# GEOMAR 

## Helmholtz-Zentrum für Ozeanforschung Kiel

# RV SONNE Fahrtbericht / Cruise Report SO234-2 

08.-20.07.2014

Durban, South Africa - Port Louis, Mauritius


Berichte aus dem GEOMAR Helmholtz-Zentrum für Ozeanforschung Kiel

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## GEOMAR

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## RV Sonne cruise SO234-2: Durban-Port Louis, July 08-20, 2014

## Introduction

Within the frame work of the BMBF-project OASIS ("Organic very short lived substances and their Air Sea Exchange from the Indian Ocean to the Stratosphere") the research cruise SO234-2 of the German research vessel SONNE was organized and conducted by the University of Oslo, Norway (www.uio.no) together with the GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany (www.geomar.de) from 08 to 20 July, 2014 in the subtropical West Indian Ocean (Figure 1). The SO234-2 cruise was primarily planned as a training and capacity building cruise for students from southern Africa and Germany within the BMBF SPACES ("Science Partnerships for the Assessment of Complex Earth System Processes") program. Fifteen students from South Africa, Namibia and Germany participated, along with 9 scientists and one observer from Madagascar. The training and research covered air-sea gas exchange between the atmosphere and the ocean, and the transport of ocean trace gases from the Indian Ocean to the stratosphere during the southwest Monsoon as well as the determination of important biogeochemical parameters. This research project was funded within the national BMBF program SPACES within the project SO235-OASIS (Grant: 03G0235A).


Figure 1: SO234-2 SPACES cruise track of RV Sonne: Durban - Port Louis (July 08-20, 2014).

## Scientific background

Trace gases, containing halogens like chlorine and bromine are broken down by solar radiation in the stratosphere, where the halogens are highly efficient at destroying ozone. Increasing emissions from human activities have led to depletion of global stratospheric ozone over the last three decades. Whereas the chlorine supply is dominated by anthropogenic compounds, a major part of the bromine is supplied by natural, short-lived species, with oceanic sources. The importance of sulphur compounds emitted from the ocean for the middle atmosphere relates to their role as precursors to aerosols in the stratospheric aerosol layer. Recently, an increase of the stratospheric aerosol background level since 2000 has been observed. However, the origin of this elevated Junge layer, made either anthropogenically or naturally, is still under investigation. The tropical oceans are a known source of reactive halogen and sulfur compounds to the atmosphere in the form of short-lived brominated and iodinated methanes, as e.g. bromoform ( $\mathrm{CHBr}_{3}$ ), methyl iodide $\left(\mathrm{CH}_{3} \mathrm{I}\right)$, dimethyl sulphide (DMS) and COS (carbonyl sulphide). Elevated atmospheric concentrations above the oceans are related to oceanic super saturations of the compounds, and to natural photochemical and biological production. Macro algae in coastal regions, as well as regionally enhanced phytoplankton, coral reefs, photochemical reactions and local anthropogenic sources all contribute to marine and atmospheric concentrations.

Trace gases enter the stratosphere principally in the tropics, where ascending warm air carries them rapidly from the ocean surface to the tropical tropopause layer. The intense vertical transport of the tropical atmosphere implies that the oceanic sources will supply significant amounts of halogens and sulfur to the upper troposphere/ lower stratosphere where they contribute to the observed halogen content and ozone changes. The subtropical and tropical Indian Ocean is a largely uncharacterized region for oceanic compounds and a projected hot spot, especially in coastal regions for their emissions and transport pathways into the stratosphere during southwest monsoon.

Spatial and temporal variability in production and sea-to-air flux of short-lived halogenated and sulfuric trace gases creates strongly varying oceanic distributions and thus also varying atmospheric contributions. The current impact of the natural ozone depleting substances is still uncertain and future changes in the mechanisms, that regulate their emissions to the atmosphere, their transport, and their chemical processing are largely unknown. Therefore the oceanic emissions have the potential to cause surprises in the evolution of the stratospheric ozone and aerosol layer in a changing climate, unless they are better understood. The measurements are thus needed to improve the understanding of future stratospheric halogen and sulphur loading and therewith on the ozone depletion and the radiative forcing of the future climate. The results of the SO234-2 campaign will contribute to new scientific insights of the United Nations Montreal Protocol on Substances that Deplete the Ozone Layer, to the United Nations Framework Convention on Climate Change, and to global climate change research.

## Objectives and measurements

The SO234-2 cruise was primary planed as a training and capacity building cruise for students from southern Africa and Germany within the BMBF SPACES ("Science Partnerships for the Assessment of Complex Earth System Processes") program. The study program onboard the SPACES cruise SO234-2 was designed to teach the students mainly about "AirSea Interactions in the western Indian Ocean". The western tropical Indian Ocean experiences the Somali current, which reverses with the different monsoon systems, the Agulhas current, open ocean denitrification and high rates of nitrogen fixation in the Arabian Sea, and a large area in the western equatorial region of high carbon dioxide drawdown. All these phenomena make the tropical Indian Ocean an excellent laboratory and classroom, allowing special focus on anthropogenic effects, global climate change and on ocean biogeochemical and physical processes.

Of particular scientific relevance during SO234-2 were oceanic and atmospheric measurements of a suite of short-lived trace gases containing bromine, iodine and sulfur in various marine biogeochemical regimes like close to the coasts, in regions of high chlorophyll, close to coral reefs (as the Toliara reef south of Madagascar) and sea banks and in $\mathrm{CO}_{2}$ sink regions, and open ocean conditions. From these measurements the climatesensitive oceanic emission strengths and their contribution to stratospheric halogen and sulfur aerosol abundances will be deduced by high resolution transport modeling.

The atmospheric structure was determined by frequent radio and ozone soundings during the cruise. Other marine trace gases as e.g. nitrous oxide ( $\mathrm{N}_{2} \mathrm{O}$ ), dimethyl sulphide (DMS), oxygen $\left(\mathrm{O}_{2}\right)$ and carbon dioxide $\left(\mathrm{CO}_{2}\right)$ were investigated as well. In situ and satellite measurements of phytoplankton groups, obtained by special retrieval methods from the SCIAMACHY and GOME-2 instruments gave further information about biogeochemical conditions during the cruise. Atmospheric concentrations of a variety of long-lived anthropogenic and natural trace gases were also determined. These measurements will help to identify transport pathways of the tropospheric trace gases to and away from the ship.

Quasi-continuous measurements of a set of halocarbons, DMS, COS and $\mathrm{CO}_{2}$ in both seawater and air were carried out in order to determine actual sea to air fluxes. Additionally, we conducted direct flux measurements of $\mathrm{CO}_{2}, \mathrm{DMS}$, isoprene and acetone with the eddy covariance technique. Together with the main scientific objective of the cruise to characterize the oceanic emissions of natural halogenated and sulphuric gases in the subtropical West Indian Ocean, the participating groups followed additional research questions, which are further outlined below by the individual working groups themes (see also Table 1).

## Working Groups

1.) HALOCARBONS: Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons, in order to calculate their air-sea fluxes.
2.) OCEANIC TRACE GASES: Oceanic concentrations of DMS, $\mathrm{COS}, \mathrm{CO}_{2}$, isoprene, CO , nitrous oxide and methane, in order to understand their distribution in the different biogeochemical regimes of the western Indian Ocean and to gain new insights into halocarbon sources.
3.) EDDY COVARIANCE FLUX: Direct measurements of DMS, $\mathrm{CO}_{2}$, isoprene, and acetone airsea exchange. When combined with bulk concentration measurements, the in-situ gas transfer coefficient is derived, which can be used for other gases measured onboard.
4.) OCEAN SENSORS: Identification of carbon dioxide and oxygen sources and sinks, separation of physical and biological factors for observed sources and sinks by CTD data temperature and salinity, joint evaluation with halocarbons, in order to understand more about their sources and sinks.
5.) RADIOSOUNDING: Identification of meteorological vertical profiles, ozone and water vapor in order to evaluate the mixing layer and tropopause height and calculate air mass back trajectories to identify origin of sampled air masses and to validate transport model results and the distribution of ozone above the tropical Indian Ocean atmosphere.
6.) AIR-SAMPLING: Determination of anthropogenic and natural trace gas concentrations by flask sampling, to identify regional and diurnal gradients of some compounds and for intercalibration of different instruments
7.) MAX-DOAS: Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy in a three dimensional field and Cavity Ring Down Spectroscopy as possible decomposition products of organic trace gases and for validation of satellite-data.
8.) GHG: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (e.g. $\mathrm{CO}, \mathrm{CH}_{4}, \mathrm{O}_{3}, \mathrm{CO}_{2}$ ) in order to investigate their spatial and temporal variability in the lower tropical marine boundary layer.
9.) AEROSOL: Major ions and halogens in aerosol samples, in order to identify their sources and quantify the halogen budget in the western Pacific atmosphere.

## Participants

| Nr. | First / Sure Name | Institute/ Country | Position | Working Group |
| :---: | :---: | :---: | :---: | :---: |
| 1. | Kirstin Krüger | UiO, Oslo, Norway | Chief Scientist / Teacher | 5.), 6.) |
| 2. | Birgit Quack | GEOMAR, Kiel, Germany | Project Pl/ Teacher | 1.), 6.), 9.) |
| 3. | Christa Marandino | GEOMAR, Kiel, Germany | Co-Chief/ Teacher | 3.), 7.) |
| 4. | Tobias Steinhoff | GEOMAR, Kiel, Germany | Scientist/ Teacher | 2.), 3.), 7.) |
| 5. | Matthew Toohey | GEOMAR, Kiel, Germany | Scientist/ Teacher | 5.), 6.), 9.) |
| 6. | Matthias Krüger | GEOMAR, Kiel, Germany | Scientist/ Teacher | 4.) |
| 7. | Folkard Wittrock | IUP, Bremen, Germany | Scientist / Teacher | 7.), 8.) |
| 8. | Helmke Hepach | GEOMAR, Kiel, Germany | Scientist | 1.) |
| 9. | Gert Petrick | GEOMAR, Kiel, Germany | Technician | 1.) |
| 10. | Serge Kenny RAKOTONJANAHARY | Madagascar | Observer |  |
| 11. | Tobias Endjambi | University of Namibia, Namibia | Student |  |
| 12. | Eric Nchindo Kamwi | University of Namibia, Namibia | Student |  |
| 13. | Blessing Kamwi Kamwi | University of Cape Town, Namibia | Student |  |
| 14. | Michael Hemming | University Hamburg, Germany | Student |  |
| 15. | Kosmas Benjamin Hench | University of Oldenburg, Germany | Student |  |
| 16. | Jessica Holterhof | WMO, Geneva, Switzerland | Student |  |
| 17. | Iris Thurnherr | ETH Zürich, Switzerland | Student |  |
| 18. | Kelley Verentina Brown | Government of South Africa, South Africa | Student |  |
| 19. | Zoleka Filander | University of Cape Town, South Africa | Student |  |
| 20. | Robyn Granger | University of Cape Town, South Africa | Student |  |
| 21. | Gesa Eirund | GEOMAR, Kiel, Germany | Student |  |
| 22. | Alina Fiehn | GEOMAR, Kiel, Germany | PhD Student |  |
| 23. | Alex Zavarsky | GEOMAR, Kiel, Germany | PhD Student |  |
| 24. | Dennis Booge | GEOMAR, Kiel, Germany | PhD Student |  |
| 25. | Steffen Fuhlbrügge | GEOMAR, Kiel, Germany | PhD Student |  |

Table 1 Participants, institutions and working groups.

## Teaching program during the SO234-2 cruise

The teaching program of SO234-2 included daily lectures in the morning, practical sessions using the > instruments on board, taking part in the day and night measurements shift of the $>40 \mathrm{hr}$ station and ended in the preparation and presentation of the student work (Table 2). The studies onboard were carried out by pairs of students, one from a southern African country and one from Germany. The pairs rotated through different measurement stations: 1) meteorology, involving radiosonde launches, 2) atmospheric physics, including spectrophotometric determination of reactive trace gases in the atmosphere 3) physical oceanography, involving deep ocean profiles (CTD casts), 4) biological production including oxygen and nutrient sea water analyses, 5) biogeochemical cycling, involving gas chromatographic and mass spectrometric analysis of seawater samples, 6) atmospheric chemistry, involving air sampling of more than 50 trace gases, and 7) direct trace gas air-sea flux measurements. The student reports are given below.


Table 2: Teaching program of SO234-2.

## Work program during the SO234-2 cruise

During the SO234-2 cruise of 'RV Sonne' from 08 to 20 July 2014 in the subtropical West Indian Ocean from Durban, South Africa to Port Louis, Mauritius a variety of chemical, biological and physical parameters within the surface waters as well as between the atmospheric boundary layer and the stratosphere have been examined with different frequencies. Data and samples were obtained using a variety of analytical instruments and sampling devices (Tables 3 and 4). Regular water samples were collected from pumps submersed in the hydrographic shaft of the ship (Appendix A). Depth profiles (Appendix B) were undertaken at selected locations to investigate the vertical hydrographic structure of the water column and to obtain trace gas profiles as well as a Lagrangian drifter following the water masses at the surface was employed. Several trace gases from sea water and surface air were analyzed directly on board the ship.

The working schedule during transit included continuous sampling of seawater, a collection of discrete air samples, the installation of optical measuring techniques and the launch of weather balloons. During the cruise samples have been obtained with 44 instruments and sampling devices (Table 3). Routinely three hourly water and air samples were taken from pump supplies submersed in the hydrographic shaft, respectively installed on the monkey deck (Working Groups 1, 2, 6). Meteorologists sent weather balloons with trace gas instruments to the stratosphere (up to 30 km height) every six hours (Working Group 5).

The optical sensors and continuous instruments have been installed in the beginning of the cruise on the monkey deck, the bow and in a research container (Working Groups 3, 7, 9). Halogenated hydrocarbons have been analyzed directly on board using three different gas chromatography/ mass spectrometry systems (Working Group 1). Oxygenated trace gases and dimethyl sulfide were also analyzed directly with a gas chromatograph/mass spectrometric system from sea water (Working Group 3), while carbon dioxide and oxygen were measured immediately with sensors within the upper oceanic layer (Working group 4). More trace gases in sea water $\left(\mathrm{N}_{2} \mathrm{O}, \mathrm{CH}_{4}\right)$ will be analyzed by gas chromatography post-cruise in the laboratory. Oxygen was measured on board directly by the Winkler method and nutrient samples were frozen until analysis during SO235. Biological sampling included parameters of organic carbon and nitrogen as well as DNA, pigments, cell sizes, the amount of small cells and the composition and activity of the phytoplankton and zooplankton (Working Group 3).

Discrete air samples were taken for partners of the "Rosenstiel School of Marine and Atmospheric Sciences" in Miami and University of East Anglia (Working Groups 6 and 9). In the respective home laboratories more than 70 anthropogenic and natural trace gases, and elements in aerosols within the marine boundary layer shall be analyzed following the cruise. Atmospheric profiles of temperature, humidity and different kinds of trace gases (e.g. ozone, nitrous oxide, bromine oxide) were examined on the basis of optical measurements, and by rises of research balloons( Working Groups 5, 6, 7, 8).

Some samples taken during the cruise have been sent by air freight and are currently analyzed in the respective home laboratories, while the containers with equipment reach Kiel by beginning of October 2014. The analysis of the extensive dataset from the ocean and the atmosphere collected during SO234-2 will bring first results in summer 2015. The new
insights into the interaction of ocean and atmosphere from the subtropical West Indian Ocean will be published in peer reviewed scientific journals.

## Instruments

| Nr . | Group | Instrument/ Method | Parameter |
| :---: | :---: | :---: | :---: |
| 1 | Halocarbons | GC/MS1 | Halocarbons |
| 2 |  | GC/ED1 | Halocarbons |
| 3 |  | GC/ED2 | Halocarbons |
| 4 | Oceanic Trace Gases | GC/MS2 | DMS |
| 5 |  | Mini-CIMS | DMS/ Isoprene / Acetone |
| 6 |  | GC/ED | N2O |
| 7 | Oceansensors | Drifter with sensors | O2/CO2/fluorometer |
| 9 |  | ADCP | Currents |
| 10 |  | CTD | Salinity, Temperature, Depth |
| 11 |  | Auto-analyzer | nmolar-nutrients (uw) |
| 12 |  | Cell counter | Flow-Cytometrie |
| 13 |  | HPLC | Pigments |
| 14 |  | Sequencing | RNS |
| 15 |  | Auto-analyzer (Seal Quattro) | $\mu$ molar-nutrients ( CTD) |
| 16 |  | TOC-Analyzer | DOC/TDN |
| 20 |  | Ion chromatograph | I-/IO3- |
| 24 |  | LWCC | CDOM |
| 25 |  | Winkler Titration | Oxygen |
| 26 | Eddy Covariance Flux | APCIMS | DMS, acetone, isoprene |
| 27 |  | Licor | CO2/ Water vapor |
| 28 |  | Campbell Sonic Anemometer | 3D-wind speed and dir (2x)/ T-flux |
| 29 |  | IMU | Motion sensor (pitch and roll) |
| 30 | Radiosounding | GPS/ Kompass | Lat/long/ speed over ground |
| 31 |  | Radiosondes | T, Td, w |
| 32 |  | Ozonesondes | Ozone |
| 33 |  | Disdrometer | Precipitation/ Raindrop size |
| 34 |  | RAMSES | Radiation |
| 35 | Air sampling | weather-station | T, Td, rain, radiation |
| 36 | MAX-DOAS | canisters | long- and short lived trace gases |
| 37 |  | DOAS/ Cavity | BrO/ Nox/ Aldehyde |
| 38 | GHG | CES-DOAS | 10 |
| 39 |  | Horiba ozone monitor | ozone |
| 40 |  | OA-ICOS | N2O/CO2/CO |
| 41 | Aerosols | GC | CH 4 |
| 42 |  | aeronet/ microtop | Aerosol |
| 43 |  | cascade impactor | Aerosol Ions |
| 44 | DSHIP | DSHIP | u,v, T, P, U |

Table 3: Installed and operating instruments on board SO234-2 (Durban-Port Louis July, 08-20, 2014).

## Measurement schedule

| Group |  |  |  |  |  |  |  |  |  |  | Time of day in UTC |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| 1 | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  |
| 2 | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  | w |  |  |
| 3 | c | c | c | c | c | C | C | C | C | c | C | C | c | c | C | c | C | C | C | C | C | c | c | C |
| 4 |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5 | r |  |  | (r) |  |  | (r) |  |  | (r) |  |  | r/o |  |  | (r) |  |  | (r) |  |  | (r) |  |  |
| 6 | a |  |  | a |  |  | a |  |  | a |  |  | a |  |  | a |  |  | a |  |  | a |  |  |
| 7 |  |  |  |  |  | c | c | c | c | c | C | c | c | c | c | c | c | c | c | c |  |  |  |  |
| 8 | c | c | C | C | C | C | C | C | C | C | C | c | C | c | C | c | C | C | C | c | c | c | C | C |
| 9 | c | c | c | c | c | c | c | c | c | c | c | c | c | c | c | c | c | C | c | C | C | c | c | c |

c: continuous
w: water sample
r: radiosonde
a: air sample
o: ozonesonde

Table 4: Underway measurement plan and sampling strategy on board FS Sonne.

## Student reports

1) Oceanic trace gases - GC-MS measurements
2) Eddy Covariance measurements
3) CTD/rosette bottle sampling
4) DOC and DIC measurements
5) Dissolved oxygen profiles from titrated samples
6) Dissolved oxygen in surface waters - underway sampling
7) CDOM
8) Meteorological measurements

## 1) Oceanic trace gases - GC-MS measurements

## Gesa Eirund and Dennis Booge

In order to study gas producing material in the upper ocean, the contribution of phytoplankton and bacteria as well as eventually biogenic produced gases were investigated.

To identify certain groups of phytoplankton and bacteria, pigment filtration and flow cytometry analysis were performed (Figure 1). Results will be gained from lab analysis later on.


Figure 1 Filtration and flow cytometry.
We also improved a purge and trap technique coupled with a GC-MS (Figure 2) to measure different non-methane hydrocarbons (NMHCs) in seawater. In addition we developed a method to quantify different NMHCs (e.g. isoprene, dimethylsulfide (DMS)) in one measurement. With this analysis of volatile trace gases it is possible to study the surface ocean cycling and air-sea exchange in order to understand their impact on the chemistry of the atmosphere.


Figure 2 GC-MS coupled with a purge and trap technique.

During a 48 h -station we performed 8 CTD-Stations. Samples were taken from 5 m to about 100 m depth in order to get information about a potential diurnal cycle in isoprene and DMS concentrations during 2 days in the euphotic zone.

The results show a slight correlation of isoprene-concentrations with chl-a (Figure 3). Even we were following with a drifter the same water mass in the upper 20 meters, the water mass below 30 m changed during the 48 h -stations after noon of the first day, which could be seen in a different profile of DMS concentrations (Figure 4).


Figure 3 Ocean profiles from isoprene ( $\mathrm{pmol} \mathrm{L}^{-1}$ ) and chl-a ( X 120 ) concentrations.


Figure 4 Ocean profiles from DMS ( $\mathrm{nmol} \mathrm{L} \mathrm{L}^{-1}$ ) concentrations on two different days.

## 2) Eddy Covariance measurements

Alexander Zavarsky

## Motivation

In order to investigate the ocean's role in the atmospheric budget of climate active trace gases, we deployed an eddy covariance (EC) direct flux measurement system onboard RV Sonne. EC can be used to perform biogeochemical cycling measurements without typical pitfalls associated with bulk flux calculations, as well as to constrain the main forcings on airsea gas exchange. Using the direct flux ( $F$ ), $F=\rho\left\langle w^{\prime} c^{\prime}\right\rangle$, from EC, we can attempt to improve the gas transfer parameterization (k) used in bulk formulas, $F=(H C w-C a)$, where $\rho$ is density, $w^{\prime}$ are the fast fluctuations in vertical wind speed, $c^{\prime}$ are the fast fluctuations in atmospheric gas concentrations (brackets denote time average), $\mathrm{C}_{\mathrm{w}}$ and $\mathrm{C}_{\mathrm{a}}$ are water and air concentrations, respectively, and H is the Henry's law solubility constant. My goal was to measure dimethylsulfide (DMS), isoprene and acetone flux. Measurements started at DOY 196 12:00 UTC (-29.62444288 LAT 58.58830401 LON) and continued until Port Louis.

## Instrumentation

Atmospheric levels of DMS, isoprene and acetone were measured using an atmospheric pressure chemical ionization mass spectrometer (AP-CIMS). Air was sampled through a $1 / 21$ tube from a mast welded to the bow (approximately 10 m above the sea surface) at a flow rate of $70 \mathrm{I} \mathrm{min}^{-1}$. To obtain turbulent wind speed measurements and sensible heat flux, a sonic anemometer was placed at the bow mast. A GPS and inertial navigation system (INS) was used for motion correction (Figure 1).


Figure 1 Set-up of instruments onboard of SO234-2, Durban South Africa.

## Preliminary results:

## Bulk air concentrations

All three trace gases, isoprene, DMS and acetone, show relatively low bulk concentrations (Figure 2). This is in accordance to findings of the report by Gesa Eirund and Dennis Booge, which report very low water concentrations of respective gases. A daily cycle, due to photolysis (sunlight creates OH which oxidizes isoprene), of isoprene can be seen.


Figure 2 Bulk air concentrations of isoprene, DMS and acetone (in ppt).

## Wind spectrum

Figure 3 shows a sample power spectrum of vertical wind speed. It reveals good agreement with the Kaimal turbulent wind spectrum. Still the motion peak at around 0.1 Hz has to be removed using data from the IMU.


Figure 3 Power spectrum of vertical wind speed.

## Trace gas spectrum

Figure 4 shows a sample spectrum of the fluctuations of acetone. However, this spectrum is promising; still an improvement of sensitivity of the mass spectrometer is needed to get good data to perform the correlation with wind data for flux calculations.


Figure 4 Power spectrum of acetone measurements.

## 3) CTD/rosette bottle sampling

Kelley Brown and Eric Kamwi Nchindo

## Introduction

During the 48 hour station, the two of us took part in profiling the ocean using the CTD/Rosette sampler. We took turns through shift work, in which we were both able to be part of four deployments each.

The CTD instrument is an acronym for Conductivity, Temperature and Depth instrument. It measures these parameters throughout the water column, during casts. The CTD is situated below the Rosette bottles, which is triggered to close, using the software, to collect water samples at given depths. From the first CTD's conducted at the beginning of the cruise, graphs were drawn, using Microsoft Excel, to view what was being observed throughout the water column.

## Preliminary results

Below is the graph (Figure 1) for temperature and the 4 casts displayed the same profile. An observation is made that surface temperature moderate for the Indian Ocean. The lowest and highest temperatures are approximately at 21 and $24{ }^{\circ} \mathrm{C}$, respectively. The possible reason for Cast 1 having a slightly warmer temperature above 500 m could be because of the Mozambican current.


Figure 1 Water temperature $\left({ }^{\circ} \mathrm{C}\right)$ versus ocean depth (m).
Figure 2 depicts temperature vs. salinity. It was observed that on the surface salinity was relatively high and this was due to high temperature. High temperature results in high
evaporation on the surface of course precipitation also played a role since we experienced just showers for some seconds, hence this did not alter the salt concentration on the surface. In addition to this, salinity decreased (observed) with increase in depth.


Figure 2 Water temperature ( ${ }^{\circ} \mathrm{C}$ ) versus salinity ( psu ).

Figure 3 is the graph that shows oxygen vs. depth (all the 4 casts displayed the same profile). We observed that oxygen concentration was high on the surface, why? This was due to primary production occurring tin the photic zone. So oxygen level decreased with increase in depth, hence a non-linear relationship was observed. However, oxygen concentration level was high again in deeper water because the deep layer is rich in oxygen due to water that is derived from the cold surface waters which sank (convection) to the bottom. Consumption is low because there are fewer organisms and less decay consuming oxygen.


Figure 3 Oxygen ( $\mu \mathrm{mol} / \mathrm{Kg}$ ) versus ocean depth (m).

Figure 4 shows fluorescence versus ocean depth. High Fluorescence concentration was observed on the surface due to primary production in the photic zone. Cast 2 and 4 displayed a high concentration level because we were close to the coast of Madagascar otherwise the other two displayed almost the same profile.


Figure 4 Fluorescence (chl-a indicator) versus ocean depth (m).

## 4) DOC and DIC measurements

Zoleka Filander and Iris Thurnherr

# DOC and DIC measurements during the SO234-2 SPACES on FS Sonne in the Southern Indian Ocean. 

By<br>Zoleka Filander<br>Offshore Benthic Ecologist at DEA, South Africa<br>and<br>Iris Thurnherr<br>MSC at ETH Zurich, Switzerland

Port Louis, Mauritius, July 19, 2014

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## 1 Introduction

It is no secret that the climate is dramatically changing globally due to anthropogenic activities. With atmospheric carbon dioxide increasing at an exponential rate it is prominent to understand the distribution and pathways taken by such an influential gas. Sea-Air interactions of most oceans have been examined and datasets analyzed. However, the Indian Ocean has received little attention over the years; and paucity on how this mass is responding to climate change still exists; especially in the Southern Indian Ocean (SIBER, 2009).
This cruise thereby aimed to evaluate the biogeochemical and atmospheric statuses of various gases in the Southern Indian Ocean, and this report will emphasize on the carbon.
Carbon is transported through different mediums (land, oceans and atmosphere) by a phenomenon referred to as the carbon cycle. In marine environments carbon is extracted from the atmosphere in an inorganic form (Dissolved Inorganic Carbon - DIC) where photosynthesis converts it to a carbohydrate with assistance of sunlight and other gases, i.e. oxygen. There are various sources that affect the concentrations DIC in the ocean such as temperature or ocean circulation. This inorganic form is thereafter found in biomass as an organic form that can be classified as either dissolved Organic Carbon (DOC) or particulate organic carbon (POC). These classes are based on size i.e. $\mathrm{POC}>=0.45 \mu \mathrm{~m}$ and $\mathrm{DOC}<=0.45 \mu \mathrm{~m}$ (Dafner et al., 2002). As in DIC, there are some sources that influence DOC. They include freshwater input, rainfall input, sedimentation etc. Both phases find their way to greater depths of the ocean.

## 2 Data and Methods

### 2.1 DOC Analysis

. DOC samples were collected from a CTD that was casted at a 6-hour interval. All samples were from shallow depths $(<100 \mathrm{~m})$ due to the high abundance of species found. Samples were then taken to the lab where 20 ml was filtered into a glass bottle. Thereafter, $8 \mu l$ of phosphoric acid was added to stabilize the gas. Bottles were then flamed sealed, and refrigerated. Analyses to be undertaken in Germany (Kiel) using a high-temperature catalytic oxidative technique (HTC). Thus, no data was available to present on the cruise.

### 2.2 DIC (Dissolved Inorganic Carbon)

$p \mathrm{CO}_{2}$ is a form of DIC, and this gas was measured from the under way system which ran at 3 hour intervals from the 10-18th July and a drifter that was operated for the 48 -hrs station. The gas was measure using a $\mathrm{CO}_{2}$ sensor which pumps the air till its dry and then passes the dry air through an infrared detector. No laboratory analysis was needed. No calibration of the data was done. Therefore preliminary results were presented on the cruise.

## 3 Preliminary Results

The partial pressure of $\mathrm{CO}_{2}$ in the surface water $\left(\mathrm{pCO}_{2}^{o}\right)$ from the underway and drifter measurement, the equilibration temperature of the underway surface water (SST) and the partial pressure of $\mathrm{CO}_{2}$ in the atmosphere $\left(p \mathrm{CO}_{2}^{a}\right)$ are shown in this section. Figure 1 shows the time series from the 10.to 18.7 .14 for the $p C O_{2}^{o}, p C O_{2}^{a}$ and SST. $p C O_{2}^{a}$ was
more or less constant during these days at a value of $386 \mathrm{ppm} . p C O_{2}^{a}$ shows values from 350 to 378 ppm (the very high and low peaks show calibration measurements). From the 15.7. 17 pm to the end of the time series $p C O_{2}^{o}$ is measured on the drifter.Around the 12.7.14, when the cruise was near the southern tip of Madagascar, the $p C O_{2}^{o}$ highest. During the drifter measurement $p \mathrm{CO}_{2}^{o}$ is relatively constant. The atmospheric values of pCO 2 are higher the the oceanic values of $p \mathrm{CO}_{2}$ during the whole time window. The SST decreased from around $25^{\circ} \mathrm{C}$ in the beginning to around $19^{\circ} \mathrm{C}$ at the end. The temperature seems to follow the decrease in oceanic $p \mathrm{CO}_{2}$ from 12. -15.7.14 but shows more variability than $p \mathrm{CO}_{2}^{o}$ from the 14. to 18 . of July.


Figure 1: Time series of partial pressure of $\mathrm{CO}_{2}$ of the surface water ( $\mathrm{pCO} \mathrm{O}_{2}^{o}$, dark blue) and atmosphere ( $\mathrm{pCO} \mathrm{C}_{2}^{a}$, bright blue) and sea surface temperature (SST, green). SST measured from underway water, $p C O_{2}^{o}$ data from underway measurement apart from the section marked with Drifter: The drifter data was measured on the drifter during the 48-hrs station.

As a rough estimate, the temperature dependence of $p \mathrm{CO}_{2}^{o}$ was calculated using the well known physical relationship between temperature and $p \mathrm{CO}_{2}$ (see Appendix). Figure 2 and three show the analysis of this relationship. The cruise was divided into two part for this analysis. The part west of $45^{\circ} E$ where the water masses are within the Mozambique channel and the part east of $45^{\circ} \mathrm{E}$ where the water masses are influenced by the circulation east of Madagascar. The "temperature dependent" $p \mathrm{CO}_{2}$ corresponds to the partial pressure of $\mathrm{CO}_{2}$ in the water if $p \mathrm{CO}_{2}^{o}$ was only dependent on temperature. This means that the measured $p \mathrm{CO} O_{2}^{o}$ and the temperature dependent $p C O_{2}^{o}$ overlay in cause measure $p C O_{2}^{o}$ depends only on temperature.

Figure 2 shows the analysis for the first part of the cruise. The temperature dependent $p C O_{2}^{o}$
shows a different time line than the measured $p \mathrm{CO}_{2}^{o}$. The temperature independent part which is the counterpart to the temperature dependent part should be the same as the temperature dependent part after it is mirrored on the measured $p \mathrm{CO}_{2}^{o}$. This is not the case in figure 2 .
Figure 3 shows the second part of cruise. The temperature dependent $p \mathrm{CO}_{2}^{o}$ and measured $p \mathrm{CO}_{2}^{o}$ do not overlay. Contrary to figure 2 the temperature independent and dependent $p \mathrm{CO}_{2}^{o}$ are mirrored along measured $p \mathrm{CO}_{2}^{o}$.


Figure 2: Time series of measured (red), temperature dependent(blue) and temperature independent(green) $p \mathrm{CO} O_{2}^{\circ}$ west of $45^{\circ} \mathrm{E}$.


Figure 3: Time series of measured (red), temperature dependent(blue) and temperature independent(green) $p \mathrm{CO} O_{2}^{\circ}$ east of $45^{\circ} \mathrm{E}$.

## 4 Discussion

Atmospheric $p \mathrm{CO}_{2}$ versus oceanic $p \mathrm{CO}_{2}$ :
The $p C O_{2}^{a}$ is larger than $p C O_{2}^{a}$ over the whole time series. This indicates that the Indian Ocean on the cruise track is a $\mathrm{CO}_{2}$ sink. Especially during the drifter measurement, the $\mathrm{CO}_{2}$ sink is strong. The decrease of SST simultaneously with the decrease of $p \mathrm{CO} \mathrm{O}_{2}^{o}$ could indicate a temperature dependence of $p \mathrm{CO}_{2}^{\circ}$. But the fluctuations of the SST from 14. - 15.7.14. do not agree support this hypothesis. The analysis of the temperature dependence in figure 2 and 3 show that temperature is not the only factor influencing $p \mathrm{CO}_{2}^{o}$ because the measured and temperature dependent $p \mathrm{CO}_{2}^{o}$ do not overlay each other. The mismatch of the temperature dependent and independent $p \mathrm{CO}_{2}^{o}$ during the first part of the cruise might be due to calculation errors or a mismatch of the time axis.

## 5 Further Studies

Temperature is not the only factor influencing $p \mathrm{CO}_{2}^{\circ}$. Thus the investigation of other parameters might give some more insights into the processes behind the measured $p \mathrm{CO}_{2}^{\circ}$. Possible parameters are biology (e.g. phytoplankton blooms), Circulation, DOC, pH of the seawater, Oxygen and Salinity.

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## 7 Appendix

Formula to calculate oceanic $p \mathrm{CO}_{2}$ depending on temperature

$$
p \mathrm{CO}_{2}^{\text {dep }}=\overline{p C O_{2}} \cdot \exp \left(0.0423 \cdot\left(T_{\text {meas }}-\text { Tmean }\right)\right)
$$

and the oceanic $p \mathrm{CO}_{2}$ if temperature had no influence

$$
p C O_{2}^{\text {indep }}=p C O_{2} \cdot \exp \left(0.0423 \cdot\left(T_{\text {mean }}-\text { Tmeas }\right)\right)
$$

. Where $\overline{p \mathrm{CO}_{2}}$ is the mean $p \mathrm{CO}_{2}$ over the calculation time, $T_{\text {meas }}$ the measured temperature and $T_{\text {mean }}$ the mean temperature over the calculation time.

## 5) Dissolved oxygen profiles from titrated samples

Tobias Endjambi and Blessing K. Kamwi

## Introduction

The southern Indian Ocean is characterized by different water masses/current that influences the vertical mixing of water. However there little is published on the phenomena that are happening in this area. To understand this, more extensive studies need to be done.

This exertion of the project was aimed at determining the oxygen profile at predetermined sampling stations in the Southern Indian Ocean, between Durban - South Madagascar Mauritius (Figure 1). Furthermore this work compared the CTD profile undertaken during the cruise to the titrated samples for calibration purpose. In addition to that, we compared the oxygen concentration during the day to the concentration of oxygen during the night


Figure 1 Proposed SO234-2 cruise track.

## Materials and methods

Samples for oxygen where taken at predetermined CTD sampling stations along the cruise track. The oxygen samples were drawn into clear bottles (labelled with different "BedfordNo") from the niskin bottles and treated immediately with sodium hydroxide and magnesium chloride then mixed by shaking for about 30 seconds before they were taken to the laboratory for analysis. Samples were covered with a cloth to prevent further photosynthesis process by phytoplankton while allowing the solution to precipitate and settle at the bottom at least for 30 minutes.


Figure 2 A TITRONIC ${ }^{\circ}$ universal Piston Burette used for titration.

A TITRONIC universal Piston Burette set was used for sample analysis (titration) and the following procedures were followed as shown in Table 1 below.

Table 1 sample analysis procedures:

## Standardization

- 50 ml deionized $\mathrm{H}_{2} \mathrm{O}$ into a glass beaker
- Add 1 ml of $50 \%-\mathrm{H}_{2} \mathrm{SO} 4$
- Switch on the stirrer
- Add NaOH
- Add $\mathrm{MnCL}_{2}$
- Add 10 ml iodate $\mathrm{KH}(\mathrm{IO})_{2}$
- Titrate with Na -thiosulphate until it turn pale yellow
- Add 1 ml of starch
- Titrate until it become clear
- NB: note down the reading on the piston burette


## Sample (bottles) titration

- Open the sample bottle and add a magnet (make sure the stirrer is off)
- Add 1 ml of $50 \%-\mathrm{H}_{2} \mathrm{SO} 4$
- Turn the magnetic stirrer on
- Titrate with Na-thiosulphate until the color turn pale yellow
- Add starch and titrate until the solution become clear
- NB: note down the reading on the piston burette


## Determination of oxygen concentration

Calculation of oxygen concentration was done following Winkler (1988)
$\mathrm{O}_{2}(\mu \mathrm{~mol} / \mathrm{L})=a \cdot f \cdot 500 /(b-2)$
$f=\frac{5}{v(m L)}$
$f$ - is the ...factor
$a$ - is the volume of the titrated Na -thiosulphate (bottle sample)
$b$ - is the volume of the bottle sample
$v$ - is the volume of the titrated Na -thiosulphate (standard)
The units ( $\mu \mathrm{mol} / \mathrm{L}$ ) of oxygen concentration were changed to ( $\mu \mathrm{mol} / \mathrm{Kg}$ ) as follow:

$$
\mu \mathrm{mol} / \mathrm{Kg}=\frac{(\mu \mathrm{mol} / \mathrm{L})}{\text { Density }(\mathrm{Kg} / \mathrm{L})}
$$

## Results and Discussion

The dissolved oxygen concentration from the six stations along the SO234-2 cruise track was determined. The CTD oxygen data from the sensor was compared to the oxygen titrated using the Winkler method. The dissolved oxygen determined from the Winkler method was converted to $\mu \mathrm{mol} / \mathrm{kg}$ for better comparison with the CDT data. The dissolved oxygen from both the CDT and the Winkler method show similar oxygen profile patterns (Figure 3 and 4).

Station one was in the Mozambique Channel and shows an oxygen maximum of CDT (192.05 $\mu \mathrm{mol} / \mathrm{kg}$ ) and Winkler ( $217.09 \mu \mathrm{~mol} / \mathrm{kg}$ ) between the depth of $10-500 \mathrm{~m}$ (Figure 3). This oxygen maximum is also depicted in stations 2 at the depth of approximately 500 m . It is also important to note that station 2 was close to the continental shelf of Madagascar where there is primary productivity. This oxygen maximum was also evident at station 3 at the same depth of 500 m . Station 4 is along the southwest Indian ridge, at this station the oxygen maxima was deeper ( 600 m ) compared to the other stations (Figure 4). This oxygen maximum along these four stations may be due to the Antarctic Intermediate Water which is reach in oxygen travelling northwards (Tomczak and Godfrey, 1994). The oxygen maxima are also observed to be sinking to deeper depth as you follow the cruise track eastward.

All four stations depict an oxygen minima zone at the depth between $1000-1300 \mathrm{~m}$ conversely as you move south east along the cruise track, the oxygen minima zone get deeper (Figure 3 and 4). These oxygen minima may be due to aged water mass which is isolated and becomes warmer. According to Rogers (2000), the Indian Ocean has an intense intermediate-depth oxygen minima zone. The oxygen concentration tend to be higher at the bottom, this may be due to the influence of Antarctic Bottom Water (AABW) water mass which flows from the Weddell Bay into the Indian Ocean at through the gap of the southwest Indian ridge and the Madagascar basin (Thomas et al., 1998).


Figure 3 Oxygen profiles from station 1 and 2 along the SO234-2.


Figure 4 Oxygen profiles from station 3 and 4 along the SO234-2.

## The 48 hours station

Along the 48 hours station eight different casts were taken with the CDT following the drifter deployed on the $16^{\text {th }}$ of July 2014. Two casts were made at midnight and two were made at mid-noon. The oxygen levels were measured at all the casts. Figure 5 shows the midnight and mid-noon oxygen profile from the Winkler method. This depicts higher oxygen levels during midnight then during mid-noon. This may be due to errors during the titration of oxygen as the levels were expected to be higher during noon due to photosynthesis.

## Day and nigth schedule



Figure 5 Day and night oxygen profile along two stations 5 and 7.

## The CTD and Winkler offset

The offset between the CTD and Winkler were determined by subtracting the CTD data from the Winkler data and then expressed in percentage as shown in figure 6. The offset increased with increasing depth. The offset is approximately $15 \%$, this is due to the calibration of the CTD or due to pressure.


Figure 6 Offset between Oxygen -sensor on CTD and direct oxygen-determination by Winkler.

## Conclusion

There appear to be a low oxygen minima zone along the cruise tracks whereas the oxygen maximum is between the depths of $100-1000 \mathrm{~m}$. This is influenced by different water masses. The oxygen levels tend to be deeper from station to station and follows a water mass. Therefore further studies should investigate the spatial and temporal variation. Comparison with other parameters such chlorophyll a and salinity and the physical dynamics of the South West Indian Ocean.

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## 6) Dissolved oxygen in surface waters - underway sampling

Robyn Granger and Jessica Holterhof
$\mathrm{O}_{2}$ is pivotal in the biogeochemical cycling of carbon, nitrogen, and others ( $\mathrm{P}, \mathrm{Fe}, \mathrm{Mn}$, etc.), and fundamental for all aerobic life. Oxygen concentrations in seawater are mainly controlled by fluxes through the air-sea interface, by biological assimilation and dissimilation, and the dynamical motion and mixing of water (Hansen, 2007).

At present, dynamics of the Indian Ocean are sparsely documented. The SO234-2 cruise therefore presents new dissolved $\mathrm{O}_{2}$ data in this seasonally variable region.

## SETTING

The Southwest Indian Ocean circulation is affected by multiple water masses, including the Southeast Madagascar Current (SEMC) and the Antarctic Circumpolar Current (ACC) waters, the former of which plays a large role in the region explored during the cruise. The winddriven, anticyclonic circulation of the Southern Indian Ocean shows two persistent features a large basin-wide circulation and a well-developed subgyre west of the Madagascar Ridge.

The ACC transports cold $\mathrm{O}_{2}$-rich bottom water in the thermohaline circulation northwards into the northern Indian Ocean. The water circulates in the Northern Hemisphere, and returns as intermediate/surface water to the southern Indian Ocean. The South Indian gyre then recirculates the water masses in the western and central parts of the basin (Stramma and Lutjeharms, 1997).


Figure 1 Schematic overview of the flow field in the South Indian Ocean (Stramma and Lutjeharms, 1997).

## METHODOLOGY

Measurements were mainly taken with an $\mathrm{O}_{2}$ optode that was installed on board of the ship. During the 40h station, the optode was deployed onto the drifter. For the in situ detection of oxygen, the optode provides a good method for measurement, as it is based on the ability of oxygen to act as a luminescence quencher (Tengberg et al., 2006). The higher the
concentration of oxygen in the water, the lower the luminescence reaction detected within the optode.
Additionally, underway samples and the uppermost 5-10 m samples of the CTD from the first four stations of cruise SO234-2 were taken into account. $\mathrm{O}_{2}$ concentrations for those samples were measured with the Winkler Titration method. The Winkler Titration is a multistep oxidation-reduction process that enables the calculation of actual oxygen concentration values within the water samples (Hansen, 2007). Through the use of multiple detectors such as the Winkler Titration of underway and CTD samples and the $\mathrm{O}_{2}$ optode, higher accuracy could be established of the dissolved oxygen using the following formula: $y=0.615^{*} x+76.498$. The calibration enabled the correction of the $\mathrm{O}_{2}$ optode data.

## RESULTS/MEASUREMENTS

The data taken represent the dissolved oxygen values in surface waters of the southern Indian Ocean, and a focus was set on the sampling of underway measurements in the top few meters of the ocean. In general, surface layers may often become saturated and sometimes slightly over-saturated due to air-sea exchange of oxygen, photosynthesis, respiration and oxidation of organic matters (Miyake and Saruhashi, 1966).


Figure 2 Dissolved $\mathrm{O}_{2}$ measurements using the Optode from 9-15 July 2014. The scale on the right side shows amounts of $\mathrm{O}_{2}$ concentrations in $\mu \mathrm{mol} / \mathrm{L}$.

Figure 2 displays the calibrated dissolved $\mathrm{O}_{2}$ concentration, which is shown to be increasing towards the southeast of the research area. Lower values can be detected in the coastal regions surrounding the southernmost tip of Madagascar. This is consistent with the underway titration $\mathrm{O}_{2}$ measurements taken within the region of the 40 hr station (at approximately $30^{\circ} \mathrm{S}$ and $60^{\circ} \mathrm{E}$ ), as they show amounts well above $230 \mu \mathrm{~mol} / \mathrm{L}$ as well. The $\mathrm{O}_{2}$ values were then used to calculate the oxygen saturation (see Figure 3 ), where results indicate a similar trend. The data suggest a slight over-saturation in the overall sampling area.

Variations in surface temperature, taken from approximately 6 m water depth using the equilibrator on board, seem to correlate with the $\mathrm{O}_{2}$ saturation data. As one moves further southeast into the gyre, temperatures decrease with a sharp gradient occurring at about $48^{\circ}$ E.


Figure 3 The uppermost figure displays the $\mathrm{O}_{2}$ saturation in \%, and the lower image shows the surface temperatures in ${ }^{\circ} \mathrm{C}$.

## REMARKS

The complex current circulation within the region gives rise to interesting physical surface properties. Changes in absolute dissolved $\mathrm{O}_{2}$ and $\mathrm{O}_{2}$ saturation could be due to the influence of the SEMC, which is in turn effected by the bathymetric profile to the south of Madagascar. Biological activity is generally considered to be an important forcing mechanism with regard to changes in dissolved $\mathrm{O}_{2}$. Whether this is the case in the southwest Indian Ocean remains to be seen, and would make for further studies.

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## 7) CDOM

## Alina Fiehn and Kosmas Hench

## What is CDOM?

Chromophoric dissolved organic matter (CDOM) is the fraction of DOM that interacts with solar radiation (280-700 nm). A fraction of it is fluorescent.

Sources of oceanic CDOM include Terrestrial humic materials from rivers and runoff as well as autochthonous production from microbial Metabolism in the open ocean. The CDOM from terrestrial sources is mostly removed in the coastal zone. CDOM production in the open ocean is a byproduct of the metabolism of zooplankton, dinoflaggelates, and macroalgae. The main sink of CDOM is in the ocean is solar bleaching. CDOM is degraded by photolysis and therefore influences the underwater radiation budget. This also means that the ocean color is greatly influenced by its CDOM content.

The absorption of light by CDOM also has implications for photochemistry and -biology in the ocean. On the one hand it limits the amount of accessible light in the visible spectral range; on the other hand it functions as a protection against UV radiation for plankton.

## Why do we measure CDOM?

Ocean color based satellite remote sensing of chlorophyll and primary productivity is biased by the CDOM fingerprint of the water color. For calibration reference measurements are necessary.

The degradation of CDOM by UV light results in the formation of trace gases. These include COS, $\mathrm{CS}_{2}$, OVOCs, formaldehyde, acetone, acetaldehyde, alkanes and alkenes (e.g. isoprene). Therefore CDOM plays a vital role in the air-sea exchange of trace gases.

## Measurement

CDOM can be optically quantified by spectrometry. A mass quantification is not possible yet, but the absorption coefficient correlates with the quantity. Still, the absorption is relative to exact composition of CDOM.


Figure 1 Absorption spectra of CDOM.

Figure 1 shows two measured absorption spectra of CDOM of this cruise. A typical spectrum has a maximum between 230 and 250 nm and then falls exponentially to a base value. In order to compare the different spectra this base value at about 700 nm and the absorption coefficient close to the maximum value are determined. The abundance of CDOM is then relative to the difference between those two values.


Figure 2 Abundance of CDOM from underway measurements.

The abundance of CDOM in terms of absorption has been determined for all underway samples from SO234-2 so far. The results are depicted in Figure 2. Normally the amount of CDOM in the surface waters is high close to the coast and decreases towards the open ocean. Figure 2 shows the lowest values close to the reef south of Madagascar and higher values in the open ocean.

CDOM abundances have also been determined for the CTD casts during SO234-2. Figure 3 shows the profiles of CDOM and isoprene from the 7 CTD casts of the 48 h station. The abundance of CDOM declined slightly with depth in the first 500m. In greater depths the abundance remained constant. This goes in accordance with the expectations as major depletion of CDOM by photolysis can only take place in surface water masses. As CDOM presents a precursor to isoprene, a relationship of the abundance of CDOM and isoprene would be plausible - yet after preliminary analysis of the CTD casts no such relation could be detected.


Figure 3 CTD profiles of CDOM (red) and isoprene (dashed) for the seven casts from the 48h station.

## Classification of CDOM

A classification of the type of CDOM and its source is possible by analyzing the spectra as well. The absorption spectra can be approximated using the following formula, where $\mathrm{a}_{\text {CDOM }}$ is the absorption coefficient, S is the exponential slope parameter and $\lambda_{0}$ is a reference wavelength:

$$
\mathrm{a}_{\mathrm{CDOM}}(\lambda)=\mathrm{a}_{\mathrm{CDOM}}\left(\lambda_{0}\right) \mathrm{e}^{-\mathrm{S}\left(\lambda-\lambda_{0}\right)}
$$

The slope parameter can be calculated by a linear fit through the logarithmic spectrum and is used to classify the CDOM. Figure 4 shows CDOM absorption spectra from different regions. Lower slope values correspond to coastal waters with high amounts of terrestrial sourced CDOM and open ocean waters show higher slope parameter values (Nelson \& Siegel, 2013).


Figure 4 CDOM spectra from different locations on the globe with normal (left) and logarithmic (right) $y$-axes. The slope of the spectrum helps classifying the type of CDOM (Nelson \& Siegel, 2013).

This method of classification has been applied to some of the CDOM spectra obtained during SO234-2. Figure 5 shows two spectra from underway measurements (black and grey) and two spectra from CTD casts (blue and red). The underway probes have been taken close to the coast of Madagascar, the CTD probes are from the 48 h station in the open ocean. The slope parameters for all spectra have been determined and are noted in the legend of the right figure. We find that the coastal spectra have higher slope values than the underway spectra from coastal waters. This corresponds to the results from Nelson and Siegel (2013).


Figure 5 Absorption spectra of CDOM from four SO234-2 CDOM measurements in linear (left) and logarithmic (right) scale. The values of the slope parameter have been determined with a linear fit.

## References

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## 8) Meteorological measurements

Steffen Fuhlbrügge, and Michael Hemming

## Introduction

34 radiosondes have been launched to date (19.07.2014, 15:00 UTC). Launch locations and horizontal flight tracks are shown in Figure 1.


Figure 1 (left) Radiosonde launch locations (circles) and horizontal trajectories for launches from 8-18 July. (right) Zonal wind speed ( $\mathrm{m} / \mathrm{s}$ ) derived from the radiosonde launches as a function of height. Cold-point tropopause heights (km) shown by markers.

Data from the radiosondes shows a high tropical cold-point tropopause at around 17 km (stars in Figure 1, right). Maximum zonal wind speeds are found a few km below the tropopause, and show a strong gradient with respect to the latitude of launch. At southernmost launch latitude, south of $\sim 28^{\circ} \mathrm{S}$, we find strong zonal winds of $\sim 80 \mathrm{~m} / \mathrm{s}$. Northward of this threshold, we find weaker maximum zonal wind speeds of $30-50 \mathrm{~m} / \mathrm{s}$.

During the portion of the cruise track closest to the Madagascarian coast, radiosondes were launched at a 3 -hourly frequency. Winds measured by these sondes show a strong wind shear in the lower troposphere, with north-easterly winds at the surface and south-westerly winds beginning at $2-5 \mathrm{~km}$ height. Figure 1 (right), which shows the zonal wind as a function of height, shows this feature for sonde launches 7-18.

A sharp gradient in the relative humidity profiles is found between 2-4 km height (not shown). Here the relative humidity decreases from $>80 \%$ to $15-30 \%$. However this gradient does not mark the upper limit of the atmospheric boundary layer per se. The moist layers up to 4 km are air masses that have been advected and do not interact with the surface by turbulent mixing processes. The mean atmospheric boundary layer height determined from the radiosonde profiles of temperature, humidity and wind is $\sim 0.8 \mathrm{~km}$ during the cruise.

Two ozonesonde launches have been performed. Due to a failure of the GPS on the first launch, altitude and position (therefore winds) are missing from the data of the first flight. Approximate heights have been estimated by comparing the measured temperature profile to the profile measured via radiosonde 6 hours earlier.

Preliminary profiles of ozone vs. height for the two ozonesonde launches are shown in Figure 2.


Figure 2 Preliminary ozone profiles (ppbv) from ozonesonde launches on 16.07.2014 and 18.07.2014. Ozone values shown in (right) linear and (left) log scales to highlight stratospheric and tropospheric values, respectively.

Surface meteorological fields measured by the ship's instruments are being collected and archived. Surface pressure, temperature, humidity and wind speed for a portion of the cruise are shown in Figure 3.


Figure 3 Surface meteorological fields as measured and archived by the Sonne systems.

## Working groups reports

1.) HALOCARBONS
2.) OCEANIC TRACE GASES
3.) EDDY COVARIANCE - TRACE GASES
4.) OCEANSENSORS
5.) RADIOSOUNDING
6.) AIR-SAMPLING
7.) MAX-DOAS
8.) GHG
9.) AEROSOL

## 1) Halocarbons in surface and deep water

Helmke Hepach, Gert Petrick, Birgit Quack (PI) (GEOMAR, Kiel, Germany)

## Background

Halocarbons are hydrocarbons in which one or more hydrogen atoms are replaced by one or more halogens. Some halocarbons are produced naturally in the oceans. Although it is commonly acknowledged that many of these compounds have a biological origin with distinct maxima in the chlorophyll a (Chl a) maximum, their cycling within the water column is still poorly understood. Other production pathways such as photochemical formation might play a significant role. Once the halocarbons are transported into the troposphere from the sea surface by air-sea gas exchange, they have very short lifetimes of less than 120 days. Bromoform $\left(\mathrm{CHBr}_{3}\right)$ and dibromomethane $\left(\mathrm{CH}_{2} \mathrm{Br}_{2}\right)$ are together the biggest carriers of organic bromine into the atmosphere, while $\mathrm{CH}_{3} \mathrm{l}$ is the most abundant organoiodine. The tropical ocean is a key region with respect to atmospheric transport processes: tropical deep convection can carry these compounds despite their short lifetimes into the stratosphere where they can deplete ozone much more effectively than chlorine. Additionally, diiodomethane $\left(\mathrm{CH}_{2} \mathrm{I}_{2}\right)$ and chloroiodomethane $\left(\mathrm{CH}_{2} \mathrm{ClI}\right)$ have recently been suggested to be similarly important for the organic iodine loading of the troposphere as CH3I. These compounds are involved in numerous chemical cycles within the atmosphere with iodinated compounds even participating in aerosol formation.

So far, large data gaps with respect to halocarbons exist in the Indian Ocean. Very few studies have focused on this region, although it might be of large importance for convective transport processes. The measurements of halocarbons during the SO234-2 cruise are the first measurements of these compounds in this region. They will help to characterize this area with respect to the global oceanic distribution of these compounds, and the contribution of the Indian Ocean to the stratospheric organic halogen loading.

## Material and methods

Halocarbons onboard the RV Sonne were measured directly after sampling. Discrete samples were collected both from the continuously working pump located in the ship's moon pool (underway) every three hours, and from the Niskin bottles attached to the CTD. Each CTD was sampled for five to eight different depths. The water was analyzed for ten brominated, chlorinated and iodinated compounds including $\mathrm{CH}_{3} \mathrm{l}$, dichloromethane ( $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ), chloroform $\left(\mathrm{CHCl}_{3}\right)$, tetrachloromethane $\left(\mathrm{CCl}_{4}\right), \mathrm{CH}_{2} \mathrm{Br}_{2}, \mathrm{CH}_{2} \mathrm{ClI}$, bromoiodomethane $\left(\mathrm{CH}_{2} \mathrm{BrI}\right)$, dibromochloromethane ( $\mathrm{CHBr}_{2} \mathrm{Cl}$ ), $\mathrm{CHBr}_{3}$, and $\mathrm{CH}_{2} \mathrm{I}_{2}$. 50 mL of the sampled water was introduced into a purge chamber. The water was purged with a stream of helium of 30 mL min- 1 while it was concurrently heated up to $70^{\circ} \mathrm{C}$. The purged gas was trapped in stainless steel tubing hanging in liquid nitrogen for 50 min . The trap was desorbed at $100^{\circ} \mathrm{C}$ and the sample was injected into a gas chromatograph attached with a detector. CTD samples were measured using combined gas chromatography and mass spectrometry (GC-MS), while underway samples were analyzed using a gas chromatograph equipped with an electron capture detector (ECD). Calibration was conducted using volumetrically prepared standards in methanol. In total, 13 CTD casts were measured, rounding up to a total of 76 samples that
were measured from the CTD, while 70 samples were taken from the underway pump system, making a total of 146 halocarbon water samples during SO234-2. Additionally, 30 air samples were measured. For these measurements, 500 mL of air was sucked from a sampling line located at the ship's main deck into a cooled trap, and then injected into a third GC-ECD for quantification.

## Preliminary results

First evaluation of the underway and CTD data reveal low concentrations of the bromocarbons $\mathrm{CHBr}_{3}$ and $\mathrm{CH}_{2} \mathrm{Br}_{2}$. Concentrations were in the range of typical open ocean concentrations during the greater part of the cruise. Higher concentrations of both compounds were measured close to the Banc de l'Etoile, a coral reef with also rich microalgal abundances close to Southern Madagascar. This was also the only region where atmospheric measurements showed elevated $\mathrm{CHBr}_{3}$ mixing ratios. Mean $\mathrm{CHBr}_{3}$ in all CTD profiles of $3.2 \mathrm{pmol} \mathrm{L}-1$ ranging only between 0 and $7.4 \mathrm{pmol} \mathrm{L}-1$ were measured with the higher values in the deeper water close to the chlorophyll a (Chl a) maximum, which is in agreement to biogenic formation of this compound. In contrast, $\mathrm{CH}_{2} \mathrm{Br}_{2}$ showed higher values with a slightly higher mean of $3.8 \mathrm{pmol} \mathrm{L}-1$ and up to $19.5 \mathrm{pmol} \mathrm{L}-1$ in the deeper water. An example for a depth profile measured during the cruise is given in Figure 1 for the first day of the 48 -h-station. $\mathrm{CHBr}_{3}$ displays low variability within the water column, but shows generally higher values in the deeper water. The variability within the $\mathrm{CH}_{2} \mathrm{Br}_{2}$ profiles is larger, showing more distinct maxima. Both show similar distributions during all day times, which is in agreement to previous studies hypothesizing similar sources for both compounds.


Figure 1 Raw Chlorophyll a (a), $\mathrm{CHBr}_{3}$ (b) and $\mathrm{CH}_{2} \mathrm{Br}_{2}$ (c) depth profiles during the 48 -h-station (day 1 ).

Surprisingly, highest concentrations of both compounds were measured in the evening where the lowest Chl a signal was detected. $\mathrm{CHBr}_{3}$ is generally assumed to be emitted in higher concentrations than $\mathrm{CH}_{2} \mathrm{Br}_{2}$. However, the higher $\mathrm{CH}_{2} \mathrm{Br}_{2}$ in comparison to $\mathrm{CHBr}_{3}$ has previously been observed in the open ocean, further away from fresh sources. The ratio of $\mathrm{CHBr}_{3}$ and $\mathrm{CH}_{2} \mathrm{Br}_{2}$ leaning towards $\mathrm{CH}_{2} \mathrm{Br}_{2}$, as is here the case, has been hypothesized to be caused by different lifetimes of these compounds (Carpenter et al., 2009), assuming that $\mathrm{CH}_{2} \mathrm{Br}_{2}$ has a longer lifetime in water than $\mathrm{CHBr}_{3}$ similarly to the atmosphere. However, Quack et al. (2007), supported by Hughes et al. (2013), suggested an additional explanation for the elevated $\mathrm{CH}_{2} \mathrm{Br}_{2}$ in the open ocean: biologically mediated conversion from $\mathrm{CHBr}_{3}$ to $\mathrm{CH}_{2} \mathrm{Br}_{2}$, possibly through heterotrophic processes. The depth profiles with largely elevated $\mathrm{CH}_{2} \mathrm{Br}_{2}$ in comparison to $\mathrm{CHBr}_{3}$ observed during 234-2 could therefore be an indicator for the latter hypothesis, which will be investigated more thoroughly during the second leg.

## Outlook

Further analysis of the data will be performed in Kiel. Once the data is fully analyzed, it will be compared to biological and physical parameters. Emissions will be calculated using discrete atmospheric samples that were taken at the same time as the water samples, and using several parameters from the DSHIP data and the continuously measuring thermosalinograph (e.g. wind speed, air pressure, water temperature, density). Furthermore, the data will be compared to pigment data, nutrients, CDOM, and iodide and iodate, which were all sampled in parallel to evaluate sources of halocarbons in the Indian Ocean and learn more about their biogeochemical cycling. The final evaluation of the 48hstation will reveal possible diurnal variability of these compounds within the water column. Sea-to-air fluxes from the Indian Ocean will be used to calculate the entrainment of halocarbons into the stratosphere.

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# 2) OCEANIC TRACE GASES - Underway measurements of $\mathrm{CO}_{2}, \mathrm{O}_{2}, \mathrm{CO}$, and $\mathrm{N}_{2} \mathrm{O}$ 

## Tobias Steinhoff, Gesa Eirund and Damian Arevalo-Martinez (GEOMAR, Kiel, Germany)

Oceanic and atmospheric measurements of $\mathrm{CO}_{2}, \mathrm{CO}$ and N 2 O were carried out by means of a continuous system based upon the off-axis integrated cavity output spectroscopy technique (RMT-200 N2O/CO Analyzer, Los Gatos research Inc.) coupled to a $\mathrm{CO}_{2}$ detector based upon non-dispersive infrared detection (LICOR, USA; LI-6252). Water was drawn on board by using a submersible pump installed in the ship's moonpool at 6 m depth and was subsequently conducted at a rate of about $5 \mathrm{~L} \mathrm{~min}^{-1}$ through the equilibrator. Sample air from the headspace of the equilibrator was continuously pumped through the instruments and then back to the equilibration chamber forming a closed loop. The air stream was dried before being injected into the analyzers in order to diminish interferences due to the water vapor content of the sample. In order to correct for potential warming of the seawater between intake and equilibrator the water temperature at the equilibrator was constantly monitored by means of a digital thermometer and at the intake by a Seabird SBE37 termosalinograph. Ambient air measurements were accomplished by drawing air into the system from a suction point located at the ships mast at about 30 m high. Control measurements and calibration procedures were performed every $\sim 6$ and 24 h respectively, by means of 3 standard gas mixtures. Fig. 1 shows the over- or undersaturation of $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}$ with respect to the atmosphere. During most of the cruise both gases were near the equilibrium, while strong supersaturation was observed when entering the coastal upwelling region along the African coast.

Underway measurements of surface water $\mathrm{O}_{2}$ and gas tension were carried out in a flowthrough box. Gas tension data are only available until 15 . July due to a broken connector at the instrument. The box was connected to the same water supply and the water flow was adjusted to approximately $20 \mathrm{~L} \mathrm{~min}^{-1}$. The following instruments were implemented: Aanderaa Oxygen Optode (model 4330), Pro Oceanus Gas tension device. The gas tension device physically measures the total pressure of all dissolved gases, i.e, $\mathrm{pN}_{2}, \mathrm{pO}_{2}, \mathrm{pH}_{2} \mathrm{O}$, and pAr as well as minor trace gases below the instrument's accuracy. As water vapour $\mathrm{pH}_{2} \mathrm{O}$ is a function of temperature and salinity, Argon pAr is constant, and Oxygen $\mathrm{pO}_{2}$ is measured by the oxygen optode, it effectively gives the pN 2 , which is a prime indicator of physical processes of gas exchange, like e.g., bubble processes, and unaffected by biology. It thus helps to separate biological and physical contributions to air-sea gas exchange of $\mathrm{O}_{2}$. This is complemented by the biology-dominated $\mathrm{pCO}_{2}$ measurements in water and air. In combination with information about the mixed layer from the CTD, the continuous underway measurement thus yield insight into major physical and biological processes at play in the surface ocean. Occasionally, discrete oxygen and salinity samples were taken from the bypass to compare these underway measurements.

Discrete comparison samples for $\mathrm{N}_{2} \mathrm{O}$ and $\mathrm{CO}_{2}$ were carried out in $8-12 \mathrm{~h}$ intervals by sampling from the same water stream that fed the underway setup. $\mathrm{N}_{2} \mathrm{O}$ and DIC/TA samples were collected and stored to be measured at the Chemical Oceanography Department of the GEOMAR in Kiel.

## Preliminary results



Figure 1 Surface water distribution of $\mathrm{pCO}_{2}, \mathrm{~N}_{2} \mathrm{O}$, oxygen saturation and sea surface temperature (SST) during SO234-2.

Figure 1 shows preliminary data of surface distributions of $\mathrm{pCO}_{2}, \mathrm{~N}_{2} \mathrm{O}$, oxygen and SST along the cruise track. Under the influence of the Mozambique Channel higher SST up to $25^{\circ} \mathrm{C}$ was observed. East of $48^{\circ} \mathrm{W}$ SST dropped and lowest temperature around $19^{\circ} \mathrm{C}$ was observed in the most easterly part of the cruise track. This differentiation between the part west and east of Madagascar can be also found in the different gases. $\mathrm{CO}_{2}$ was undersaturated with respect to the atmosphere during the whole cruise with lowest values in the eastern part. $\mathrm{N}_{2} \mathrm{O}$ surface water concentrations were around equilibrium with the atmosphere during most of the time. Only in the Mozambique Channel slight supersaturation was observed. The oxygen data are not calibrated yet and the shown saturation values seem to be too low. But the observed pattern in the oxygen saturation can also be found in the SST data. Warmer waters have a slightly higher saturation than colder waters.

## 3) EDDY COVARIANCE - trace gases

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## Motivation

Despite their low abundances, short-lived trace gases produced in the oceans play an important role in biogeochemical cycling and atmospheric processes. Some examples of such climate active gases that are measured on board the SO234-2 cruise are dimethylsulfide (DMS), isoprene, acetone, and carbonyl sulfide (OCS). These gases react rapidly when emitted to the atmosphere, with lifetimes between 1 hour and 1 month. They participate in ozone and hydroxyl radical cycles and in the formation of aerosols and cloud condensation nuclei. The biogeochemical and physical factors influencing the production and destruction of these compounds in the surface ocean are only marginally constrained for gases such as DMS, OCS, and acetone, while very little information about isoprene cycling is known. In addition, quantifying the air-sea exchange of these compounds is further hindered by the lack of direct flux measurements and poor constraints on the factors controlling their fluxes (e.g. the gas transfer coefficients, presence of vertical gradients, etc.). The goal of this cruise is to understand what controls the biogeochemical cycling of these gases in the surface ocean, in depth profiles, and their exchange with the atmosphere.

In order to investigate the ocean's role in the atmospheric budget of these trace gases, bulk atmospheric and oceanic concentration measurements and ancillary data (such as colored dissolved organic matter, cell counts, and DNA), as well as direct air-sea exchange, have been measured. We deployed three different instruments to measure underway and CTD seawater samples for trace gas concentrations and three instruments to measure air concentrations. An eddy covariance (EC) direct flux measurement system has also been deployed, which can be used to perform biogeochemical cycling measurements without typical pitfalls associated with bulk flux calculations, as well as to constrain the main forcings on air-sea gas exchange. Measurements of the precursors and sinks of these trace gases were measured in order to better understand and quantify surface ocean cycling. The main factor thought to influence these gases is biological activity. Therefore, samples for DNA and cell counts (i.e. flow cytometry) were taken for later analysis. Because the degradation of CDOM by UV light results in the formation of trace gases, such as OCS, acetone, and isoprene, CDOM quantities were also measured.

## Methods

This working group is responsible for the following measurements:

1. Continuous eddy covariance fluxes of DMS, isoprene, acetone using atmospheric pressure chemical ionization mass spectrometry (AP-CIMS)
2. Continuous eddy covariance fluxes of $\mathrm{CO}_{2}$ using infrared absorption (LICOR 7200)
3. Three hourly underway and CTD water concentrations of DMS (and related compounds such as DMSP, DMSO), and isoprene with purge and trap gas chromatography-mass spectrometry (GC-MS)
4. Continuous underway water concentrations of DMS, isoprene, and acetone using an equilibrator coupled to AP-CIMS
5. Continuous underway water levels of OCS using an equilibrator coupled to a cavity ring down spectrophotometer (MICA), with hourly valve switches to measure air mixing ratios for 15 minutes
6. Quantification of CDOM (both underway and at depth with the CTD) using UV-visible absorption (qualification may be attempted with a fluorescence spectrophotometer, but this has not yet been accomplished)
7. Sampling and preparation of DNA and flow cytometry samples for identifying types and amount of biological activity

## Eddy covariance

The eddy covariance direct flux (F) is computing with the following equation,
$\left.F=\rho<w^{\prime} c^{\prime}\right\rangle$
where $\rho$ is the density, $w^{\prime}$ are the vertical wind fluctuations, and $c^{\prime}$ are the concentration fluctuations (brackets denote time average). Using this technique, we can attempt to improve the gas transfer parameterization ( $k$ ) used in the commonly employed bulk formula,
$F=k\left(H C_{w}-C_{a}\right)$,
where $C_{w}$ and $C_{a}$ are water and air concentrations, respectively, and $H$ is the Henry's law solubility constant. The goal was to measure dimethylsulfide (DMS), isoprene and acetone flux with the AP-CIMS and $\mathrm{CO}_{2}$ flux with the LICOR 7200. Measurements started at DOY 196 12:00 UTC (-29.62444288 LAT 58.58830401 LON) and continued until Port Louis.
Air was sampled through a $1 / 2 \prime$ tube from a mast welded to the bow (approximately 10 m above the sea surface) at a flow rate of $70 \mathrm{I} \mathrm{min}^{-1}$ to the AP-CIMS and approximately $25 \mathrm{I} \mathrm{min}^{-}$ ${ }^{1}$ to the LICOR. To obtain turbulent wind speed measurements and sensible heat flux, a sonic anemometer was placed at the bow mast, which measured three dimensional wind speed and the speed of sound. A GPS and inertial navigation system (INS) was used for motion correction (Figure 1). The AP-CIMS can discriminate gases using a single quadrupole mass spectrometer. The gases are ionized at atmospheric pressure using $\mathrm{H}_{3} \mathrm{O}^{+}$as the reagent gas and electrostatically steered to the quadrupole. The ions are detected using a counting electron multiplier. The LICOR measures $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ using infrared absorption.


Figure 1 Eddy covariance setup on the R/V Sonne.

## Purge and trap GC-MS

We improved a purge and trap technique coupled with a GC-MS (Figure 2) to measure different non-methane hydrocarbons (NMHCs) in seawater. In addition, we developed a method to quantify different NMHCs (e.g. isoprene, dimethylsulfide (DMS)) in one measurement using isotopically labeled internal standards. A 40 ml discrete water sample was taken, bubble free, and purged with approximately $30 \mathrm{ml} \mathrm{min}^{-1}$ of helium for 15 minutes and trapped with liquid nitrogen on an empty u-shaped trap. The frozen gas was then injected with boiling water into the GC. Each analysis took approximately 13 minutes.


Figure 2 Purge and trap GC-MS aboard R/V Sonne.

## Instruments coupled to equilibrators

A miniature AP-CIMS and a cavity ring down spectrophotometer (MICA) were each coupled to a membrane equilibrator to measure trace gases. The AP-CIMS measured DMS and isoprene, while the MICA measured OCS (there were also hourly valve switches to measure air mixing ratios with the MICA). Each equilibrator had approximately $5 \mathrm{I} \mathrm{min}^{-1}$ water flow and a counterflow of purified air of $\sim 300 \mathrm{ml} \mathrm{min}^{-1}$. The AP-CIMS air stream was dried with a Nafion dryer and diluted with dry purified air with a flow of $1100 \mathrm{ml} \mathrm{min}^{-1}$. All gas flows were controlled with mass flow controllers and all liquid flows were measured and recorded.

## Ancillary measurements

Samples for DNA, cell counts, and CDOM were also taken from both the underway system and the CTD and preserved for later analysis. 2 I of water for DNA were filtered through 0.2 micron filters and mixed with 0.5 ml of RNA later before shock freezing and final storage in the -80C freezer. The samples will be shipped to Hong Kong for analysis. 4.5 ml of water were taken for phytoplankton and bacteria cell counts, each, and were preserved with GDA ( 20 and 200 microliters, respectively) before final storage in the $-80 C$ freezer. The samples will be shipped by to Kiel for flow cytometry analysis. 50 ml of water was filtered through 0.2
micron filters for CDOM quantification. The samples were stored in the refrigerator until shipboard analysis, between 1 and 48 hours. Measurements were made using a UV-visible spectrophotometer. Milliq water was used as a reference. The CDOM value was computed by subtracting the absorbance at approximately 700 nm from that at 350 nm . All values are reported in absorbance units and reflect relative amounts.

## Preliminary results

## Bulk air values - Eddy covariance system

Figure 3 shows the bulk air concentrations of isoprene, DMS, and acetone measured with the AP-CIMS during the 48 hour station. All three trace gases show relatively low bulk concentrations. This is in accordance with the results from the surface seawater measurements of the same gases, which were also low. A daily cycle, due to photolysis (sunlight creates OH which oxidizes isoprene), of isoprene can be clearly seen, especially because the lifetime of isoprene in the atmosphere is on the order of 1 hour. The DMS lifetime is on the order of 1 day, and a less clear diurnal pattern is evident.


Figure 3 Trace gas measurements in the atmosphere during the 48 hour station using the AP-CIMS and the inlet on the eddy covariance mast.

## Eddy covariance wind measurements

Vertical wind speed power spectra are in good agreement with the empirically determined Kaimal turbulent wind spectrum (Kaimal et al., 1972; Figure 4), which is used as the standard for all turbulence measurements. The high frequency portion of the spectrum exhibits the appropriate slope, but the peak at around 0.1 Hz is due to the motion of the ship. This must be removed from the wind data in post processing, using the data from the IMU situated on the mast.


Figure 4 Sample power spectrum of vertical wind speed.

## Eddy covariance trace gas measurements

It is clear that trace gas spectra show the same features as the wind spectrum, in accordance with the Kaimal curve (Figure 5). Therefore, the trace gas measurements can be correlated with the vertical wind speed measurements to obtain the eddy covariance flux. However, this data must be post processed to correct for high and low frequency interferences and the possibility of flow distortion.


Figure 5 Sample power spectrum of the turbulent fluctuations of acetone.

## GC-MS measurements



Figure 6 Diurnal isoprene cycle plotted with fluorescence values from the CTD.

During a 48 h -station we sampled from 8 CTD-Stations. Samples were taken from 5 m to about 100 m depth in order to get information about a potential diurnal cycle in isoprene and DMS concentrations during 2 days in the euphotic zone (Figures 6,7 ). The results show a slight correlation of isoprene-concentrations with chl- $a$. It appears however, that despite following the same water mass with a drifter in the upper 20 meters, the water mass below 30 m changed during the 48 h -stations after noon of the first day. This could also be detected in the evening profile of DMS concentrations from the first day (Figure 7, left). Values for both DMS and isoprene were below the global annual average.


Figure 7 Diurnal DMS from CTDs during the 48 hour station, left) first day, right) second day.

## OCS measurements

Preliminary mixing ratios of OCS in air and water are shown in Figure 8. The values appear to be below the expected levels by approximately $40 \%$. We believe this is due to dirty mirrors inside the cavity and can be corrected during post processing. The water values exhibit the expected diurnal cycle, which is related to the CDOM photolysis source of OCS. It appears that OCS was undersaturated in the water during most of the cruise, which is unusual and may have to do with the low SSTs.


Figure 8 OCS mixing ratios (ppt). Top constant value is the air mixing ratio, while the cycling lower values are in the water.

## CDOM measurements

Figure 9 shows two measured absorption spectra of CDOM from this cruise. A typical spectrum has a maximum between 230 and 250 nm and then falls exponentially to a base value. The abundance of CDOM in terms of absorption has been determined for most underway samples from SO234-2 (Figure 10). Normally the amount of CDOM in the surface


Figure 9 Absorption spectra of CDOM from two underway samples.


Figure 10 CDOM underway samples.
waters is high close to the coast and decreases towards the open ocean. However, we observed the lowest values close to the reef south of Madagascar and higher values in the open ocean.

CDOM abundances have also been determined for the CTD casts during SO234-2. Figure 11 shows the profiles of CDOM and isoprene from the 7 CTD casts of the 48 h station. The abundance of CDOM declined slightly with depth in the first 500 m . In greater depths the abundance remained constant. This goes in accordance with the expectations as major depletion of CDOM by photolysis can only take place in surface water masses. As CDOM could be a precursor to isoprene, a relationship of the abundance of CDOM and isoprene would be plausible - yet after preliminary analysis of the CTD casts no such relation could be Figure 10. Relative abundances of surface seawater CDOM.

A classification of the type of CDOM and its source is possible by analyzing the spectra as well. The absorption spectra can be approximated using the following formula, where $\mathrm{a}_{\text {CDOM }}$ is the absorption coefficient, S is the exponential slope parameter and $\lambda_{0}$ is a reference wavelength:

$$
\mathrm{a}_{\mathrm{CDOM}}(\lambda)=\mathrm{a}_{\mathrm{CDOM}}\left(\lambda_{0}\right) \mathrm{e}^{-\mathrm{S}\left(\lambda-\lambda_{0}\right)}
$$

The slope parameter can be calculated by a linear fit through the logarithmic spectrum and is used to classify the CDOM. Figure 12 shows CDOM absorption spectra from different regions. Lower slope values correspond to coastal waters with high amounts of terrestrial sourced CDOM and open ocean waters show higher slope parameter values (Nelson \& Siegel,
2013).


Figure 11 CTD profiles of CDOM (red) and isoprene (dashed) for the seven casts from the 48 h station.

This method of classification has been applied to some of the CDOM spectra obtained during SO234-2. Figure 13 shows two spectra from underway measurements (black and grey) and two spectra from CTD casts (blue and red). The underway samples have been taken close to the coast of Madagascar, the CTD samples are from the 48h station in the open ocean. The slope parameters for all spectra have been determined and we find that the coastal spectra have higher slope values than the underway spectra from coastal waters. This corresponds to the results from Nelson and Siegel (2013).


Figure 12 Examples of CDOM spectra from various source regions, where the right side is the log of the left side. The slopes of the different curves is given in the legend of the right panel and can be used to determine the source regions of CDOM (Nelson and Siegel, 2013).


Figure 13 Analysis of SO234-2 CDOM samples in the method of Nelson and Siegel (2013). See Figure 12 above.

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## 4) OCEANSENSORS

## 4A) Conductivity Temperature Density (CTD)

## Matthias Krüger (GEOMAR, Kiel, Germany)

During SO234-2, 13 profiles of pressure ( P ), temperature ( T ) and conductivity (C) were recorded. These CTD profiles usually ranged to the bottom, on the 48 h station to the bottom and some to 750 m . We used a Seabird Electronics (SBE) 9plus system, attached to the water sampler rosette, and the latest Seabird Seasave software. The system had the following sensors: p \#64860, T \#2135, c \#1854, Oxygen (O) \#1902 and a Dr. Haardt Fluorometer. Conductivity will be calibrated using a linear relation in $p, T$ and $c$. This relation will be obtained by fitting the according CTD salinity to 37 water samples, which will be analyzed with a salinometer later on. Oxygen will be calibrated using a linear relation in $p, T$ and O . Winkler titration of 312 bottle samples gives the accurate value of absolute oxygen in the water.

A potential temperature - salinity diagram of the first four CTD stations is shown in Figure 1, with such a diagram the water masses can be easily detected.


Figure 1 Temperature - salinity diagram of the first four stations.

## Preliminary results

A vessel mounted Acoustic Doppler Current Profiler (ADCP) continuously recorded current velocities. We used a RD Instrument Ocean Surveyor 38 kHz (OS38) mounted in the ship's hull. The instrument was run in two configurations: one configuration in broadband mode (BB) and one configuration in narrowband mode (NB). Usually NB is for the deeper regions of the ocean. The main reason to choose the less robust $B B$ mode was the higher possible resolution in space and time. The two configurations of OS38 were: a) NB mode, 55 bins of 32 m , range 1000 m ; b) BB mode, 80 bins of 16 m , range 800 m .

Due to the extremely low abundance of acoustic scatters in parts of the cruise area, there are sometimes lacks of interpretable acoustic backscatter signals, even when using the more robust NB mode.

A time series showing the velocity structure in the upper 1000 meters of the water column is shown in Figure 2, where enhanced internal wave activity is evident.


Figure 2 Velocity time series ( $\mathrm{m} / \mathrm{s}$ ) at the beginning of the 48 h station, data from 38 kHz ADCP. Enhanced internal wave activity is apparent in the upper 800 m .

## 4B) Surface drifter

## Tobias Steinhoff (GEOMAR, Kiel, Germany)

During one station a 48h (Lagrangian) drift experiment was conducted. In order to follow a water parcel in a quasi-Lagrangian approach a surface drifter was used to mark a water patch and follow it with the ship for 48 h (Figure 1). The drifter was further equipped with autonomous instrumentation at approx. 15 m water depth for in situ measurements of Salinity and Temperature (Seabird MicroCat), pCO2 (Contros HydroC), O2 (Aanderaa Oxygen Optode, Model 4330), Chlorophyll (Trios Micro flu) and Nitrate (Trios Props). The continuously recorded data need to be processed and will be available after the cruise. During the drift experiment the ship approached the drifter every 6 hours in order to conduct a CTD hydrocast ( 750 m max. depth) next to it. Samples were taken and analyzed for various parameters. Most of sampling and measurement procedures are described in the cruise report of other groups.


Figure 1 Track of the surface drifter during the deployment of 48 h ; photo of the drifter on 17.07.2014 @Folkard Wittrock).

## 5) RADIOSOUNDING - meteorology measurements

## Matthew Toohey, Steffen Fuhlbrügge (GEOMAR, Kiel, Germany), Michael Hemming (University Hamburg, Germany), and Kirstin Krüger (PI - UiO, Oslo, Norway)

## Introduction

34 radiosondes were launched until 19.07.2014, 15:00 UTC. Launch locations and horizontal flight tracks are shown in Figure 1.


Figure 1 (left) Radiosonde launch locations (circles) and horizontal trajectories for launches from 8-18 July. (right) Zonal wind speed derived from the radiosonde launches as a function of height. Cold-point tropopause heights shown by markers.

## Preliminary results

Data from the radiosondes shows a high tropical cold-point tropopause at around 17 km (stars in Figure 1, right). Maximum zonal wind speeds are found a few km below the tropopause, and show a strong gradient with respect to the latitude of launch. At southernmost launch latitude, south of $\sim 28 \mathrm{~S}$, we find strong zonal winds of $\sim 80 \mathrm{~m} / \mathrm{s}$. Northward of this threshold, we find weaker maximum zonal wind speeds of $30-50 \mathrm{~m} / \mathrm{s}$.

During the portion of the cruise track closest to the Madagascarian coast, radiosondes were launched at a 3 -hourly frequency. Winds measured by these sondes show a strong wind shear in the lower troposphere, with north-easterly winds at the surface and south-westerly winds beginning at 2-5 km height. Figure 1 (right), which shows the zonal wind as a function of height, shows this feature for sonde launches 7-18.

A sharp gradient in the relative humidity profiles is found between 2-4 km height (not shown). Here the relative humidity decreases from $>80 \%$ to $15-30 \%$. However this gradient does not mark the upper limit of the atmospheric boundary layer per se. The moist layers up to 4 km are air masses that have been advected and do not interact with the surface by
turbulent mixing processes. The mean atmospheric boundary layer height determined from the radiosonde profiles of temperature, humidity and wind is $\sim 0.8 \mathrm{~km}$ during the cruise.

Two ozonesonde launches have been performed. Due to a failure of the GPS on the first launch, altitude and position (therefore winds) are missing from the data of the first flight. Approximate heights have been estimated by comparing the measured temperature profile to the profile measured via radiosonde 6 hours earlier.
Preliminary profiles of ozone vs. height for the two ozonesonde launches are shown in Figure 2.


Figure 2 Preliminary ozone profiles from ozonesonde launches on 16.07.2014 and 18.07.2014. Ozone values shown in (right) linear and (left) log scales to highlight stratospheric and tropospheric values, respectively.

Surface meteorological fields measured by the ship's instruments are being collected and archived. Surface pressure, temperature, humidity and wind speed for a portion of the cruise are shown in Figure 3.


Figure 3 Surface meteorological fields as measured and archived by the Sonne systems.
The pyrgeometer and pyranometer, measuring atmospheric emission longwave (LW) and solar shortwave (SW) radiation, respectively, and precipitation measuring disdrometer were working fine and collecting data continuously. Figure 4 shows a preliminary version of data collected to date.


Figure 4 Radiative and precipitation quantities measured by the radiometers and disdrometer, respectively.

## 6) AIR-SAMPLING - for atmospheric trace gases

## Elliot Atlas (RSMAS, Miami, USA), and Birgit Quack (GEOMAR, Kiel, Germany)

94 canister samples of air have been collected in 2 L stainless steel tanks, being pressurized to 2 bar for RSMAS with a metal bellows pump and will be analyzed for a variety of trace gases as natural and anthropogenic hydrocarbons and halocarbons, DMS, $\mathrm{N}_{2} \mathrm{O}$, alkyl nitrates, CO and other long-lived anthropogenic and natural trace gases on different instruments at the Rosenstiel School of Marine and Atmospheric Sciences in Miami.

Long lived anthropogenic gases producing halogen radicals can account for about 3400 ppt of chlorine and about 15-16 ppt of bromine in the stratosphere, depleting ozone.

Other gases with shorter lifetimes, the so-called very short-lived substances (chemical lifetimes shorter than 6 months) like bromoform ( $\mathrm{CHBr}_{3}$ ) or dibromomethane $\left(\mathrm{CH}_{2} \mathrm{Br}_{2}\right)$ as well as iodinated methanes with the ocean as their main source also may have a significant impact on the stratospheric bromine loading. Deep convection within the tropics could provide a fast pathway for these substances to be transported in significant abundances into the stratosphere. The quantification of this input to the budget of stratospheric bromine and iodine from the Indian Ocean during southwest monsoon was a major objective of the cruise. It will give information about natural background halogen loading of the stratosphere and improve the projections of future stratospheric ozone concentrations.

With the help of the anthropogenic and terrestrial trace gases and calculated trajectories oceanic, land-based and anthropogenic sources and possibly source strengths can be determined.

## 7) MAX-DOAS

## Folkard Wittrock (IUP, University of Bremen, Germany)

During the SO234-2 cruise in the Indic from July 8 to July 20, 2014, measurements of different reactive trace gases were carried out using the Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) technique (Wittrock et al., 2004 and Wittrock, 2006). The Bremian MAX-DOAS setup was running almost continuously for the whole cruise without having any serious problems (starting already early in the morning on July 7 in the port of Durban). Since the MAX-DOAS technique is based on solar stray light, measurements were only possible during daytime short before sunrise until sunset ( $96^{\circ} \mathrm{SZA}$ ). In addition some complementary parameters were obtained: surface ozone with an in situ ozone monitor (Horiba), meteorological parameters (wind speed and direction, total solar radiation, UV radiation, precipitation, humidity, pressure and temperature). Starting July 18 denuder tube sampling was carried out to quantify the amount of molecular iodine. Furthermore the MAX-DOAS is also collecting AIS data from passing ships which might help to explain measured pollution levels.
The MAX-DOAS setup used on the ship was covering a wavelength range of approximately 300 to 470 nm with a medium resolution (FWHM 0.8 nm ). This enables us to retrieve the following trace gases: $\mathrm{IO}, \mathrm{BrO}, \mathrm{CHOCHO}, \mathrm{HCHO}, \mathrm{H}_{2} \mathrm{O}, \mathrm{O}_{3}, \mathrm{NO}_{2}$, and $\mathrm{SO}_{2}$. From O 4 measurements the aerosol extinction profile and the AOD can be derived. The telescope was installed on the starboard side of the ship and was collecting spectra toward three different azimuth angles possibly identifying horizontal gradients of trace gases. In addition the waterleaving radiance was measured once per measurement cycle (Peters et al., 2014).
During the cruise a first analysis was carried out. For the halogen oxides BrO and IO no clear indications of levels above the detection limit ( $\sim 0.5 \mathrm{ppt}$ ) was found. For the tropospheric pollutants $\mathrm{NO}_{2}$ and $\mathrm{SO}_{2}$ elevated levels up to several ppb were measured in Durban and when passing the main shipping routes close to Madagascar. In case of HCHO similar values ( $\sim 0.6$ to 0.8 ppb ) as published in Peters et al. have been retrieved. AOD levels were in general very low with values around 0.06. A detailed analysis of the whole data set taking into account detailed radiative transfer calculations will be done at the IUP Bremen as soon as possible. Preliminary and raw data have been uploaded to the cruise data base.


Figure 1 MAX-DOAS telescope on RV Sonne heading to starboard. During SO234-2 the telescope was scanning different azimuth angles to identify spatial inhomogeneities in trace gas distributions.

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8) GHG (see work group reports 2 and 3)

## 9) AEROSOLS

## 9A) Alex Baker (UEA, Norwich, UK)

Aerosols play a key role in halogen cycling in the marine atmosphere, with Cl being transferred to the gas phase by acid displacement reactions, Br release being induced by reaction of ozone on sea salt particles and iodine chemistry promoting transfer of $\mathrm{Cl}, \mathrm{Br}$ and I to the gas phase via halogen activation reactions. Ultimately aerosols appear to be net sources for Cl and supermicron Br and net sinks for I and submicron Br .

During the SO234-2 cruise two day aerosol samples were collected for determination of Cl -, Br - and iodine speciation, as well as a number of other aerosol ionic components which will provide us with useful information on aerosol background chemistry. 6 fourtyeight hour aerosol samples of about 600 L of air have been collected with a multistage aerosol impactor.

The data obtained will allow us to examine the potential strength of the aerosol Br source along the transect and investigate the role of iodine chemistry in halogen activation, as well as providing a unique opportunity to compare atmospheric iodine source (trace gas) and sink (aerosol) strengths in the Indian Ocean for the first time.

## 9B) Matthew Toohey (GEOMAR, Kiel, Germany)

The microtops sun photometer (Figure 1 left) is being used to measure aerosol optical thickness in cloud-free conditions. Based on satellite AOT retrievals, we expect weak aerosol levels in this region at this time of year, with values below 0.2 and often below 0.1. Microtops measurements are in line with this expectation (Figure 1 right). Larger AOT values are expected in the later portion of the cruise as the ship gets in closer proximity to India.


Figure 1 (Left) Microtops sun photometer; (right) aerosol optical thickness (AOT) as measured by the Microtops handheld sun photometer during the cruise.

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I would like to thank the scientific team on board for their extra-ordinary hard work to setup and operate the instruments additional to their teaching duties during the 12 days of SO234-2. Thanks in particular to all of you who have looked after several measurement and sampling devices and that you have worked day and night to get samples every 3 hours. During the 48 hour station, this was only possible with the help of our wonderful students, who did a great job carrying out the measurements at day and night and who also survived the turbulent classes during strong storm and wave events. Despite these tough times, all of you together managed to create a pleasant and professional working environment. Next to an inspiring and fruitful exchange with our SPACES students we were also able to gain a great and unique data set of the subtropical West Indian Ocean. The analysis and evaluation of the data are still ongoing for the next months and I am very much looking forward to see the final scientific results.

During our SO234-2 cruise we managed to set up our instruments quickly, supported also by the expertise of the professional ship's crew, who was always there, when we faced technical problems. The ships' crew was very helpful and we had the best cooking team on board. Special thanks go to the WTD and the electrician, who rapidly repaired our breakdowns with insight and care. Thanks also to the decks crew for all helping hands and friendly support of our activities and the machinery for the smooth maintenance of all technical details of this fine ship. SO234-2 succeeded not last due to the professional cooperation between the captain, the crew and the scientists, so we were able to carry out all of our work together during SO234-2 to the best results. I would also like to especially thank the captain of RV Sonne for his careful and considerate navigation through the rough subtropical West Indian Ocean.

Finally, I would like to thank my colleagues Birgit Quack and Christa Marandino for their collaboration and support with the SO234-2 SPACES SONNE project and ship cruise.

Last but not least, I am very grateful to the BMBF for funding the SO235 OASIS/ SO234-2 SPACES project (BMBF grant 03G0235A) and the SO234-2 SPACES SONNE cruise, Barbara Tanner, Susanne Korich and the PTJ for taking care of the student, project and the ship cruise administration and the Geoscience Department at University of Oslo and GEOMAR Kiel for supporting our SO234-2 activities.

All together you were a wonderful, hard-working and very successful SO234-2 team!

Yours Kirstin Krüger (Chief Scientist, UiO)

Appendix A: Sample lists for underway samples


Appendix B: Sample lists for CTD samples

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