all other | to (control)  | 0    | 0,12     | 0,00     | 0,46          | 0,01     | 1,12      |
| 08.11.2002 | nut add   | to (nut. add) | 0    | 8,88     | 0,00     | 1,24          | 1,63     | 5,76      |
| 10.11.2002 | Control   | t2            | 48   |          |          | 0,37          | 0,04     |           |
| 10.11.2002 | nut add   | t2            | 48   | 8,88     | 0,03     | 0,85          | 1,64     | 9,66      |
| 10.11.2002 | steril    | t2            | 48   |          |          | 0,05          | 0,04     |           |
| 10.11.2002 | Tricho    | t2            | 48   |          |          | 1,45          | 0,04     |           |
| 10.11.2002 | dark      | t2            | 48   |          |          | 0,29          | 0,04     |           |
| 10.11.2002 | DOC add   | t2            | 48   |          |          | 0,29          | 0,04     |           |

Some of the treatments did not contain the expected plankton composition e.g. the sterile

treatment contained massive amounts of bacteria, the *Trichodesmium* treatment had many microzooplankton organisms enriched as well, obviously excreting large amounts of ammonia. Therefore, a pronounced decrease in primary production between the start of the experiment and after 48 hours was observed (Figure 25). This was apparent in all treatments being strongest in the control and in the samples enriched with *Trichodesmium*. The highest primary production after 48 hours was found in the samples with nutrient additions.

Bacterial production showed the opposite effect and increased strongly between the start of



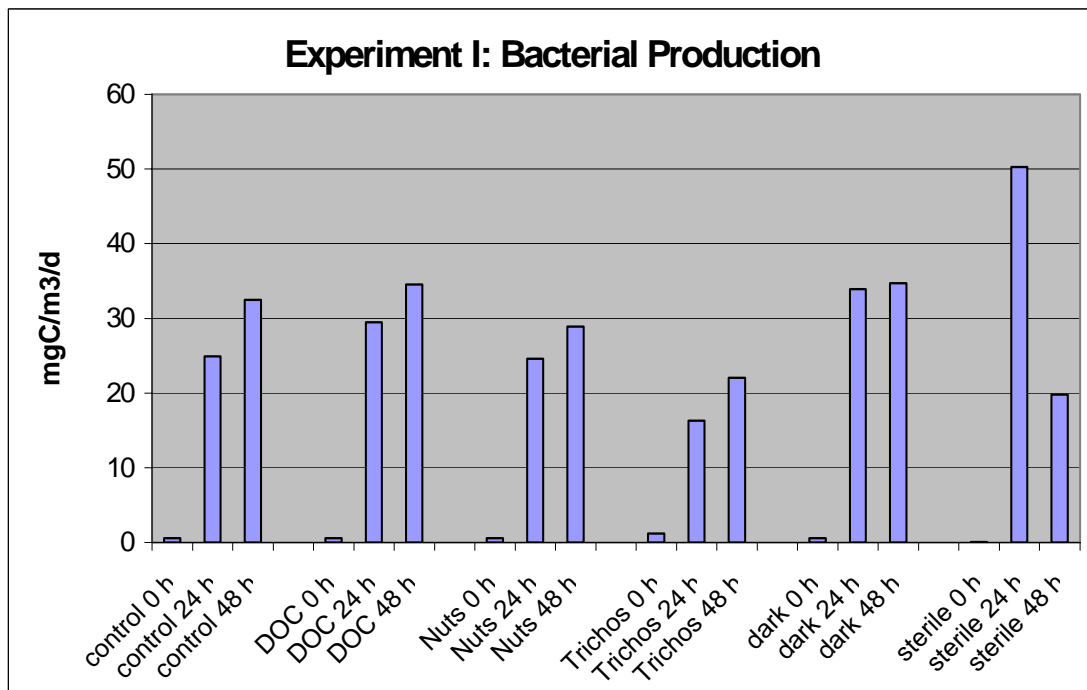
**Figure 25:** Results from primary production measurements in the first experiment in selected treatments.

the experiment and 24 or 48 hours of experiment duration (Figure 26). The high values in the “sterile” treatment show clearly that this sample was not free of bacteria. It appears rather that all grazers of bacteria were removed and bacteria developed explosively. The bacterial production was nearly as high or higher than primary production.

The results imply that during the incubation phytoplankton did not grow but rather decreased. The causes for this may be damage due to high light intensities or high grazing pressure. Heterotrophic bacteria seemed to have taken advantage of this mortality leading to a mass development of bacteria with extremely high growth rates. Differences between treatments are difficult to discern.

Concentrations of  $N_2O$  were analysed from the DOC and *Trichodesmium* enriched treatments. Both did show no difference in the in  $N_2O$  concentration in the beginning of the experiment and after 48 hours.

Preliminary results from VOC and alkyl nitrates from the first incubation experiment showed concentrations of methyl nitrate increasing in all the treatments, with the largest increases being seen in the nutrient and DOC enriched bottles. Methyl iodide also increased, although in the control and dark bottles, concentrations peak after 12 hours, and had decreased after 48 hours. It was not possible in this experiment to differentiate between any of the treatments.



**Figure 26:** Results from bacterial production measurements in the first experiment.

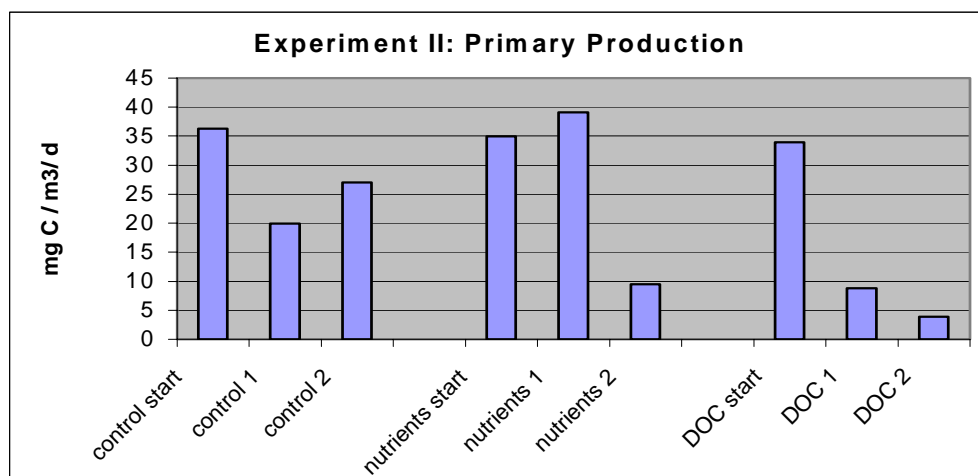
### Experiment II

The 2nd experiment was conducted Monday, November 11. in similar waters. Niskin bottles were also filled in 10m depth and the water transferred into 12l incubation bottles.

The chosen experimental treatments were:

- Full supplemented of inorganic nutrients (10 $\mu$ M NO<sub>3</sub>, 1 $\mu$ M NH<sub>4</sub>, 1  $\mu$ M PO<sub>4</sub>, 5 $\mu$ M Si(OH)<sub>4</sub>), plus Saharan-dust
- Dissolved organic carbon enriched ( 10 $\mu$ M amylo-pectin )
- Control: unenriched water sample

In the second joint experiment primary production did not decline so strongly after 48 hours of experiment duration, except in the treatment with DOC addition (Figure 27).



**Figure 27:** Primary production as measured during Experiment 2.

There was a clear difference between the two parallel treatment of nutrient additions. While

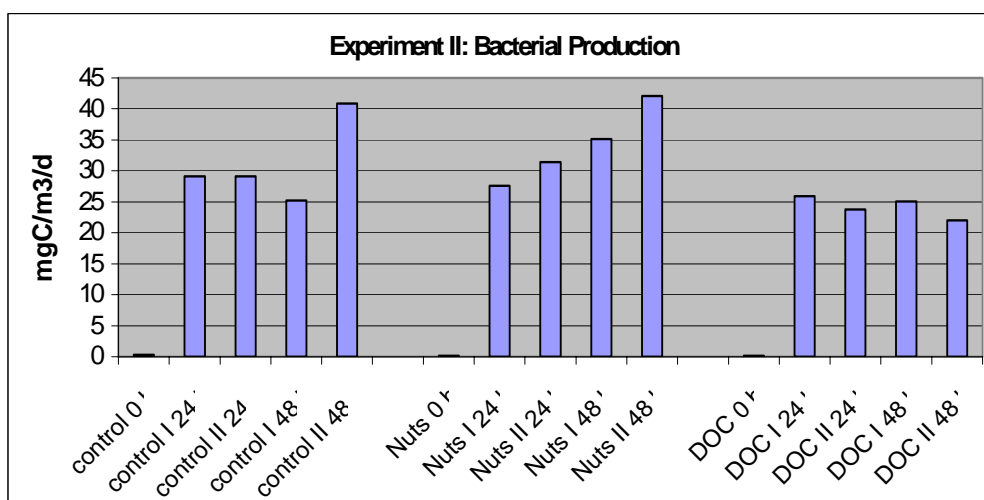
sample “Nutrients I” increased slightly in production relative to the start values, sample “Nutrients II” declined strongly. DOC additions suppressed primary production significantly.

**Table 14:** Nutrient data from the 2nd Meteor 55 Joint Experiment. na = not available.

| date       | treatment       | time point      | hour | NO3<br>[μMol] | NO2<br>[μMol] | mean<br>NH4<br>[μMol] | PO4<br>[μMol] | SiO4<br>[μMol] |
|------------|-----------------|-----------------|------|---------------|---------------|-----------------------|---------------|----------------|
| 11.11.2002 | all other       | to<br>(control) | 0    | na            | na            |                       | na            | na             |
| 12.11.2002 | nut<br>addition | to (nut<br>add) | 0    | na            | na            |                       | na            | na             |
| 12.11.2002 | Control 1       | t1              | 24   | 0,04          | 0,01          |                       | 0,08          | 1,15           |
| 12.11.2002 | Control 2       | t1              | 24   | 0,03          | 0,01          |                       | 0,03          | 0,90           |
| 12.11.2002 | nut add 1       | t1              | 24   | 9,05          | 0,02          |                       | 1,65          | 5,19           |
| 12.11.2002 | nut add 2       | t1              | 24   | 9,46          | 0,11          |                       | 1,95          | 7,71           |
| 12.11.2002 | DOC add 1       | t1              | 24   | 0,15          | 0,03          |                       | 0,09          | 1,31           |
| 12.11.2002 | DOC add 2       | t1              | 24   | 0,05          | 0,01          |                       | 0,04          | 0,90           |
|            |                 |                 |      |               |               |                       |               |                |
| 13.11.2002 | Control 1       | t2              | 48   | 0,04          | 0,02          | 0,40                  | 0,05          | 1,60           |
| 13.11.2002 | Control 2       | t2              | 48   | 0,01          | 0,01          | 0,10                  | 0,03          | 1,35           |
| 13.11.2002 | nut add 1       | t2              | 48   | 9,02          | 0,02          | 1,55                  | 1,66          | 5,40           |
| 13.11.2002 | nut add 2       | t2              | 48   | 9,22          | 0,02          | 1,60                  | 1,75          | 5,53           |
| 13.11.2002 | DOC add 1       | t2              | 48   | 0,00          | 0,01          | 0,33                  | 0,02          | 1,23           |
| 13.11.2002 | DOC add 2       | t2              | 48   | 0,00          | 0,01          | 0,29                  | 0,02          | 1,09           |

Also in this experiment bacterial production increased dramatically in all treatments between the start of the experiment and 24 hours of experiment duration (Figure 28). The strongest response was seen in the nutrient addition. There is no obvious difference between both parallel nutrient addition treatments in respect to bacterial production. Addition of DOC did not stimulate bacterial production to the same degree. This may indicate that nutrient limitation and competition between phytoplankton and bacteria dominates this system. Amendments with DOC therefore cause increased competition for nutrients which may be the reason for the strongly decreased primary production in the DOC treatments.





**Figure 28:** Results from the bacterial production measurements in the 2<sup>nd</sup> experiment.

The results from VOC and alkyl nitrates from the second incubation experiment show very little change in the methyl nitrate concentrations in any of the treatments. Methyl iodide, which was also measured in the incubations, showed evidence of increasing concentrations in both the DOC enriched, and nutrient enriched bottles. However, different results were obtained in the duplicated bottle for all three treatments.

These preliminary findings do not yet allow us to draw any clear conclusions of the mechanisms behind the generation and/or destruction of the compounds investigated. Joint interdisciplinary experiments are certainly the right tool to approach the above discussed questions which process might be responsible for generation and destruction of organic gaseous and other volatile compounds. Hopefully more opportunities in new projects or other cruises come up and more work will be done together on this interesting scientific question.

## 5. The Weather during Meteor 55

RV METEOR left the port of Willemstad/Curacao 12 hours earlier than originally planned for a West-East transect across the Atlantic along 11° North. The weather was cloudy and the winds came from eastsoutheast force 6 to 7. Due to the political situation at the Ivory Coast - the original destination – it was necessary to decide for an alternative port of call. This was Douala in Cameroon. Since this port is about 840 nautical miles further to the east, FS METEOR had to save time and left Curacao earlier than planned. Until Trinidad and Tobago southeasterly winds predominated and the sky was partly sunny, partly cloudy. Significant weather occurred only in form of light and short rainshowers.

On October 16 the cruise leader decided to move the transect to 10° North. The reason was Seawifs-pictures, on which the marine biologists detected a more interesting distribution of chlorophyll. During the next days winds of Bft 4 or 5 from northeast to east predominated. On October 16 the wind was backing southeasterly and decreasing to 3-4 Bft. During this period it was mainly sunny or cloudy with only some light showers. During the night from October 21 to 22, a denser cloud area crossed the investigation area with thunder showers. On October 23 the sky was overcast and the precipitation observed was rain with interruptions. On October 24 the weather became partly sunny with northeasterly winds force 4 or 5. Until October 26 the wind abated. With the approach of a branch of the ITCZ isolated showers occurred. On October 27 at 10.00° N 26.42W METEOR headed south. An intensive convective and thundery cluster of the ITCZ lay between 07°N, 13°N, 34°W, and 26°W, which caused rain showers until October 29. On the course to the equator the wind was backing southerly mainly with force 4 or 5. Approaching the equator the weather became sunny.

On October 30 near 00°N 23°W a sediment trap of the University of Bremen was lifted up. On the late afternoon of October 30 METEOR headed northerly until 11°N. The ITCZ extended from 07.30°N until Sierra Leone and expanded northerly until 13 to 15 °N. Thus until November 03 dense clouds and convective precipitation occurred very often. On the track to the north the wind had turned to northeasterly directions and the wind force encountered was 4 or 5. On November 04, in the coastal waters of Guinea, the sky became sunny and the wind was light (Bft 2) from eastnortheast. To this time a second branch of the ITCZ with intense convective clouds and embedded thunderstorms lay along a line from 04°N 22°W to the Ivory Coast. This branch moved northwest, causing precipitation in the following night. On November 06 METEOR was more northerly and only lightning was observed. On the following day the sky was mainly clear.

On November 08 the northern branch of the ITCZ extended from 10°N 40°W until Mauritania and the southern part from 02°N 08°W until Sierra Leone and Liberia. Near 11°N 20°W METEOR met POLARSTERN between these two branches of the ITCZ within fair weather and northeasterly winds of Bft 3-4. A mutual visit was possible for some hours.

Then POLARSTERN left the meeting point for the voyage to Cape Town and the Antarctic. The southern branch of the ITCZ became denser on the next day, expanding to the west and crossing METEOR with high convective clouds. The wind had turned to southeast and increased to 4 or 5 Bft. In the evening first heavy showers occurred, accompanied by thunderstorms with gusts of 20 m/s. Until noon of November 11 METEOR was influenced by big cluster off the coast of Guinea and Sierra Leone and during the following night heavy thundery showers were encountered. The precipitation was 10 mm within 2 hours. The showers did not cease until the end of the leg due to large cloud clusters, tracking westwards along the coast of Ghana and Ivory Coast.

## 6. Station List

| Station Number | Station Date/Time |                | Station Start |           | Station End |           |
|----------------|-------------------|----------------|---------------|-----------|-------------|-----------|
|                | Start             | End            | Latitude      | Longitude | Latitude    | Longitude |
| 1              | 16.10.02 09:45    | 16.10.02 13:00 | 11.000        | -56.752   | 11.000      | -56.640   |
| 2              | 16.10.02 19:45    | 16.10.02 20:47 | 11.000        | -55.575   | 11.000      | -55.575   |
| 3              | 17.10.02 09:00    | 17.10.02 12:29 | 10.552        | -53.730   | 10.552      | -53.730   |
| 4              | 17.10.02 19:45    | 17.10.02 23:24 | 10.291        | -52.660   | 10.292      | -52.661   |
| 5              | 18.10.02 08:01    | 18.10.02 11:07 | 10.000        | -51.410   | 10.000      | -51.405   |
| 6              | 18.10.02 18:45    | 18.10.02 20:14 | 10.002        | -50.125   | 10.003      | -50.122   |
| 7              | 19.10.02 08:00    | 19.10.02 11:01 | 10.000        | -48.056   | 10.000      | -48.056   |
| 8              | 19.10.02 18:45    | 19.10.02 20:17 | 10.000        | -46.785   | 10.001      | -46.784   |
| 9              | 20.10.02 08:22    | 20.10.02 10:42 | 10.000        | -44.926   | 10.000      | -44.926   |
| 10             | 20.10.02 18:45    | 20.10.02 20:17 | 10.001        | -43.755   | 10.004      | -43.755   |
| 11             | 21.10.02 08:00    | 21.10.02 13:02 | 10.000        | -41.731   | 10.007      | -41.734   |
| 12             | 21.10.02 18:49    | 21.10.02 19:52 | 9.998         | -40.773   | 10.001      | -40.774   |
| 13             | 22.10.02 08:04    | 22.10.02 11:58 | 10.000        | -38.990   | 10.011      | -39.001   |
| 14             | 22.10.02 18:50    | 22.10.02 20:00 | 10.000        | -38.164   | 10.001      | -38.164   |
| 15             | 23.10.02 08:01    | 23.10.02 12:01 | 10.000        | -36.233   | 10.024      | -36.222   |
| 16             | 23.10.02 18:50    | 23.10.02 20:34 | 10.001        | -35.187   | 10.003      | -35.186   |
| 17             | 24.10.02 07:41    | 24.10.02 09:44 | 10.000        | -33.396   | 10.002      | -33.398   |
| 18             | 24.10.02 17:45    | 24.10.02 19:50 | 10.001        | -32.152   | 10.006      | -32.153   |
| 19             | 25.10.02 07:00    | 25.10.02 10:51 | 10.000        | -30.283   | 10.004      | -30.283   |
| 20             | 25.10.02 17:48    | 25.10.02 22:15 | 10.000        | -29.099   | 10.000      | -29.095   |
| 21             | 26.10.02 07:00    | 26.10.02 10:02 | 10.000        | -27.558   | 10.001      | -27.554   |
| 22             | 26.10.02 15:00    | 26.10.02 16:41 | 10.000        | -26.667   | 10.002      | -26.662   |
| 23             | 27.10.02 12:30    | 27.10.02 13:11 | 6.551         | -26.433   | 6.551       | -26.432   |
| 24             | 29.10.02 07:00    | 29.10.02 10:51 | 0.000         | -26.000   | 0.000       | -25.996   |
| 25             | 29.10.02 17:46    | 29.10.02 18:51 | 0.000         | -24.939   | 0.002       | -24.936   |
| 26             | 30.10.02 07:00    | 30.10.02 09:41 | 0.000         | -23.500   | 0.003       | -23.497   |
| 27             | 30.10.02 15:30    | 30.10.02 19:20 | 0.001         | -23.500   | 0.001       | -23.499   |
| 28             | 31.10.02 07:00    | 31.10.02 10:14 | 1.949         | -23.500   | 1.951       | -23.500   |
| 29             | 31.10.02 17:47    | 31.10.02 18:50 | 3.266         | -23.650   | 3.268       | -23.649   |
| 30             | 01.11.02 07:00    | 01.11.02 10:28 | 5.290         | -24.027   | 5.290       | -24.019   |
| 31             | 01.11.02 17:48    | 01.11.02 20:58 | 6.498         | -24.250   | 6.501       | -24.241   |
| 32             | 02.11.02 07:17    | 02.11.02 09:41 | 8.218         | -24.572   | 8.224       | -24.574   |
| 33             | 02.11.02 17:47    | 02.11.02 18:45 | 9.508         | -24.814   | 9.510       | -24.815   |
| 34             | 03.11.02 06:15    | 03.11.02 08:29 | 10.500        | -25.000   | 10.499      | -25.000   |
| 35             | 03.11.02 18:12    | 03.11.02 19:32 | 11.000        | -23.518   | 11.007      | -23.526   |
| 36             | 04.11.02 06:41    | 04.11.02 09:30 | 11.000        | -21.667   | 11.002      | -21.667   |
| 37             | 04.11.02 17:08    | 04.11.02 18:12 | 11.000        | -20.334   | 11.002      | -20.335   |
| 38             | 05.11.02 06:15    | 05.11.02 08:36 | 11.500        | -18.733   | 11.500      | -18.733   |
| 39             | 05.11.02 16:15    | 05.11.02 17:32 | 11.967        | -17.518   | 11.967      | -17.518   |
| 40             | 05.11.02 19:31    | 05.11.02 20:58 | 11.649        | -17.500   | 11.649      | -17.500   |
| 41             | 06.11.02 06:00    | 06.11.02 08:02 | 10.417        | -16.833   | 10.419      | -16.836   |
| 42             | 06.11.02 14:30    | 06.11.02 19:22 | 11.035        | -17.699   | 11.028      | -17.698   |
| 43             | 07.11.02 06:15    | 07.11.02 08:07 | 11.000        | -18.833   | 11.000      | -18.833   |
| 44             | 07.11.02 15:20    | 07.11.02 21:08 | 11.001        | -19.751   | 11.001      | -19.753   |
| 45             | 08.11.02 06:30    | 08.11.02 09:24 | 11.000        | -20.417   | 11.003      | -20.418   |
| 46             | 08.11.02 17:21    | 08.11.02 18:23 | 10.999        | -19.987   | 11.000      | -19.986   |
| 47             | 09.11.02 06:31    | 09.11.02 10:27 | 9.308         | -19.004   | 9.308       | -19.004   |
| 48             | 09.11.02 17:06    | 09.11.02 18:53 | 8.402         | -18.501   | 8.402       | -18.499   |
| 49             | 10.11.02 06:32    | 10.11.02 08:40 | 6.998         | -17.083   | 6.998       | -17.083   |
| 50             | 10.11.02 16:48    | 10.11.02 18:48 | 6.104         | -15.904   | 6.101       | -15.898   |
| 51             | 11.11.02 07:30    | 11.11.02 08:07 | 5.401         | -13.999   | 5.401       | -13.999   |

## 7. Publications and Presentations of Meteor 55 Results

The M55 cruise has already resulted in submission and publication of a large number of publications as well as numerous presentations at international meetings. We reproduce here a list of presentations and abstracts of manuscripts that have resulted directly from work done on the cruise. We anticipate that several additional manuscripts will make use the M55 data in the near future.

### 7.1 Conference Presentations

American Geophysical Union and the European Geophysical Society; Joint Congress, Nice, April 2003; M 55 Posters and Talks:

“Meteor 55 Exchanges between the Surface Ocean and the Lower Atmosphere in the Tropical Atlantic: Results from the 1st German SOLAS cruise.” D. Wallace and M55 participants. POSTER

“Photochemical versus biological production of methyl iodide during Meteor 55”. Richter, U. and Wallace, D. POSTER

“Assessment Of Nutrient Limitation On The Primary Production And N<sub>2</sub> Fixation Across The Tropical Atlantic”. Ridame, C., Mills, M., Davey, M., La Roche, J. and Geider, R. POSTER

“Bromoform in the tropical Atlantic: Distributions, Sources and Air-Sea-Fluxes”. Quack, B., Wallace, D., Petrick, G., Stange, K. TALK

“Atmospheric and Oceanic Measurements Of Reactive Organic Species From The Tropical Atlantic Ocean”. J. Williams, R. Holzinger, V. Gros, Xiaobin Xu and D. Wallace. POSTER

“Nitrous oxide in the tropical Atlantic: First results from the German SOLAS cruise M55”. S. Walter, H. Bange, D. Wallace. TALK

“The Tropical Atlantic Ocean as Source Of Atmospheric Nitrous Oxide”. H.W. Bange, S. Walter, D.W.R. Wallace. POSTER

“Biological Investigations During The 1st German SOLAS Cruise, Meteor 55” .I. Peeken, K. Lochte, L. Hoffmann, P. Croot. TALK

### 7.2 Published Peer-Reviewed Manuscripts based on Meteor 55 Data

Lelieveld, J., J. van Aardenne, H. Fischer, M. de Reus, J. Williams and P. Winkler (2004) Increasing ozone over the Atlantic Ocean. *Science* 304, 1483-1487. (This paper is based partly on Meteor 55 data).

All the remaining papers in this list are based on data that were collected PRIMARILY OR EXCLUSIVELY during the Meteor 55 cruise:

Mills, M.M., C. Ridame, M. Davey, J. LaRoche, R. Geider, Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic, *Nature* 429, 292 - 294 (20 May 2004); doi:10.1038/nature02550

Gros V., J. Williams, M. G. Lawrence, R. von Kuhlmann, J. van Aardenne, E. Atlas, A. Chuck, D. P. Edwards, V. Stroud, M. Krol (2004), Tracing the origin and ages of interlaced atmospheric

pollution events over the tropical Atlantic Ocean with in situ measurements, satellites, trajectories, emission inventories, and global models, *J. Geophys. Res.*, 109, D22306, doi:10.1029/2004JD004846.

#### Geophysical Research Letters Special Section

Baker, A. R. (2004), Inorganic iodine speciation in tropical Atlantic aerosol, *Geophys. Res. Lett.*, 31(23), L23S02, doi:10.1029/2004GL020144.

Croot, P. L., P. Streu, and A. R. Baker (2004), Short residence time for iron in surface seawater impacted by atmospheric dry deposition from Saharan dust events, *Geophys. Res. Lett.*, 31(23), L23S08, doi:10.1029/2004GL020153.

Croot, P. L., P. Streu, I. Peeken, K. Lochte, and A. R. Baker (2004), Influence of the ITCZ on H<sub>2</sub>O<sub>2</sub> in near surface waters in the equatorial Atlantic Ocean, *Geophys. Res. Lett.*, 31(23), L23S04, doi:10.1029/2004GL020154.

Körtzinger, A., A significant CO<sub>2</sub> sink in the tropical Atlantic Ocean associated with the Amazon River plume, *Geophys. Res. Lett.*, 30(24), 2287, doi:10.1029/2003GL018841, 2003.

Quack, B., E. Atlas, G. Petrick, V. Stroud, S. Schauffler, and D. W. R. Wallace (2004), Oceanic bromoform sources for the tropical atmosphere, *Geophys. Res. Lett.*, 31(23), L23S05, doi:10.1029/2004GL020597.

Richter, Uwe; Wallace, Douglas W. R., Production of methyl iodide in the tropical Atlantic Ocean, *Geophys. Res. Lett.*, 31(23), L23S03, doi:10.1029/2004GL020779.

Voss, M., P. Croot, K. Lochte, M. Mills, and I. Peeken (2004), Patterns of nitrogen fixation along 10°N in the tropical Atlantic, *Geophys. Res. Lett.*, 31(23), L23S09, doi:10.1029/2004GL020127.

Walter, S., H. W. Bange, and D. W. R. Wallace (2004), Nitrous oxide in the surface layer of the tropical North Atlantic Ocean along a west to east transect,, *Geophys. Res. Lett.*, 31(23), L23S07, doi:10.1029/2004GL019937.

Wallace, D. W. R., and H. W. Bange (2004), Introduction to special section: Results of the Meteor 55: Tropical SOLAS Expedition, *Geophys. Res. Lett.*, 31, L23S01, doi:10.1029/2004GL021014.

Williams, J., R. Holzinger, V. Gros, X. Xu, E. Atlas, and D. W. R. Wallace (2004), Measurements of organic species in air and seawater from the tropical Atlantic, *Geophys. Res. Lett.*, 31(23), L23S06, doi:10.1029/2004GL020012.

#### Submitted

Tengberg, A., J. Hovdenes, J.H. Andersson, O. Brocandel, R. Diaz, D. Hebert, T. Arnerich, C. Huber, A. Körtzinger, A. Khripounoff, F. Rey, C. Rönning, S. Sommer and A. Stangelmayer (2005). Evaluation of a life time based optode to measure oxygen in aquatic systems. *Limnol. Oceanogr.: Methods*, submitted.

Stramma, L., J. Schafstall and S. Hüttl (2005) Water masses and currents in the upper tropical Northeast Atlantic off northwest Africa, *J. Geophys. Res. (Oceans)*, submitted.

Langlois, R., J. LaRoche, and P. Raab (2005) Diazotroph Diversity and Distribution in the Tropical and Subtropical Atlantic Ocean, *Appl. Environ. Microbiol.*, submitted.

### 7.3 PhD and Diplom Theses

The following Ph.D and Diplom theses are or will be based to a significant extent on work conducted during M55:

Uwe Richter (2003) Factors influencing methyl iodide production in the ocean and its flux to the atmosphere. PhD Dissertation, University of Kiel.

Lynn Hoffmann (2003): Vergleich der Phytoplanktonökologie in verschiedenen Biogeographischen Provinzen des tropischen Atlantiks. Diplomarbeit, Universität Kiel.

Wilhelm Gaul (2005) Untersuchungen zur Produktion und zum Mikrobiellen Umsatz von  $\beta$ -Dimethylsulphoniopropionat. PhD Dissertation, University of Kiel.

Sylvia Walter (2005) Nitrous oxide in the North Atlantic Ocean. PhD Dissertation (expected Summer 2005).

## 8. Acknowledgements

The Chief Scientist wishes to acknowledge his colleague Dr. Hermann Bange who assisted all Meteor 55 participants with good organisation, good planning and good fun. The success of this SOLAS pilot study would not have been possible without the support of the METEOR Leitstelle and, of course, the expert assistance of Kaptn. Papenhagen and the crew of FS METEOR. All participants were impressed by the professionalism and friendliness of the officers and crew.