RV SONNE - Cruise report

Cruise SO218

Singapore to Manila, Philippines

15 to 29 November 2011

(In the frame work of the SHIVA Western Pacific campaign in November and December 2011.)

SHIVA

SHIVA (EU- Grant: 224644)

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RV Sonne cruise SO218: Singapore-Manila, 15-29 November 2011

Within the frame work of the EU-project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) the research cruise SO218 of the German research vessel SONNE was organized and conducted by the Leibniz-Institute of Marine Sciences (IFM-GEOMAR, http://www.ifm-geomar.de/) from 15 to 29 November 2011 in the South China and Sulu Sea. The cruise was mainly bound to investigate tropical trace gas emissions in Malaysian and Philippine waters of various biogeochemical regimes between Singapore and Manila (Philippines) and their contribution to stratospheric halogens. Partners on board were from the European project SHIVA - Stratospheric halogens in a varying atmosphere - (http://shiva.iup.uni-heidelberg.de/) and from Malaysia, the University of Malaya, Kuala-Lumpur (IOES) Universiti of Malaya, Sarawak (UNIMAS), Universiti of Malaya, Sabah) and the University of the Philippines Diliman, Quezon.

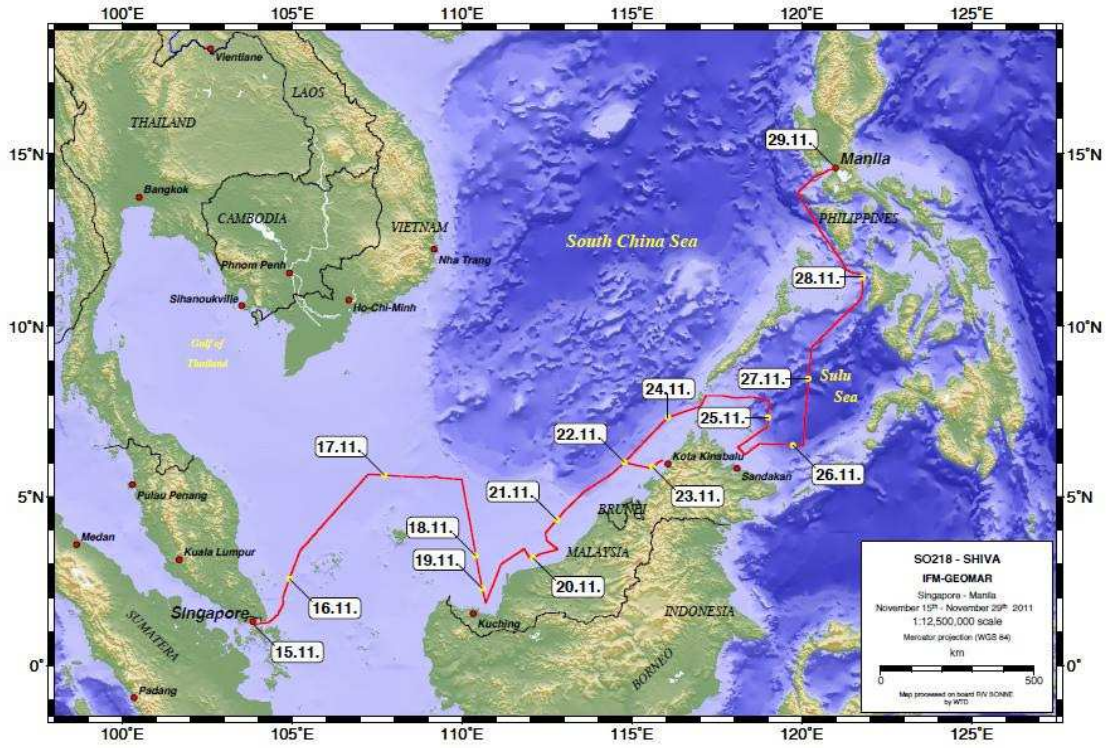

Figure 1: Cruise track of RV Sonne: Singapore-Manila (15-29 November 2011).

Scientific background

Trace gases, containing halogens as 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 tropical oceans are a known source of reactive bromine and iodine to the atmosphere in the form of short-lived brominated and iodinated methanes as e.g. bromoform ($CHBr_3$). Elevated atmospheric concentrations above the oceans are related to oceanic supersaturations of the compounds, and to natural photochemical and biological production. Macro

algae in coastal regions, as well as regionally enhanced phytoplankton, river outflow, 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 upwards. The intense vertical transport of the tropical atmosphere implies that the oceanic sources could supply significant amounts of halogens to the upper troposphere/ lower stratosphere where they may contribute to the observed ozone amounts and trends. The tropical western Pacific is a largely uncharacterized region for the oceanic compounds and a projected hot spot, especially in coastal regions for their emissions and transport pathways into the stratosphere.

Spatial and temporal variability in production and sea-to-air flux of the short-lived halogenated trace gases create strong varying marine and atmospheric distributions and thus also varying stratospheric contributions. The current impact of the natural ozone depleting substances is still highly 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 future evolution of the ozone layer in a changing climate, unless they are better understood. The measurements were thus needed to improve the understanding of future stratospheric halogen loading and therewith ozone depletion. The results of the SHIVA-SONNE campaign will contribute to the scientific underpinning 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, participating institutions and measurements

Of particular relevance during SO218 were oceanic and atmospheric measurements of a suite of short-lived trace gases containing the halogens chlorine, bromine and iodine in various marine biogeochemical regimes, as close to the coasts, in regions of high chlorophyll, close to coral reefs, in oceanic upwelling regions and in river outflow, compared to more open oceanic conditions and under differing meteorological conditions. From these measurements the climate-sensitive oceanic emission strengths and real contributions of the emissions to stratospheric halogens will be characterized by modeling.

The atmospheric structure was determined by intense radio and ozone sounding during the cruise. Other marine trace gases as i.e. nitrous oxide (N_2O), dimethylsulfide (DMS), oxygen (O_2) and carbon dioxide (CO_2), 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 ship expedition. 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 towards and away from the ship. The measurements on RV SONNE in the South China Sea and along the coastline of Peninsula Malaysia and Borneo in conjunction with Malaysian research partners were accompanied by parallel measurements with the DLR Falcon and land-based investigation teams (see: The SHIVA Western Pacific campaign in November and December 2011, Post-campaign Activity Report by Pfeilsticker, 2012).

The instruments on board of the ship made quasi-continuous measurements of VSLS and related species in both seawater and air to determine actual sea to air fluxes, whilst the aircraft carried out surveys of the larger scale concentrations in the marine boundary layer and in the convective outflow at altitudes up to ~13 km.

Together with the main scientific objective of the cruise to characterize the oceanic emissions of natural halogenated gases in the western Pacific, the participating groups followed additional research questions. Thus, more specifically, the overall scientific program of SO218 included the following themes, which can roughly be assorted to the individual working groups (Table 1):

1.) HALOCARBONS: Atmospheric and oceanic concentrations of bromine, iodine and chlorine containing halocarbons, in order to derive their sea to air fluxes.

2.) PHYTO-OPTICS and PLANKTON: Phytoplankton pigments, species and size distribution, radiation and absorption spectra of seawater and plankton content in order to characterize the phytoplankton and zooplankton composition and to validate satellite data from the western Pacific.

3.) OCEANIC TRACE GASES: Oceanic concentrations of dimethyl sulfide and related compounds (DMS, DMSO, DMSP), nitrous oxide and methane, in order to understand their distribution in the different biogeochemical regimes of the western Pacific and to gain new insights into halocarbon sources.

4.) OCEANSENSORS: Identification of carbon dioxide and oxygen sources and sinks; separation of physical and biological factors for observed sources and sinks, temperature and salinity; joint evaluation with halocarbons, in order to understand more about their sources and sinks.

5.) RADIOSOUNDING: Identification of meteorological vertical and ozone profiles in order to evaluate the mixing layer and tropopause height and to calculate air mass back trajectories to identify origin of sampled air masses. Finally, to validate chemical transport model results and the distribution of ozone in the western Pacific atmosphere.

6.) AIRSAMPLING: 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.) SPECTROSCOPY: Identification of reactive trace gases BrO and IO with Multi-Axis Differential Optical Absorption Spectroscopy (MAX DOAS) 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.) µ-DIRAC: Quasi-continuous measurements of some VSLS in the marine atmospheric boundary layer (15 m altitude) for realtime concentrations. For details of the measured parameters, please refer to Table 2.

9.) Atmospheric trace gases: Continuous measurements of the atmospheric mixing ratios of a suite of pollution indicators and greenhouse gases (CO, CH_4, O_3, CO_2) in order to investigate their spatial and temporal variability in the lower tropical marine boundary layer.

10.) CIMS-REACTIVE COMPOUNDS; Continuous measurements of Br_2, BrCl, HOBr, BrO, and $ClNO_2$ and HNO_3, HCl, SO_2, and HBr in the marine boundary layer with two Atmospheric Chemical Ionization Mass Spectrometers, a LIF Instrument for IO and a NOx detector, which were deployed inside a specifically designed 10 ft container on the forecastle deck of the ship.

11.) ATMOSPHERIC AEROSOL: Major ions and halogens in aerosol samples, in order to identify their sources and quantify the halogen budget in the western Pacific atmosphere.

Table 1: Scientific groups. participating institutions and contacts:

	Principal Investigator (PI)	groupno.+ name	Last Name	Fore Name	Function	University
	Ship					
			Quack	Birgit	chief scientist	IFM-GEOMAR
			Sapii	Mohamad Zaid bin	observer	NHD-Malaysia
			Magura	Benjamin Z. Magura	observer	Navy-Philippines
in water	Quack	1a: Halocarbons MS	Hepach	Helmke	student	IFM-GEOMAR
			Raimund	Stefan	technician	IFM-GEOMAR
	Wallace	1b: Halocarbons ED	Qiang	Shi	student	IFM-GEOMAR
	Bracher	2a: Biology; Pigments	Altenburg Soppa	Mariana	scientist	AWI- BREMERHAVEN
			Wiegmann	Sonja	technician	AWI- BREMERHAVEN
			Cheah	Wee	scientist	AWI- BREMERHAVEN
	UM/UNIMAS	2b: Biology, speciation	Idid	Rizman	scientist	Universiti Malaya Kuala Lumpur
			Muhajid	Aazani	scientist	University Malaysia Sarawak
	Palermo		Palermo	Joseph	scientist	University of the Philippines Diliman
	Marandino	3a: OVO, C	Zindler	Cathleen	student	IFM-GEOMAR
	Quack	3b: Ox, Nuts	Marandino	Christa	student	IFM-GEOMAR
	Bange	3c: N_20, CH_4, DMS				
	Körtzinger/Tanhua	4: P_{CO2}, P_{O2}, S,T	Schneider	Anke	scientist	IFM-GEOMAR
in air	Krüger	5: radiosonding	Krüger	Kirstin	scientist	IFM-GEOMAR
			Bieligk	Henner	scientist	IFM-GEOMAR
			Fuhlbrügge	Steffen	student	IFM-GEOMAR
	Atlas	6: air sampling	Wittke	Franziska	scientist	IFM-GEOMAR
	Pfeilsticker	7: CE- DOAS	Lampel	Johannes	student	Uni Heidelberg
	Harris/ Kreher	8: µ- DIRAC	Kinzel	Julian	scientist	Cambridge/IFM-GEOMAR
	Schlager	9: CO, CO_2, CH_4, O_3	Sentian	Justin	scientist	University Malaysia Sabah
			Abdullah	Nur Aleesha	scientist	Malaysian Meteorological Dep.
	Voigt	10a: CIMS, Br	Jurkat	Tina	student	DLR
			Schäuble	Dominik	scietist	DLR
	Heard	10b: IO, OH, Hox	Ingham	Trevor	scientist	Uni Leeds
	Hofmann		Bunyan	Hannah	student	Uni Leeds
	Baker	11: Aerosol				UEA-Norwich

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IFM-GEOMAR	Leibniz-Institut für Meereswissenschaften, Düsternbrooker Weg 20, D-24105 Kiel, Tel: +431 6004206, Fax: +431 6004205, email: bquack@ifm-geomar.de ; New name for IFM-GEOMAR since 1. January 2012: Helmholtz-Zentrum für Ozeanforschung Kiel | GEOMAR, bquack@geomar.de, kkrueger@geomar.de
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Philippine-Navy	ENS Benjamin Zambrano Magura, email: mantarayz12@yahoo.com
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UM	Institute of Biological Sciences, Faculty of Science, 50603 Kuala Lumpur, Dr.Mohammed Rizman Idid, email: rizman@um.edu.my
UM SABAH	Borneo Marine Research Institute (BMRI), Universiti Malaysia Sabah Jalan UMS, 88400 Kota Kinabalu, Sabah, email: aanton@ums.edu.my
UNI LEEDS	School of Chemistry, University of Leeds, LS2 9JT, UK, email: t.ingham@leeds.ac.uk
UNIMAS	Department of Aquatic Science, Faculty of Resource Science & Technology, University Malaysia Sarawak, 94300 Kota Samarahan, Sarawak Malaysia, Aazani Mujahid, email: maazani@frst.unimas.my
UNI MAINZ	Institute for Analytical Chemistry, D-55128 Mainz, Thorsten Hoffmann, Ru-Jin, Huang, email: rujin@uni-mainz.de

UPHI Biological Oceanography and Modeling of Ecosystem Lab., The Marine Science Institute, University of the Philippines, Diliman, Quezon City, 1101 Philippines, email: jaydeepalermo@gmail.com

Table 2: Installed and operating instruments on board SO218 (Singapore-Manila; 15.-29. November 2011)

	Group	Instrument	Parameter
1	Halocarbons	Agilent GC/MS	iodinated, brominated and chlorinated VSLS
2	Halocarbons	Fisons GC 8000	iodinated, brominated and chlorinated VSLS
3	Phytoplankton/AWI	Pigments/Filtration	phytoplankton pigments, chlc3, chlc1+2,
4		Flowcytometry	phytoplankton size classes
5		Remote sensing (chla maps)	phytoplankton speciation
6		FRRF_Fluorometer	chla
7		Peristaltik/Pump	water supply
8		Microscopy	phytoplankton species
9	Radiation	RAMSES/ Container top	Radiane/Irradiance
10		RAMSES/ Monkey deck	Radiane/Irradiance
11		Fasttracka/ CTD	Radiane/Irradiance
12	Phytoplankton/Malaysia	UW Phyt. + Bacteria / Filter (150L water)	molecular characterization
13		CTD Phyt. + Bacteria / Filter (150L water)	zooplankton
14		Bongo Net/Plankton Net	zooplankton
15	Phytoplankton/Philippines	Infinity ME/ station/ fluorescence	phytoplankton
16	OVOC	GC/ MS	acetone, acetaldehyde, propanal, butanal, butanon
17		CDOM	humic acdis
18	DMS	GC	DMSP, DMSO, DMS
19	Ox/Nuts	Oxygen	CTD- discrete Winkler Oxygen
20		Nutrients	NO^{3-}, PO_4^{3-},
21		N2O; CH4	nitrous oxide, methane
22	Tracer	Freon samples	CFC water age
23	PCO2	PCo_2	CO_2 pressure in seawater
24		PO_2 (Oxygen optode)	Oxygen in Seawater
25		T	SST from Optode
26		Gas tension device	Total gas pressure in water
27	CTD	CTD	Temperature and Salinity profiles
28		Rosette sampler	water depth samples
29		Fluorometer	chlorophyll
30	Thermosalinograph	T/S	Temperature and Salinity continuous
31		meteorology	air temp, humidity, wind speed and direction,
32	Hydrographic shaft	CTD	temperature and salinity continuous
33		ADCP	ocean surface currents
34		sun-Pump	water samples from 4m depth
35		lowara	water samples from 4m depth
36	Radiosounding	Radiosondes	air temp, humidity, wind speed and direction profiles
37		Disdrometer	rain dropsizes
38		Rainsensor (Rudolph IRSS88)	rain
39		Ozon- sondes	ozone profiles
40	Air- sampling	Atlas flasks	> 50 trace gases, hydro-, halocarbons, freons, alkylnitra
41		Baker Aerosol	aerosol bromine, iodine speciation
42	Max Doas	Max Doas HD /Spectrometer (Acton)	BrO, IO
43		Max Doas HB/Spektrometer Shamrock 303i	BrO, IO,
44		Cavity HD	IO
45	µ-dirac	GC	$CHBr_3$, CH_2Br_2, and chlorinated compounds
46	DLR	cavity ring down (CO2, CH4,H2O)	CH_4, CO_2; O_3; CO
47		UV-absorp., VUV-fluoresc. (CO/O3)	carbon monoxide, ozone
48		CIMS1(BrO, Br_2, HOBr)	Br, HBr, BrO
49		CIMS2 (SO_2,HCl, HBr)	SO2,HCl, HBr, nitril chloride
50	Leeds	LIF (IO)	IO
51		Nox-Box (NO_2)	nitrous oxide
52		Denuder-Hofmann (I_2)	I_2

Work program during the cruise

During the SO218 cruise of 'RV Sonne' from 15 to 29 November 2011 in the South China and Sulu Sea between Singapore and Manila (Philippines) a variety of chemical and physical parameters within the surface waters as well as between the atmospheric boundary layer and the stratosphere have been examined with different measurement frequencies. Data and samples were obtained using a variety of analytical instruments and sampling devices (Tables 1 and 2). Regular water samples were collected from pumped supplies submersed in the hydrographic shaft of the ship. Depth profiles were undertaken at selected locations to investigate the vertical hydrographic structure of the water column and to obtain trace gas profiles (Appendix 3). Deep profiles of anthropogenic tracers were determined in the Sulu Sea to determine the water mass age. Several VSLS from sea water and air were analyzed directly on board the ship.

Table 3: Underway Work plan and sampling strategy on board FS Sonne.

Zeit	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Group																								
1	w/a	w	w	s	w	w	w/a	w	w	s	w	w	w/a	w	w	s	w	w	w/a	w	w	s	w	w
2	w	c	c	c	c	c	c	w	c	c	c	c	c	w	c	c	c	c	c	w	c	c	c	w
3		w			w			w			w			w			w			w				w
4	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c
5	r						r						r/w/o						r					
6	(a)	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	a	(a)	(a)	(a)	(a)	(a)	2a	(a)	(a)	(a)	(a)	(a)
7	c	c	c	c	c	c	c	c	c	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
10	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c	c

w: water sample
a: air sample (occasional)
c: continuous
r: radio sonde
o:ozone sonde
st: standard

The working schedule during transit included continuous sampling of seawater, a collection of discrete air samples, the installation of optical measuring techniques and the uplift of research balloons. During the cruise samples have been obtained with 52 instruments and sampling devices (Table 2). Routinely hourly to three hourly water and - air samples have been taken from pump supplies submersed in the hydrographic shaft, respectively installed on the monkey deck (Work Groups 1,2,3,4,6). Meteorologists sent weather balloons with trace gas instruments to the stratosphere (up to 30 km height) every six hours (Work Group 5), with an increased frequency of two hours on the two diurnal stations on 18./19th and 21./22nd November , which were conducted in open waters each roughly 60 nm off-coast from Kuching and Kota-Kinabalu.

After these stations boats from our Malaysian partners at Kuching from the University of Malaysia-Sarawak, at Kota-Kinabalu from the University of Malaysia, Sabah visited the RV Sonne. During these local ship cruises, water samples were taken (at 1 km, 5 km, 10 km, 15 km, and 20 km off-coast) and exchanged with samples taken in the open ocean by the RV Sonne team. The local boat water samples were analyzed for their content of trace gases and phytoplankton on board RV SONNE. Open ocean measurements were thus complemented by near shore and coastal gradients from the local ships and atmospheric measurements through the troposphere by the aircraft Falcon, starting at the same height of 15m above sea level as air samples were taken on board SONNE.

Figure 2: Meetings and simultaneous measurements of RV SONNE and DLR aircraft Falcon – stationed in Miri on Borneo during the SHIVA campaign- were and performed on 19th November, 12 o'clock local time and on 21st November, 11o' clock local time (Photo: Torsten Bierstedt).

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 (Work Groups 3, 7, 8, 9, 10).

Various halogenated hydrocarbons have been analyzed directly on board using a gaschromatography/ mass spectrometry system (Work Group 1). Oxygenated trace gases and dimethyl sulfide were also analyzed directly with a gas chromatograph/mass-spectrometric system from sea water (Work Group 3), while carbon dioxide and oxygen were measured immediately with sensors within the upper oceanic layer (Work group 4). More trace gases in sea water (N_2O, CH_4) will be analyzed by gas chromatography post-cruise in the laboratory. Biological sampling included parameters of organic carbon and nitrogen as well as pigments, the amount and sizes of cells and the composition and activity of the phytoplankton and zooplankton (Work Group 3). The optical properties of seawater and its ingredients were measured as reference spectra for the validation of satellite data analysis and models, in order to detect the composition, distribution and productivity of phytoplankton (Work Group 3).

Figure 3: Local boats visited the RV Sonne from our Malaysian partners (University of Malaysia-Sarawak) at Kuching on 19th November at noon and the University of Malaysia, Sabah.at Kota-Kinabalu on 22nd November.

Discrete air samples were taken for partners of the Universities Norwich (15 samples) as well as the 'Rosenstiel School of Marine and Atmospheric Sciences" in Miami (200 samples) (Work Groups 6, 11). 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, nitric oxide, bromine oxide, carbon monoxide) were examined on the basis of optical measurements, by rises of research balloons and mass spectrometers (Work Groups 5, 6, 8, 9, 10).

The majority of 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 end of January 2012 and the dangerous goods container end of February 2012. The analysis of the extensive dataset from the ocean and the atmosphere collected during SO218 will bring first results in late summer 2012. The new insights into the interaction of ocean and atmosphere, which will be gained in the next months, will be presented at international conferences (SOLAS, EGU and AGU conferences) and will be published in peer reviewed scientific journals.

Figure 4: Release of an ozone-sonde at night (photos: Johannes Lampel).

Short cruise reports and participating institutions

In the following, short cruise reports from the participating institutions are presented which give an insight into their objectives, methods and some preliminary results.

1a Halocarbons in the South China and Sulu Sea

Helmke Hepach, Birgit Quack, Stefan Raimund, IFM-GEOMAR, Kiel

Introduction

The oceans have strong influence on the trace gas concentrations in the atmosphere by sea-air-exchange processes. Halogenated hydrocarbons (halocarbons) such as methyl iodide (CH_3I), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) are important trace gases and are biologically and (photo) chemically produced in the water column. Macroalgae along the coast and waters with high phytoplankton densities are known sources for such compounds. River outflow, photochemical reactions and anthropogenic discharges (e.g. treatment of waste water) are other important sources and together with the biological sources cause a highly variable pattern of oceanic halocarbon distribution.

Halocarbons influence the atmospheric chemistry by contributing to the atmospheric halogen pool and consequently influencing the 'oxidizing capacity' of the troposphere and the stratosphere. Whereas naturally produced halocarbons mostly supply to the bromine and iodine pool, anthropogenic halocarbons elevate the atmospheric chlorine pool. In the troposphere, halocarbons influences the NO/NO_2 cycle, stimulates catalytic ozone depletion cycles and influences the life times of other trace. Rapid deep convection can transport halocarbons to the lower stratosphere where they may represent significantly to stratospheric halogens and consequently contribute to ozone depletion.

For a better understanding of chemical processes in the atmosphere (especially in a changing atmosphere with elevated greenhouse gases), it is necessary to measure oceanic halocarbon concentrations in so called “hot spots” around the globe. Tropic gas emissions from the ocean towards the atmosphere are highly interesting, because in those areas, trace gases can enter the stratosphere where ascending warm air lifted them upwards. Here, when deep convection events occur, air masses are transported from the troposphere to the lower stratosphere (passing the tropical tropopause layer, which is the typical barrier for ascending air masses in higher latitudes).

Method

During this cruise (15 to 29 November 2011), we investigated halocarbon distributions in the South China and Sulu Sea along the coast off Singapore, Malaysia, Borneo and the Philippines on board the German research vessel SONNE during the SHIVA (Stratospheric Ozone: Halogen Impacts in a

Varying Atmosphere) campaign. Samples were taken along the cruise track at 73 different positions using a submerged water pump under the ship`s keel. Moreover, profiles were taken at 10 CTD stations with a 24-bottle CTD rosette (10-L-Niskin bottles). At each station samples were collected in the entire water column with the focus on the upper 150m (surface layer, chlorophyll maximum layer, lower layers).

Halocarbons were analysed using a purge-and-trap technique and GC-MS. The halocarbons were quantified in single ion mode. Quantification of volatiles was performed by external liquid standards. Liquid standards were diluted in seawater and treated like a normal sample. For more details see Quack et al. (2007).

First results

We were able to measure 13 different halocarbons along the cruise track (at 73 positions) and in the water column at 10 different positions. First results show, that halocarbon distribution is highly variable along the cruise track. Near shore samples show typically elevated concentrations, while samples off shore contain lower halocarbons concentrations. The CTD profiles indicate that bromoform has a source near or within the Chl-a maximum. However, those findings need to be carefully confirmed by a thorough data analysis later. Together with the discrete air measurements (canisters will be measured by Elliot Atlas, RSMAS), our data set will be used to calculate the sea-to-air gas exchange, after careful intercalibration of data.

1b Methyl iodide and more halocarbons in the South China and Sulu Sea

Qiang Shi, IFM-GEOMAR, Kiel

Methyl iodide (CH_3I) and other volatile iodocarbons are major carriers of iodine from the ocean to the atmosphere. If methyl iodide goes into the atmosphere, the carbon-iodine bond in methyl iodide can be easily broken by solar UV radiation (260 nm). This reaction yields methyl radicals and iodine radicals. The iodine radicals react fast with ozone forming oxygen molecules and iodine monoxide. These two reactions lead to the destruction of ozone.

From 15.11.11 (Singapore) to 29.11.11 (Manila) the focus was on under way samples. In the first under way sample, which was closest to Singapore, we can find higher concentrations of halogen compounds. The preliminary analysis showed concentration of methyl iodide of 9 pmol/L, of dibromo methane of 15 pmol/L, and of bromoform of more than 70 pmol/L. The variations of bromoform and dibromomethane in the under way samples were similar. From sample 27 to samples 36, we can find higher concentration of bromoform and dibromomethane. The highest concentration of methyl iodide was 11 pmol/L from the sample 26. The reason for the increasing concentration needs further analysis.

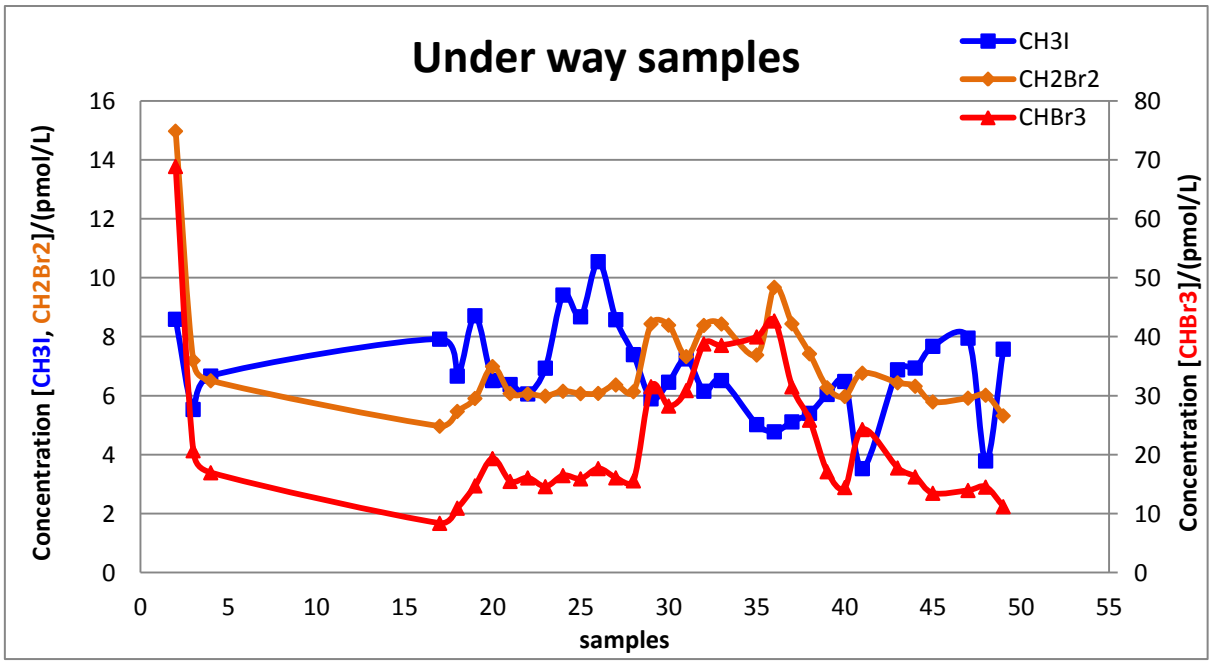

Figure 1: Preliminary concentration of methyl iodide, dibromomethane and bromoform in the under way samples.

During the cruise I have analysed 12 local boat samples also (6 samples from Kuching, the rests from Kota Kinabalu).

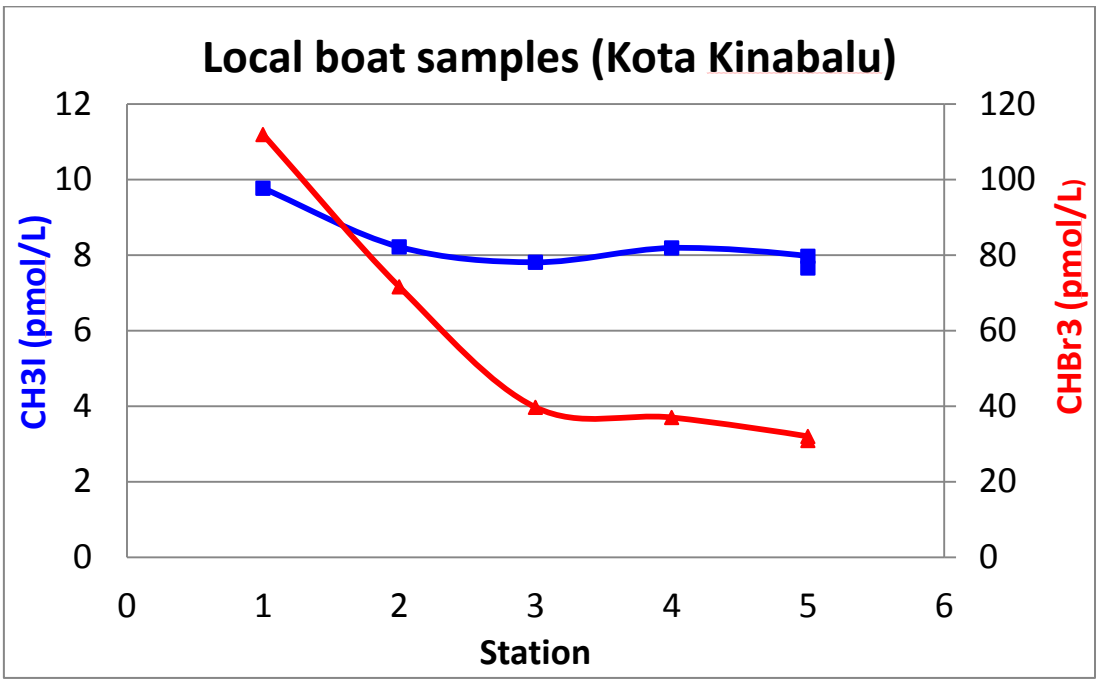

Figure 2: The local boat samples by Kota Kinabalu (preliminary concentrations).

Between land and ship we had analysed 5 samples from 5 stations. Station 0 is close to land, and station 6 is our ship. We can clearly find, the concentration of methyl iodide and bromoform decreased from land to ship, especially bromoform. The concentration of bromoform in the station 1 was more than 100 pmol/L, then decreased to 30 pmol/l in the station 5, which was very closed to our ship. For methyl iodide, the variation of concentration was small from station 2 to station 5, the concentration of methyl iodide was kept at 8 pmol/L.

2a The relationship between phytoplankton composition and biogenic trace gases during the SHIVA-Sonne SO218 campaign

Expeditioner: Wee Cheah[1], Sonja Wiegmann[1], Mariana Altenburg-Soppa[1], Joseph Dominic Palermo[2]

Principal Investigator: Astrid Bracher[1] (not on board)

[1] Phytooptics Group, Alfred-Wegener-Institute for Polar and Marine Research, Bremerhaven, Germany

[2] Marine Science Institute, University of the Philippines, Quezon City, Philippines.

Objective

The ocean is the largest source of biogenic trace gases, especially short-lived halocarbons. These short-lived halocarbons are primary halogen carriers to the troposphere and lower stratosphere, and catalyse ozone depletion. Although it is widely believed that phytoplankton and other marine primary producers contribute to the production of biogenic trace gases in both coastal waters and the open ocean, the mechanisms in the production and release of these halogens into the atmosphere are largely unknown. Further field studies are required if we are to better estimate the contribution of these halogens in the atmosphere, especially ozone depletion. The objective of this project is to investigate the link between phytoplankton compositions and biogenic traces gases around the Malaysian and Philippines waters. These regions are believed to be an upwelling hotspot for short-lived halogens, but have received little attention.

This project utilised both remote sensing technique and in situ observation to achieve the study goal. Field measurements of phytoplankton pigment and group composition, optical characteristics of phytoplankton, and physiological conditions of phytoplankton were investigated on board R.V. Sonne from 15 – 29 Nov 2011 in the South China Sea and Sulu Sea as part of the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) campaign. Underwater reflectance and light availability that are highly precise and essential input parameters for the satellite retrievals and modeling were also measured.

Sampling strategy (Water samples)

Discrete surface seawaters were collected from the ship's underway system and at six different depths from the CTD/Rosette Niskin Bottle during CTD stations. Sampling that were performed on board included: (1) filtration of water samples onto GF/F filters for high performance liquid chromatography (HPLC) pigment analysis, particulate absorption (PABS) and particulate organic carbon (POC) measurements; (2) water samples were preserved for flow cytometric measurements and microscopy for later analysis in the laboratory at the Alfred-Wegener-Institute for Polar and Marine Research at Bremerhaven, Germany; (3) filtered seawater were collected for analysis of coloured dissolved organic matter (CDOM) fluorescence at University of Kiel.

In-situ optical and fluorescence measurements (1) A Fast Repetition Rate Fluorometer (FRRF) (Chelsea Technology Group) was used in a flow-through system to provide online data of variable chlorophyll a (chl a) fluorescence during the cruise; (2) a second FRRF and a multi-excitation fluorometer were deployed in the water down to 150 m during CTD stations to obtain the vertical profiles of phytoplankton pigments fluorescence; (3) in-water downwelling spectral irradiance and upwelling spectral irradiance and radiance sensors were also deployed together with the FRRF during CTD stations with a set of three TriOS's Ramses spectroradiometers, while a fourth sensor is mounted on deck and measures downwelling irradiance at the sea surface.

Data description

Below are the list of parameters that were measured during the cruise and data that will be obtained after the cruise.

1. Phytoplankton pigment concentration (mg/m3)
2. Phytoplankton species composition
3. Particulate organic carbon, POC (mgC/m3)
4. Phytoplankton cell size and count
5. Particulate absorption (m2)
6. Maximum photochemical efficiency of photosystem II, Fv/Fm (dimensionless)
7. Relative absorption spectra of phytoplankton at 375, 400, 420, 435, 470, 505, 525, 570, 590 nm
8. Downwelling irradiance at sea surface, Eo [mW/(m^2 nm)]
9. Downwelling irradiance in water, Ed [mW/(m^2 nm)]

10. Upwelling irradiance in water, Eu [mW/(m^2 nm)]
11. Upwelling radiance in water
12. Photosynthetic active radiation in water, PAR (µmol quanta/m^2/s)

Preliminary results

Underway FRRF measurements showed higher maximum photochemical efficiency of PSII (Fv/Fm) in waters near to the Malaysian Peninsular, which are at the western end of the cruise transect. Fv/Fm represents the photochemical efficiency of phytoplankton, which is the probability that light energy captured by photosynthetic apparatus is being utilised as photochemistry. Higher Fv/Fm values in waters near the Malaysian Peninsular suggest that environmental conditions are more favourable to phytoplankton in the area compare to other sampling sites. Further analyses between phytoplankton photosynthetic performance, concentration, halogens, and environmental variables will be carried after the cruise.

2b Diversity, Abundance and Molecular Identification of Zooplankton in the South China Sea

Mohammed Rizman Idid

Institute of Ocean and Earth Sciences, University of Malaya

Objective:

1) To determine the diversity, abundance, species composition of zooplankton in South China Sea.
2) To identify species of zooplankton based on morphological characters and also confirmation by molecular genetic techniques, eg. DNA sequencing.
3) To relate distribution patterns and the zooplankton communities to the water conditions and environmental parameters, particularly from coastal to the open sea.

Sampling Strategy

Sampling of zooplankton on RV Sonne was performed based on 3 approaches (due to what was permissible by diplomatic approvals):

1) **Continuous Underway Sampling** (every 3 hours) - water of 5m depth was continuously pumped from the moon pool and filtered using a plankton net with 147µm mesh size. The usual rate of water flow for the duration of the cruise was approximately 15.4L/min, and the water was sampled for 30 minutes at every 3 hour intervals.
2) **CTD Water Samples**- a total of 120 L of water from Niskin bottles of the CTD deployed at CTD stations was filtered into plankton net with 147µm mesh size. Water was mostly collected from depths that showed chlorophyll maxima of phytoplankton.
3) **Vertical Tow of Bongo Net** – water column was sampled vertically using bongo nets with 200µm and 140µm mesh size. Maximum depth sampled was at 65m depth.

All zooplankton samples were washed through a mesh and preserved with 95% undenatured ethanol. Samples obtained from the bongo-net usually contained gelatinous zooplankton and were separated from other zooplanktons before preservation. All samples will be analysed in the laboratory using light microscopy for species identification. This will be complemented by molecular identification using PCR amplification and DNA sequencing of 'barcoding' genetic markers.

Data Description

A total of 92 water samples were collected from the underway sampling covering areas in Malaysia and Philippines. Preliminary observations of these samples may indicate that samples from Philippines contained more zooplankton from the Malaysian waters. In general more zooplankton were found during night sampling rather than the day. Some of the common zooplankton obtained from this method were copepods, jellyfish larvae and chaetognaths.

Fifteen CTD samples were obtained which ranged from 10m- 65m in Malaysia and Philippine waters. Not all samples contained visible zooplankton, and will need closer inspection using microscope. This sampling method was the least successful in obtaining zooplankton as very little water was collected.

Eight samples from the bongo net trawls were obtained from the Malaysian waters only. Deployment of bongo nets in Philippine waters was prohibited and therefore sampling by this method was omitted. Initial inspection showed that this is the best method to obtain many zooplankton species. Other than the common copepods and chaetognaths, species of shrimps, crab and fish larvae, comb-jellies, salps, isopods have been observed. Night sampling also yielded many species, possibly due to the bright lights on the ship's deck.

Expected Outputs

1) Results from this survey cruise will contribute to the species inventory of zooplankton in this region.
2) Diversity, abundance and distribution pattern of zooplankton and its relationship with coastal and offshore conditions.
3) Contribute to the 'barcoding' database of zooplankton. Molecular identification of zooplankton in this region is fairly new.

2b Morphological and molecular characterization of phytoplankton, assessment of the microbial communities, primary productivity fronts

Dr Aazani Mujahid
Faculty of Resource Science and Technolog, Universiti Malaysia Sarawak (UNIMAS)

Background

From the 25th – 29th July 2011, I was kindly invited to be one of five Malaysian counterparts onboard the Research Vessel (RV) Sonne Cruise No. SO218. Such vital research is timely especially for Sarawak (and Malaysia in general) as the spatial and temporal coverage of the many aspects of the SHIVA-Malaysia (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere, campaign in Malaysia) research, as well as the objectives to be achieved are unprecedented. Similar expeditions in the past are rarely done and hardly published.

The equatorial waters of the South China Sea (SCS) surrounding Malaysia and the Philippines are highly productive (as seen in reports from the SEAFDEC's East Coast of West Malaysia 1995-1996 cruises and SEAFDEC's Sabah, Sarawak and Brunei Darussalam cruises in 1996-1997) while facing relatively high human pressures. It hosts many thriving mixed marine ecosystems such as mangroves endorsed by RAMSAR Wetlands, islands with UNESCO heritage site status, and coral reefs which are recognised as the world's apex for marine biodiversity and partially included into the Coral Triangle Initiative (CTI) network.

The research here is made possible with the kind permission from the Malaysian and Philippines Government and was largely funded by IFM-GEOMAR and other related SHIVA counterparts in Germany and Britain.

Scope of Research

As the UNIMAS counterpart, I have been collecting and preparing samples for Malaysian colleagues throughout the SO218 cruise which complement SHIVA-Malaysia's main aims. Samples are taken for (i) Lim Po Teen, Prof Ann and Prof Phang, with UNIMAS counterparts who will be studying the morphological and molecular characterization of phytoplankton species in the SCS; (ii) Moritz Müller who will be assessing the microbial communities in SCS waters (especially three clusters which are closely related to phytoplankton blooms and utilize dimethylsulfoniopropionate or DMSP); (iii) I am

however interested in efforts detecting primary productivity fronts of SCS using Chlorophyll a and temperature inferred from cruise and satellite dataset. This would include learning to calibrating/ validating with the case-2 data products from the MERIS satellite sensors with suitable in-situ data obtained in collaboration with the PHYTOOPTICS Group under Prof. Dr. Astrid Bracher (AWI). Besides that, I will continue to work with Prof Azizan and Lt Cmdr Zaid (Malaysian observer from the National Hydrography Centre) to process CTD and shallow water ADCP data from SO218. There are many elements for post-cruise processing in the laboratories which will not be covered in this report.

Methodology

Work on board SO218 mainly involved filtering and fixing of phytoplankton and microbial samples of seawater sampled from; (i) 5 m depth moon pool pumped into the Geology Lab; (2) rosette Niskin bottle sampling at discreet depths; (iii) 20 µm plankton net tow from 30 m depths from back deck; (iv) leftover seawater samples from all depths of the rosette. A summarized schematic of the sampling method is found in Figure 1.

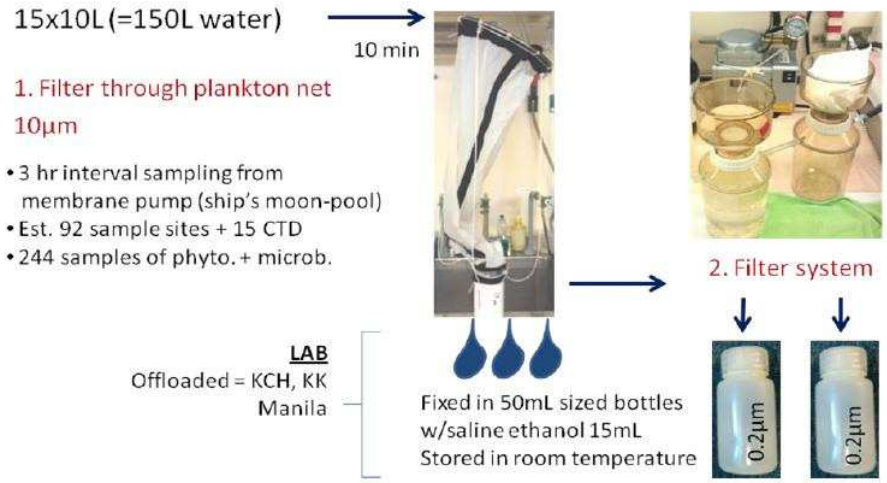

Figure 1: Schematic of sampling method employed on RV Sonne SO218. This includes filtration of estimated 150L of seawater through a 10 µm plankton net, and further filtration using filtration system then stored in 50 mL screw cap bottles with 15 mL saline ethanol at room temperature. Samples come offboard the RV Sonne in Kuching (KCH), Kota Kinabalu (KK) and Manila.

Processing includes filtration of an estimated volume of more than 150 L of seawater through a 10 µm plankton net, and further filtration through 0.2 µm nylon membrane filters. The process takes about an hour per sample site. This method is employed for all the samples mentioned (i – iv) mentioned, with

tows and rosette bottles having lesser volumes of water. The sampling detailed notes are in Appendix 1. As seen in Figure 2 below, in total there are 106 sample sites, with each site having samples for both phytoplankton and

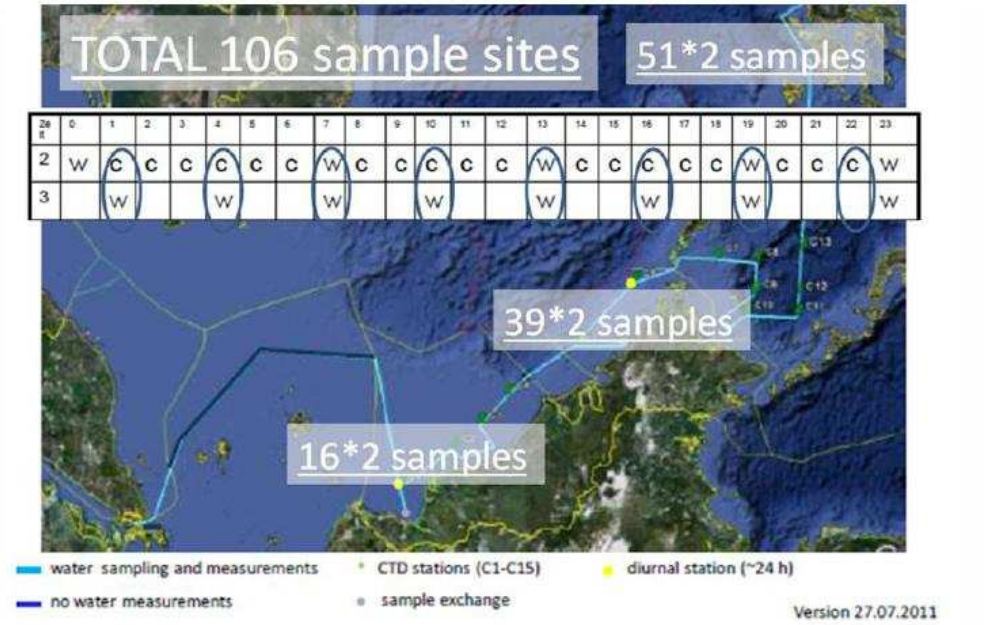

Figure 2: Map of sampling cruise track of the RV Sonne SO218. The 24 hour operation would sample water (marked w) every 3-hourly, starting at 0100 everyday. A total number of 106 sites in the SCS have been sampled, with underway 3 hourly sampling bottles of 32 (phytoplankton and microbial) samples come offboard the RV Sonne at Kuching (KCH), 78 samples offboard in Kota Kinabalu (KK) and 102 samples offboard in Manila. The rest of live samples and CTD samples are taken from Manila to Kuching**.**

Expected Outcomes and Early Results

The expected outcomes from the RV Sonne sampling would be to: (i) determine the phytoplankton and microbial biomass, composition and distribution in SCS waters; (ii) identify the distribution of Harmful Algal Bloom species (HABs); (iii) relate the phytoplankton composition with environmental conditions from the shipboard cruise profile measurements (CTD, fluorometer, ADCP for water properties and currents) and sea surface satellite parameters (especially Chlorophyll and Temperature); (iv) detecting species and investigating phytoplankton communities using selected genetic markers and genotyping systems respectively; (v) studying the role of Rosebacter sp. in DMS release in coastal waters. From the CTD and fluorometer profiles during the 15 casts, we observed various profiles of temperature, dissolved oxygen, salinity and chlorophyll which vary spatially between depths and among the stations.

On several occasions, interesting ‘steps’ and gradients of the profiles may visually be seen to be corresponding with environmental factors such as currents at depths (from ADCP), weather (rain, windspeed from shipboard weather station) or even position (GPS near coast with river plumes compared to deep open ocean casts). These are all preliminary assumptions and much more work will need to be done post processing of samples and data from all groups.

Future Outlook

Further work especially within the coastal waters can be done to improve patchy knowledge of the spatial/ temporal variability of phytoplankton and microbial communities with relation to the various environmental conditions. We intend to expand into the novel use of multi-platform tools and technology, and merging of the satellite, in situ and laboratory results. We also personally hope to continue such collaboration to improve the gaps of knowledge within the 2011 SHIVA-Malaysia campaign with our five year in situ data of phytoplankton and microbial communities, and environmental conditions in selected Malaysian coastal waters, as well as other CTD and cruise datasets previously unpublished.

3a Shiva Sonne Cruise Report: Dimethylsulfide and oxygenated volatile organic compounds

Christa Marandino, Cathleen Zindler, IFM-GEOMAR

Dimethylsulfide

Objective: To investigate seawater cycling of dimethylsulfide (DMS), dimethylsufidepropionate (DMSP), and dimethylsulfoxide (DMSO). The relationship between the concentrations of these compounds and a variety of biological, chemical and physical parameters will be examined in order to determine what factors control the magnitude and distribution of the compounds in the surface ocean.

Background: DMS is the most abundant biogenic sulfur compound emitted to the atmosphere. It is mainly produced in the surface ocean from the precursor DMSP, a compound excreted by phytoplankton. Once in the atmosphere, DMS is rapidly oxidized to sulfur dioxide (lifetime approximately 1 day). The oxidation products of DMS can form aerosols and cloud condensation nuclei, thereby influencing the Earth's radiative properties and climate. It was proposed by Charlson et al. (1987) that this air-sea cycling of DMS may be a natural negative feedback loop on Earth's climate system. This so called CLAW hypothesis has yet to be proven.

In addition, it is still not possible to predict the concentrations and distribution of DMS in the surface ocean. Although many individual components of surface ocean DMS cycling have been studied, such as production of DMSP by dinoflagellates and cleavage of DMSP into DMS via DMSP lyase, the surface ocean concentrations of DMS seem to be due to a combination of factors. One part of the cycle, DMS oxidation, produces the product, DMSO. DMSO is found throughout the water column, even into the deep ocean. More studies investigating exactly what factors (e.g. phytoplankton species, bacteria abundance, UV radiation, etc.) control the surface ocean cycling and concentrations of DMS are still needed.

Methods: DMS, DMSP (dissolved and particulate), and DMSO are measured by purge and trap gas-chromatography (GC) coupled to a flame photometric detector (FPD). Triplicate samples, 10 mL in volume, are sparged for 10 minutes with a helium flow of approximately 30 mL per minute. The samples are dried with potassium carbonate and trapped with liquid nitrogen before being injected on the GC with boiling water. DMSP and DMSO are quantitatively converted to DMS via

chemical reaction after the sample has been sparged of the ambient DMS. The subsequent concentrations of DMS are measured in the way described above.

Preliminary results: Unfortunately, the GC-FPD system did not exhibit adequate sensitivity during the cruise. Most samples were measured with the gas chromatograph-mass spectrometer system described below. Separate samples were preserved for DMS, DMSP, and DMSO detection later. The DMS values measured in situ will be compared to the preserved values.

DMS concentrations appear to be in the low range of <1 to 1 nM. This may be beneath the GC-FPD detection limit, but could be seen with GC-MS. The spatial distribution of DMS over the cruise track is yet to be determined.

Oxygenated volatile organic compounds

Objective: To measure the air-sea concentration gradient of 11 different oxygenated volatile organic compounds (OVOCs): methanol, ethanol, n-propanol, isopropanol, 1-butanol, 2-butanol, acetaldehyde, propanal, butanal, acetone, and butanone. Isoprene and DMS air-sea concentration gradients were also measured.

Background: OVOCs can influence the oxidative capacity of the atmosphere by contributing to peroxyacetylnitrate and secondary organic aerosol formation, and HO_x and ozone chemistry. They are especially important in regions of the atmosphere where water vapor levels are low, such as in the upper troposphere. The region of the Shiva Sonne cruise track is especially interesting because of the highly convective air in this region. Gases produced at the air-sea interface can be transported more quickly and directly to the upper troposphere/lower stratosphere, where they have the greatest impact on atmospheric chemistry. Whether the ocean is a source or a sink of these compounds to the atmosphere is still an open question. In addition, surface ocean processes of OVOCs are largely uncharacterized, but it is largely thought that OVOCs are produced by photochemical reactions of color dissolved organic matter (CDOM) and by biology in the surface ocean. Uptake of these compounds also seems to be related largely to biological processes.

Methods: The trace gases in seawater were measured via purge and trap gas chromatography coupled to a mass spectrometer detector (GC-MS). 10 mL samples were sparged with 30 mL per

minute of helium for 20 minutes through a potassium carbonate drying trap. The trap was then flushed at 40 mL per minute for an additional 10 mins. The sparged gases were trapped with liquid nitrogen then injected onto the GC column with boiling water. The masses of each compound were detected with the MS. Trace gases in air were trapped for 10 minutes in liquid nitrogen headspace from the bow of the ship using a small pump (flow = approx. 80 mL per minute). Potassium carbonate was again used to dry the samples. The gases were desorbed with boiling water and refocused using liquid nitrogen before being injected on the GC and detected in the same way as the liquid samples. Standards for both air and water were measured daily and 3 4 to 5 point calibrations for air and water were performed over the entire cruise track.

CDOM fluorescence was measured to characterize the chemical makeup of the CDOM. CDOM absorbance was measured to determine the quantity in the seawater samples.

Preliminary results: Methanol, acetone, isopropanol, DMS and 1-butanol were observed in almost every sample. Acetaldehyde, ethanol, propanol, and 2-butanol were also regularly measured. Propanal, isoprene, butanal, and butanone were either extremely small (below the detection limit) or not present in most of the samples measured. The air-sea gradient and spatial distribution over the cruise track is yet to be determined. CTD profiles for DMS and the CTD chlorophyll maximum depth for OVOCs and isoprene were also measured but the results are not yet known. CDOM values will be will be analyzed upon return to Germany.

3c Sampling of dissolved nitrous oxide (N_2O) and methane (CH_4) during the SHIVA-Sonne SO218 campaign

Exepditioner: Franziska Wittke, Principal investigator: Hermann W. Bange (not on board)
Marine Biogeochemistry, IFM-GEOMAR, Kiel, Germany.

Background

Nitrous oxide (N_2O) and methane (CH_4) are atmospheric trace gases, which, directly and indirectly, influence the present-day climate of the Earth. Thus, an assessment of the natural and anthropogenic sources and sinks as well as the formation pathways of N_2O and CH_4 is essential both to understand past Earth's climate variability and to estimate the future development of Earth's climate. The world's oceans including its coastal zones, as natural sources of N_2O and CH_4, play a major role in the global budget of atmospheric N_2O, but only a minor role in the global budget of atmospheric CH_4. However, measurements of oceanic N_2O and CH_4 are still sparse and the derived emission estimates are associated with large uncertainties.

N_2O in oceanic environments is mainly formed as a byproduct during nitrification ($NH_4^+ \rightarrow NH_2OH \rightarrow NO_2^- \rightarrow NO_3^-$) and as an intermediate during denitrification ($NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow N_2$). In both processes, the yield of N_2O strongly depends on the concentration of dissolved oxygen (O_2). Both, nitrification and denitrification are microbial processes and can occur in the water column, in the sediments and in the interior of suspended particles. CH_4 is formed during the decomposition of organic material by microbial methanogenesis. Since CH_4 formation requires strictly anaerobic conditions, CH_4 is produced in anoxic environments such as sediments, in the interior of suspended particles, in zooplankton guts during grazing or from biological cleavage of dissolved precursors such as DMSP and methylphosphonate. Additionally, CH_4 is oxidized under aerobic as well as anaerobic conditions in the water column and in the sediments. On the continental shelf so-called geological CH_4 can be released directly to the water column through mud volcanoes, via groundwater input, or seepage from gas/oil fields.

Sampling

Samples for the determination of dissolved N_2O and CH_4 have been taken in triplicates from both the continuous surface seawater supply and the CTD/rosette casts. Samples have been poisoned

with HgC_{l2} (aq) immediately after sampling. All samples were shipped back to our lab in Kiel for the analysis of dissolved N_2O and CH_4: N_2O and CH_4 will be determined by applying the static headspace equilibration method. Gaseous subsamples of the equilibrated headspace will be injected onto a separation column filled with 5A molsieve followed by detection of N_2O and CH_4 with an electron capture detector (ECD) and a flame ionization detector (FID), respectively.

106 underway samples have been sampled for N_2O and CH_4 in triplicates every 3h from the continuous surface seawater supply. 14 CTD/rosette casts and 7 CTD/rosette casts have been sampled for N_2O and CH_4, respectively. The final N_2O and CH_4 data will be archived in MEMENTO (The MethanE and NiTrous Oxide database: https://memento.ifm-geomar.de/).

4 Underway measurements of CO_2, oxygen and total gas pressure

Anke Schneider, Tobias Steinhoff

IFM-GEOMAR, Kiel

On Sonne cruise SO218 we ran several underway instruments to measure the following parameters: dissolved oxygen, total gas pressure of all dissolved gases and partial pressure of CO_2 ($/p/CO_2$). The instruments were fed with a seawater flow from a submersible pump that was installed in the ships moonpool (~ 5m depth). All sensors were deployed in a bath (Coleman® cooling container) that was flushed with the seawater at a typical flow rate of 20 L min^-1 .

Underway measurements

/pCO_2 /

For the determination of $/p/CO_2$ a submersible sensor was used (HydroC-CO_2). A flat silicone membrane acts as an equilibrator between the seawater and the inner gas volume of the sensor. The CO_2 concentration in the air circuit is measured by means of NDIR detection.

/Oxygen/

Dissolved Oxygen was determined via an optode (Aanderaa Instruments AS, Bergen, Norway). This technique is based on dynamic luminescence quenching. The raw data will be processed after the cruise (applying lab determined calibration function and correction for SSS).

/Gas Tension/

The PSI-GTD-Pro (Pro-Oceanus Systems Inc., Halifax, Canada) measures the total dissolved gas pressure of all gases. A small sample volume of air is equilibrated to all dissolved gases in the water through a special membrane. The GTD was also installed in the water bath.

/Sea surface temperature (SST) and salinity (SSS)/

SST and SSS were measured by a thermosalinograph (Eco-Probe, ME-Grisard, Germany) which was installed in the ships moonpool next to the seawater pump.

Discrete samples

50 discrete samples for the determination of dissolved inorganic carbon (DIC) and alkalinity (TA) were sampled twice a day. They were collected in 500 mL glass bottles with glass stoppers. They were poisoned with 100 µL saturated HgCl_2 solution to prevent biological activity (respiration) and stored in dark. The samples will be measured in the laboratory at the IFM-GEOMAR in Kiel.

5 SHIVA SONNE SO218: Radio- and Ozonesounding

GRAW radiosounding and ECC ozone sondes:

Kirstin Krüger, Steffen Fuhlbrügge, Henner Bieligk (IFM-GEOMAR)

Scientific background

Although the first signs of the ozone recovery have been recognized in the upper stratosphere since the beginning of 2000 (WMO, 2007), still unexpected high ozone loss is eventually reported over polar latitudes since then, i.e. the record ozone loss over Antarctica in 2006 und more recently the first "Arctic ozone hole" during the winter 2010/2011 (Manney et al., 2011 Nature). Especially the timing of full ozone recovery in the Northern hemisphere (NH) is quiet uncertain due to the high natural variability of stratospheric temperatures during winter and the impact of naturally produced halocarbons chemical compounds, which are yet not adequately addressed in current ozone projections for the 21st century (CCMVal 2010; WMO, 2011; Manney et al., 2011 Nature).

Despite the well known threat of anthropogenic produced halo fluorocarbons (HFCs) on the ozone layer, very short-lived substances (VSLS) as bromine and iodine compounds and other natural trace gases have to be considered for the ozone depletion as well. These chemical species are produced in the ocean, probably through the metabolism processes of microorganisms called phytoplankton. To better understand the relationship between marine biochemistry and atmospheric chemistry and physics our SO218 SONNE expedition aims to investigate these relations into more detail. The tropical Western Pacific is especially suitable for these VSLS-transport examinations for two reasons: First, the tropical West Pacific is known to be a source region for halocarbons and has not yet been examined especially the southern part of the South China Sea. Second, this region exhibits strong convective activity throughout the year. Thus, active gas exchange between the marine boundary layer and the stratosphere (altitudes: 17-50 km), where the protective ozone layer exists. Regular (6-hourly) weather balloons are launched to improve the global meteorological assimilations, which are used as input data for trajectory and chemical transport calculations within SHIVA project, starting from the ocean surface well into the stratosphere. The ozonesonde measurements should detect direct chemical effects of the halocarbons or other chemical relevant trace gases in the atmosphere along and above our ship track.

Scientific goals

From the SO218-SONNE expedition we will derive new results concerning the atmospheric structure and content over the southern part of the South China Sea from the marine boundary layer well into the stratosphere. Given that the expedition cruised well within the tropical belt, we do not expect high variations in the meteorological parameters. Along the ship cruise from 1° N to 15° N deeper cold point temperatures within the Tropical Tropopause Layer (TTL) should be measured during November compared to boreal transition or summer seasons. Given that the cruise takes place in November starting in Singapore, we expect to be close to the Inner Tropical Convection Zone (ITCZ) with enhanced convective activity. After the ship cruise we will analyse the air mass pathways (trajectories) from the surface into the stratosphere. The radiosounding of temperature, wind, humidity and ozone will be used to validate the meteorological input data and will serve as a starting point for the trajectory calculations with the Lagrangian dispersion model FLEXPART.

Measurements

We have carried out 6-hourly radiosoundings of temperature, wind, and humidity, using 350 gr balloons inflated with roughly 25 kbar Helium. This routine observational program was carried out with DFM-09 radiosonde from GRAW. These radiosondes are characterized by their small lightweight package and easy handling which bears great advantage on an expedition that does not provide dedicated balloon filling and launching facilities. Also, the ground receiver equipment (antenna, radio data acquisition) was made available at no cost from the Germany Weather Service (DWD) in Lindenberg and could be easily installed on the vessel.

Ozone sondes were launched along the western and northern coast of Borneo usually at 19 LT (11 UTC) together with a GRAW radiosonde (DFM-97), using a TOTEX balloon with 1200 gr weight and about 80 kbar Helium filling. In total 6 ozone sondes were started during our South China Sea passage as well as more 73 radiosondes. For the ozonesonde launch a DFM-97 radiosonde was tight together with the ozone instrument equipped with a 30 m enroller. These large balloons had to be filled in on deck. In order to avoid premature burst of the balloons during filling, a special cover net (“balloon launcher”) was used for protection. The balloons and the balloon launcher were produced by the Japanese company TOTEX. The balloon launches were greatly supported by the scientists and the ship crew by securing the filling and launching equipment on deck. The balloons reached frequently altitudes above 25 km. Only one small balloon burst just before starting off due to the narrow passage between the fill-in and

another 20 feed container. The individual starts of the two described instruments are listed in the appendix.

First results

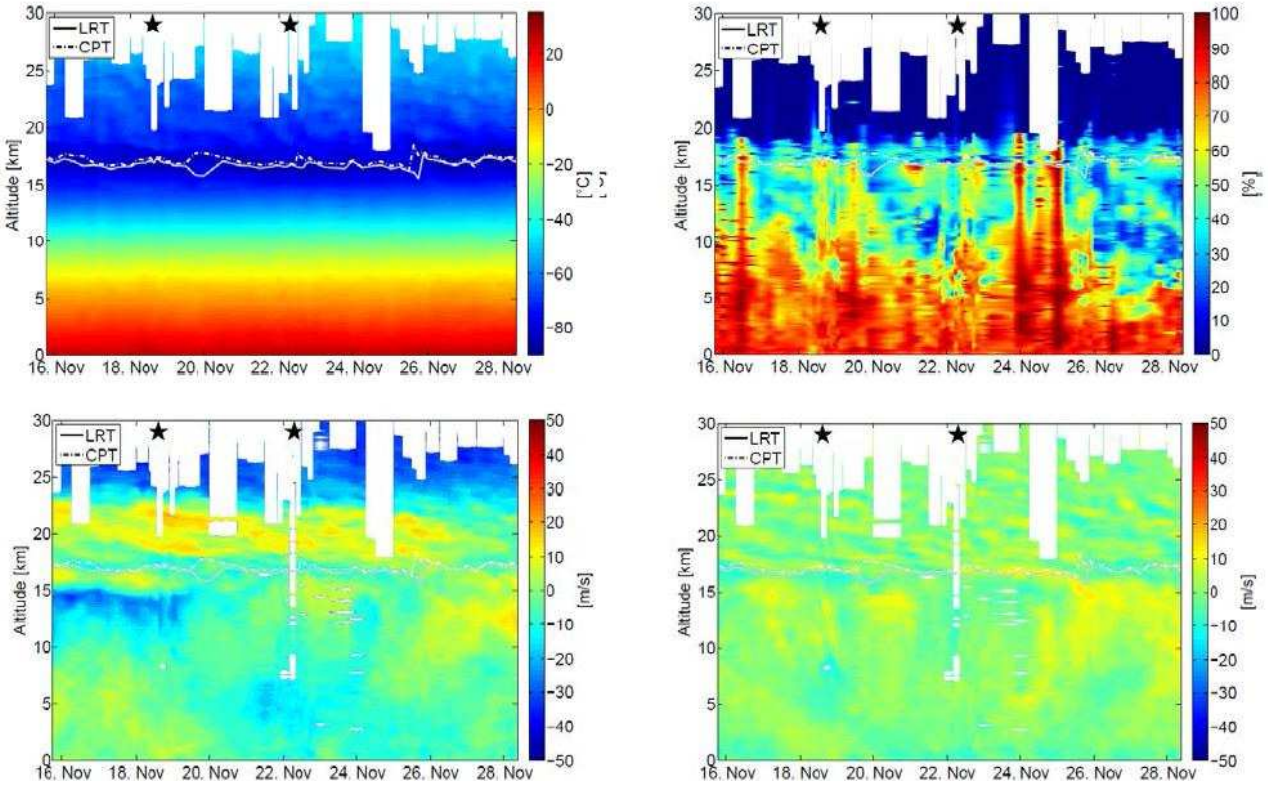

Figure 1: Profiles obtained from the radio sounding: Left: Temperature (°C), the dashed line shows the cold point temperature (CPT) and the solid line displays the lapse rate temperature (LRT); Right: Relative humidity (in %); Bottom: zonal and meridional wind components (m/s).

Preliminary analysis of our atmospheric profiles reveals first results. The atmosphere along out trip showed throughout tropical character with minimum temperatures reaching below -85° C around 17 km altitude (90 hPa), marking the lower boundary of the stratosphere (Figure 1 left). The tropical wind regime in the stratosphere the Quasi Biennial Oscillation (QBO) is in its Easterly phase above ~23 km altitude (50 hPa) (Figure 1 bottom). Surface winds were dominantly North Easterlies with maximum wind speeds reaching regularly above 10 m/s, the typical trace winds (Figure 2 left). Surface air temperature varied between maximum 29° C minimizing up to 26 °C (Figure 2 right). Sea surface temperatures (SSTs) stayed above 29 °C most of the time (not shown here), which may be influenced by the La Nina in the tropical West Pacific. Enhanced convective activity with thunder storms and lightning occurred in Singapore and at the Northwestern tip of Borneo (Figure 1 right).

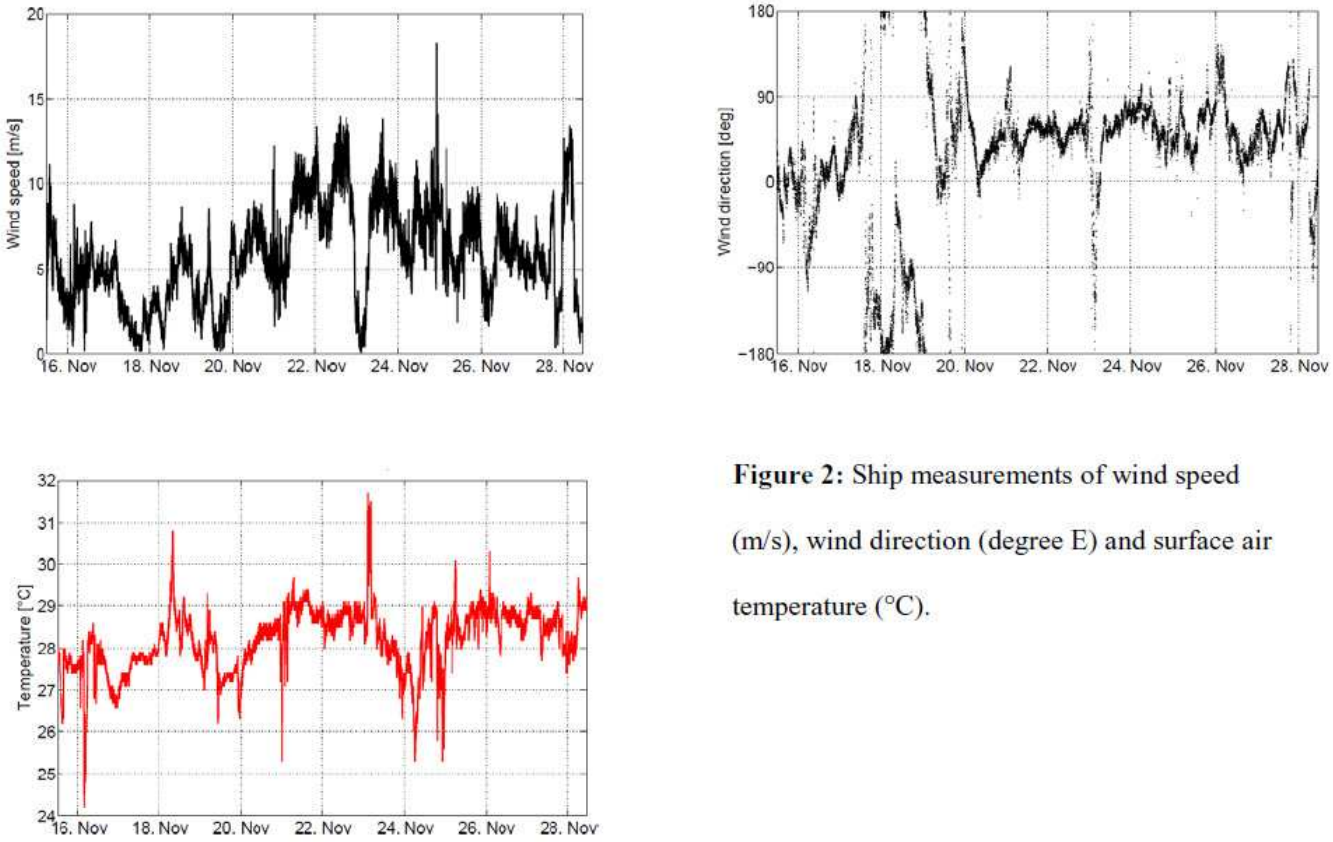

Figure 2: Ship measurements of wind speed (m/s), wind direction (degree E) and surface air temperature (°C).

6 Determination of trace gas concentrations in the marine boundary layer

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200 Canister air samples were taken for GC/MS- Analysis of trace gases in Miami. The air samples were taken three hourly and the sampling frequency was increased to 1 sample per hour at the diurnal stations and close to the northern coastal Borneo, where we expected interesting diurnal patterns as well.

7 Trace Gas Measurements using MAX-DOAS and CE-DOAS instruments

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Motivation

Reactive halogen species (RHS) are known to play an important role in the troposphere as well as in the stratosphere by, among other processes, catalytically taking part in ozone destruction, NOx and HOx cycles and thus actually influencing the oxidation capacity of the atmosphere.

They can be created by oxidizing directly emitted halogen compounds, by photolysis of VSLS emitted from the ocean or in chemical reactions upon surfaces. Iodine compounds can significantly increase ozone destruction compared to bromine compounds. Additionally eventually form aerosol particles via self-reactions.

MAX-DOAS measurements provide the possibility of calculating trace gas profiles. It is possible to measure RHS as well as providing HCHO, NO_2 and other data at the same time. Some uncertainties of concentrations can originate from radiative transport modelling. The in-situ cavity measurements have a rather well-defined path-length and thus enable us to have additional ground measurements, even though only a few trace gas species can simultaneously be measured with one instrument due to technical limitations.

Method

DOAS: (Differential Optical Absorption Spectroscopy) is a method to detect trace gases within air by measuring light spectra, calculating optical thicknesses and finally fitting trace gas absorption cross sections known from literature to these to obtain column densities and finally mixing ratios. Differential means that Mie and Rayleigh scattering are accounted for by removing the broad band structures from the optical thickness and also reducing the trace gas cross sections to their differential part. The type and number of trace gas mixing rations which can simultaneously be retrieved depends on the wavelength range used.

MAX-DOAS: (Multi AXial DOAS) This particular method uses the sun as light source. . Due to changes in the solar zenith angle and especially by looking at different elevation angles with a telescope results in different light-paths in the strato- and troposphere. Radiative transport models are used to obtain the