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Abstracts

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1. Sea-to-air fluxes of N₂O and CO₂ in the Benguela upwelling system

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High resolution measurements of surface oceanic and atmospheric N₂O and CO₂ were carried out during two cruises off Angola/Namibia in July-August 2013. A novel system based upon off-axis integrated cavity output spectroscopy (OA-ICOS) was coupled to a well-established GO System (General Oceanics, Inc.) in order to perform a detailed survey of the surface distributions of these gases during the upwelling season. Our observations show high supersaturations of both gases all along the cruise tracks as well as stronger gradients in transects closer to the coast, suggesting strong (though localized) N₂O and CO₂ outgassing to the atmosphere. Here we present the preliminary results of these surveys and explore the potential mechanisms explaining the distribution and sea-to-air fluxes of both gases.

2. Vertical particle flux in acidifying oceans – Impact on future ocean carbon export potential

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The sinking of particles from the euphotic surface layer to deeper waters is mainly driving the vertical carbon export in the oceans. Biomass quantity and the fraction of biogenic minerals such as opal and calcium carbonate influence particle sinking speed, determining the length scale of organic matter degradation. Pelagic large-scale mesocosms (KOSMOS³) were used to investigate the impact of future ocean acidification on the export potential of enclosed

plankton communities off the coast of Norway in 2011. The stepwise acidification of the enclosed water bodies induced very diverse responses of the plankton communities, with clearly negative consequences on the vertical particle flux with increasing $p\text{CO}_2$. Filter feeding appendicularians (*Oikopleura dioica*) and calcifying coccolithophores (*Emiliania huxleyi*) were strongly driving the community particle formation and sinking velocity.

Representing a coastal Atlantic plankton food web, our study showed the potential of ocean acidification to alter future ocean carbon export.

³ Kiel Off Shore Mesocosms for future Ocean Simulations

3. Turbulence in the upper-ocean mixed layer

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Variability on scales smaller than the local Rossby radius of 10 - 50 km -- i.e. the submesoscale -- are of major importance in the surface mixed layer of the ocean for realistic large-scale simulations of air-sea gas exchange. Therefore, they have to be parameterized in coarse ocean models to simulate realistic air-sea gas exchanges (e.g. Oschlies (2002).

In this study, we investigate two different parameterizations for mixed layer eddies. One is based on a scaling of the potential energy release, PER, (following Fox-Kemper et al., 2008). The other one is based on linear stability analysis, LSA, (Stone, 1966) and a scaling that uses the time and length scale of the fastest growing mode (Killworth, 1997).

Highly resolved simulations of two different mixed layer type scenarios are used to evaluate the parameterizations for a wide range of dynamical regimes that may occur. The first scenario consists of an equilibrated statistically steady flow and the second on a re-stratifying density front. It turns out that the mean deviation between both parameterizations and the diagnosed eddy fluxes is less than a factor of two. While PER performs slightly better in the spin-down scenario, LSA performs better in the equilibrated scenario. In both scenarios the vertical structure of the horizontal eddy fluxes is better captured by LSA.

4. Spatio-Temporal Variability in the Marine Carbon Cycle at CVOO

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Understanding the global carbon cycle and its variation requires a dense network of observations. Despite a growing data base for marine CO₂ surface observations (SOCAT v2) large parts of the oceans still remain uncharted both in space and time (e.g., Southern Ocean, Arabian Sea). Moreover, the impact of mesoscale processes on the marine carbon cycle is still not well understood due to a lack of high resolution in situ observations.

Recently, small-sized and submersible pCO₂ and O₂ sensors can be used to overcome these constraints. Thus, next to ship-based observations new platform technologies such as profiling floats or gliders come into reach.

A multi-platform approach was used in order to assess the spatio-temporal variability of the carbon cycle in the eastern tropical North Atlantic. Within the framework of the Cape Verde Ocean Observatory (CVOO) biogeochemical observations from both classical time-series measurements as well as from floats and gliders were performed. The following results were achieved:

1) Temporal variability: Measurements of pCO₂ and O₂ performed on a profiling float as well as CVOO time-series measurements were used to derive precise air-sea fluxes and production estimates which are consistent with time-series data from the Cape Verde Ocean Observatory (CVOO) and

2) Spatial variability: A suite of synergetic autonomous O₂ observations (glider, float, mooring) revealed mesoscale processes that featured unexpected open ocean subsurface hypoxia and anoxia.

5. Nitrous oxide gradient in top 10 meters of coastal upwelling waters off Peru

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Sea-to-air gas fluxes in upwelling systems may be overestimated when inferring them from bulk formulae and concentration measurements at 5 to 10 meters depth. We find support for this statement from nitrous oxide (N₂O) measurements in the eastern boundary upwelling system off Peru. During Meteor SOLAS cruise M91 in 2012 in the framework of an integrated study to quantify trace gas emissions, shallow N₂O measurements between 0.1 and 10 meters depth were performed at 4 stations away from ship influence. These profiles suggest that vertical gas gradients in the top 10 meters exist, particularly in the strong coastal upwelling where high N₂O supersaturations were found. The strongest observed N₂O gradient translates to a flux overestimation of factor 1.5. Such overestimation of sea-to-air flux may explain part of the issues with N₂O budgets not closed in upwelling regions (Kock et al., 2012). These findings may also have implications for estimates of other trace gas emissions.

6. Aerosols trace metal and chemical composition of Saharan dust

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Long term chemical characterization of Saharan dust has been performed at the Cape Verde Atmospheric Observatory (CVAO). Both size resolved and bulk PM₁₀ particles have been analyzed. The main chemical components investigated were inorganic ions including sulfate, nitrate, ammonium, sea salt ions, organic and elemental carbon and trace metals. Results show strong seasonal variation in the chemical components. Sulfate concentrations were higher during summer months while ammonium concentrations were higher in the spring months. Dust concentrations were higher during the winter with peak concentrations of about

900 $\mu\text{g}/\text{m}^3$ observed during Saharan dust storms. Iron and other crustal elements such as Ti, Mn were mostly found in coarse particles. Iron solubility showed strong increase with pH with about 3 orders of magnitude observed.

7. The contribution of oceanic halocarbon emissions to marine and free tropospheric air during SHIVA

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Tropical oceans, in particular coastal regions, are known to contribute through emissions of organic halocarbons (methyl iodide, bromoform, dibromomethane) to the atmospheric halogen burden. Here in this study, we investigate the contribution of their oceanic emissions to the marine atmospheric boundary layer (MABL) and to the free troposphere during the SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere) ship and aircraft campaign in November 2011 in the South China and Sulu Seas. Although oceanic emissions were rather high during SHIVA, mean atmospheric mixing ratios in the MABL were only small-to-medium abundant with 0.39ppt for methyl iodide, 2.08ppt for bromoform and 1.17ppt for dibromomethane. Local oceanic emissions contributed 79% for methyl iodide, 48% for bromoform and 23% for dibromomethane MABL concentrations. While mean free tropospheric bromocarbon concentrations, measured on board of Falcon, can be explained by the delivery from the MABL, methyl iodide free troposphere observations were higher than expected.

8. Changes in optical characteristics of surface microlayers in the upwelling region off Peruvian coast hint to photochemically and microbially-mediated DOM turnover

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Sea-surface microlayer (SML) and underwater (ULW, ~20 cm below) samples were collected in December 2012 during SOPRAN M91 cruise in the upwelling region off Peruvian coast. Polysaccharidic marine gels (Transparent Exopolymer Particles, TEP), total and dissolved organic carbon (TOC and DOC), bacterial abundance and chromophoric dissolved organic matter (CDOM) were measured. Spectral slopes (S) values were estimated based on CDOM absorption coefficients in the wavelength ranges 275-295 nm (S_1), and 350-400 nm (S_2). The ratio $S_1:S_2$, referred to as Slope Ratio (S_R), as well as S_1 and S_2 have been used as a proxy to track changes in molecular weight of DOM, either induced by microbial processes or photobleaching, as well as potential indicators of DOM sources. Moreover, the specific UV absorption (SUVA₂₅₄) correlates with DOM aromaticity. By applying these parameters, possible composition, origin and fate of gel-like components suggested to be highly concentrated in the SML will be discussed.

9. Sahara dust impact on solar radiation at Cape-Verde islands – A synthesis of ground-based radiation and aerosol measurements

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The overall goal of this project is to investigate the impact of Sahara soil dust and aerosols, through the associated changes in spectral radiance (solar forcing) on the radiative forcing of the eastern subtropical Atlantic Ocean. The investigation is being made around the Cape-

Verde islands over the subtropical North Atlantic where the wind mobilization of desert dust results in a dust aerosol signal large enough to outweigh other aerosols such as anthropogenic and marine aerosols. The in-situ measurements of solar radiation time-series exist from March 2008 onwards. Since January 2012, a sun-photometer is installed at the Cape-Verde ground station which measures the column Aerosol Optical Depth (AOD) at a high temporal resolution (every 15 minutes during the sunlit time of the day). The installed sun-photometer is a part of the worldwide NASA Aerosol Network (Aeronet), providing a standard AOD product from the raw instrument data. In addition to the AOD, the sun-photometer measurements offer additional valuable aerosol parameters such as water vapor, aerosol inversions, Angstrom parameter and cloudiness etc.. Results are presented from one major cloud-free dust outbreak event. Estimated optical thickness of the atmosphere agrees well with MODIS products available simultaneously. From the measurements the dust forcing efficiency is estimated using shortwave radiation fluxes at sea level and at the top of atmosphere.

10. Radar Backscatter measurements on FINO-2

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One of the conventional approaches to use remote sensing data to estimate gas transfer velocities is based on scatterometer winds which are used together with empirical gas transfer velocity-wind speed relationships. In order to find a more direct link between the radar cross section (RCS) and the gas transfer velocity, Multi³Scat measurements were carried out on FINO-2 from September 2011 to November 2013. We present first examples of the radar backscatter measured and their sensitivities to environmental parameters at five frequencies and four polarization-combinations and at three incidence angles. As is to be expected, the results show that for all radar bands and incidence angles the RCS increase with wind speed. Furthermore, at moderate wind speeds and steep incidence angles the radar backscatter depends only slightly on the azimuth direction. Our results are in good agreement with the radar backscatter theory.

11. Processes contributing to halocarbons in the equatorial Atlantic mixed layer

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Short lived halogenated substances (halocarbons) from the marine environment contribute to atmospheric halogens, are involved in ozone depletion, and influence aerosol formation. Oceanic upwelling regions are characterized by high biological activity with associated increased halocarbon abundance of e.g. bromoform (CHBr_3) and dibromomethane (CH_2Br_2). Photochemistry plays an important role in the formation of methyl iodide (CH_3I), but can also have a significant influence on the degradation of halocarbons, e.g. diiodomethane (CH_2I_2) within the water column.

The SOPRAN cruise MSM 18/3 on board the RV *Maria S. Merian* from June and July 2011 covered the Equatorial Upwelling region as a potential source of halocarbons for the atmosphere. Surface concentrations of CHBr_3 and CH_2Br_2 were comparably elevated to the Mauritanian upwelling. CH_3I in contrast to the Mauritanian upwelling showed a similar distribution as CHBr_3 and CH_2Br_2 possibly indicating a biogenic production in the Equatorial region. CH_2I_2 concentrations in contrast were very low, likely as a result of rapid photolysis in the surface layer.

12. Simultaneous Measurements of Solubility and Diffusion Coefficients in Liquids

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This poster presents a new technique for simultaneous measurements of the solubility and diffusion coefficient in water of environmentally important volatile tracers. For many tracers the solubility is not known with sufficient accuracy and the diffusion coefficients of many species dissolved in water has only been estimated theoretically but not been measured at all. Absolute measurements of the diffusion coefficients in water are very difficult. Therefore the idea came up to measure them only relative to tracers with well known diffusivity such as carbon dioxide, hydrogen, and noble gases. This type of measurements can be done in a small gas-tight stirred tank and also delivers solubility data. Concentrations will be measured both in air and water using membrane-inlet mass spectrometry. The poster describes the apparatus and the measuring procedure. The technique works for tracers up to medium solubility (partition coefficient < 100). For the measurement of the solubility of volatile species with higher solubility, the solubility can be measured with a simple bubble column. It is planned to measure all tracers of interest to the SOPRAN project in a temperature range from 0 to 40 degree Celsius in fresh water and sea water. Suggestions for tracers to be measured are welcome.

13. Measurement of wind wave statistics from specular reflections

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The Reflective Stereo Slope Gauge (RSSG) [1] was deployed to two cruises in the tropical Pacific Ocean in Dec. 2011 and Dec. 2012 to measure statistics of small-scale wind waves. During the cruises, both open ocean (Samoa – Hawaii, OSSPRE 2011 on R/V Kilo Moana) and coastal upwelling (off Peru, M91 on German FS Meteor) areas were studied.

Surface displacement (wave height time series with 50 Hz sampling rate) was measured by a stereo system with two light sources (Helmholtz stereopsis), while statistics of surface slope were obtained using a method related to Cox & Munk's sun glitter technique [2]. Furthermore, information on the scale of the smallest waves was gained from the brightness of specular reflections (which is related to surface curvature). This parameter is useful for determining the presence of surface slicks.

The results underline the importance of monitoring parameters other than wind speed during gas exchange measurements. The presented methods allow for robust estimates of surface slope statistics under a wide range of conditions.

[1] Kiefhaber, D., Rocholz, R., Balschbach, G. and Jähne, B., Improved optical instrument for the measurement of water wave statistics in the field, in: Gas Transfer at Water Surfaces, Kyoto University Press, 2011.

[2] Cox, C. and W. Munk (1954a), Measurements of the roughness of the sea surface from photographs of the sun's glitter, J. Opt. Soc. Amer., 44 (11), 838-850.

14. MEMENTO, the Marine Methane and Nitrous Oxide database is now online!

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MEMENTO is an initiative started in 2009 that aims to collect available oceanic and atmospheric methane and nitrous oxide data into a global database for the computation of global concentration and flux fields. Currently, data from about 150 campaigns with more than 120,000 nitrous oxide and 20,000 methane measurements have been collected. All data submissions undergo a first order quality control on the availability and range of essential and ancillary data and their metainformation before they are imported into the database. The database is now accessible through the MEMENTO webpage (<https://memento.geomar.de>).

15. Surface Ocean – Lower Atmosphere Study (SOLAS)

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The Surface Ocean - Lower Atmosphere Study is an international research initiative focusing on biogeochemical interactions at the air-sea interface in the context of climate and global change co-sponsored by SCOR (Scientific Committee on Oceanic Research), IGBP (International Geosphere-Biosphere Programme), WCRP (World Climate Research Programme) and iCACGP (Commission for Atmospheric Chemistry and Global Pollution). Since publication of its Science Plan and Implementation Strategy in 2004, SOLAS has facilitated communication, coordinated research, and fostered new projects.

In 2013 two publications were released: One article in Environmental Chemistry detailing research strategies developed since 2008 (Law et al.) and a book synthesizing major achievements of the SOLAS knowledge over last decade (Liss et al.). This and the last SOLAS Open Science Conference 2012 in USA demonstrated that there is still a lot to

understand and accomplish in the field of SOLAS science. With this in mind, the SOLAS Scientific Steering Committee and SOLAS community started to map out themes of major importance to the new course of the project.

Reference link <http://www.solas-int.org/resources/books.html>

16. High-resolution 2-D fluorescence Imaging of Gas Transfer at a Free Water Surface

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A novel 2-D fluorescence imaging technique has been developed to visualize gas exchange between air and water using ammonia as a tracer. Fluorescence is stimulated by high-power LEDs and is observed from above with a low-noise, high-resolution and high-speed camera. The invasion of ammonia into water leads to an increase in pH (from a starting value of 4), which is visualized with a fluorescent dye. The flux of ammonia can be controlled by controlling its air-side concentration. A higher flux leads to an increase of the thickness of the layer, from which fluorescent light is emitted (pH > 7). In this way, a varying fraction of the thickness of the aqueous mass boundary layer is imaged. In addition to the fluorescence measurement, we conducted collocated and simultaneous thermography and wave imaging measurements. With this data set, it is possible to compare heat and gas transfer and to investigate the effect of waves on both transfer processes. First results will be presented.

17. Physics Based Modeling of Air-Sea Gas Transfer

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The exchange of trace gases across the air-sea boundary layer is characterized by the gas transfer velocity $k = 1/\beta u^* Sc^{-n}$, with the friction velocity u^* (a measure for momentum input into the water), the tracers Schmidt number Sc , and the Schmidt number exponent n which changes gradually from $n=2/3$ for a smooth water surface, to $n=1/2$ for a rough and wavy surface. β denotes the momentum transfer resistance, a dimensionless scaling parameter. In recent years, many new insights into the transition of the Schmidt number exponent n from smooth to rough conditions were acquired in detailed lab studies, while there is a lack of studies focusing on β . Using experimental data from various wind-wave tank laboratories, we found that β , just like the Schmidt number exponent n , is not a constant but depends on the state of the water surface as well as the degree of contamination of the water surface with surface active material.

18. Air-Sea Gas Exchange under Nature-Like Surfactant Influence in the Lab

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For the first time, air-sea gas exchange measurements under the influence of four surface active substances also found in the sea surface microlayer were performed in the Aeolotron wind-wave tank. Chosen surfactants were Dextran which is water soluble, as well as the insoluble substances Mono-Galactosyl-Diacylglycerol, Palmitic Acid and

Phosphatidylglycerol. Gas transfer velocities of N₂O and C₂H₆F₅ were measured using a mass balance approach combined with FT-IR spectroscopic methods. In addition, wave parameters like the mean square slope of the water surface were monitored. It was found that Dextran alone does not significantly decrease the gas transfer velocity compared to the clean water surface, while reduction for the full mix of surfactants was as high as 70%. For the full mix of surfactants, at a wind speed of around 7m/s the surfactant film ruptured and was mixed

19. Model cross-validation against data from mesocosm experiments

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In our study we wish to identify benefits and drawbacks of some recent approaches to marine ecosystem modeling. This objective will be achieved by systematic data-model comparisons and model parameter optimization. Our primary technical task is to setup a mesocosm model environment in R. For this a wrapper function has been devised that allows us to make model calls from any R-script. Concurrently, we organized data from three mesocosm experiments, PeECE I, II, and III respectively. For our model environment we also prepared forcing files for single mesocosms. On our poster first technical achievements and preliminary scientific results are presented. We show results from a model cross-validation against PeECE experimental data. Simulation results are evaluated with respect to different parameterization of calcification. Also, we test whether a single set of parameter values, apart from initial values, can resolve differences between mesocosms within one experiment and between experiments.

20. Overview of Reactive Halogen Species in the Marine Boundary

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Reactive halogen species (RHS) in the in the marine boundary layer have the potential to influence the ozone budget on a global scale. The aim is to clarify interdependencies of RHS and their precursors as well as to estimate their overall abundance. Measurement campaigns were conducted to obtain a picture of the global distribution of RHS in the marine boundary layer and their driving mechanisms.

Iodine monoxide measurements over the open tropical ocean show agreement for different measurements, most measurement techniques and different campaigns.

Obtaining values for BrO volume mixing ratios in the marine boundary layer apart from so-called 'BrO-events' in the upwelling regions of the eastern tropical Atlantic remains challenging due to technical reasons. Furthermore MAX-DOAS measurements on the open ocean regularly showed lower values than on Cape Verde. To clarify this, a reanalysis of MAX-DOAS data will be presented.

Upper limits for atmospheric Glyoxal were found for Pacific and Atlantic at roughly to 20-30ppt.

21. A short circuit for oceanic N loss

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The constancy of the average oceanic NO₃ to PO₄ ratio, the Redfield ratio, has been interpreted as evidence of strong negative feedback mechanisms that reduce N inventory oscillations relative to the more slowly overturning phosphorus inventory. Using a biogeochemical ocean circulation model we find that negative N inventory stabilizing feedbacks cannot persist if a close spatial association of N₂ fixation and denitrification

occurs. Enhanced denitrification generates nitrogen deficient waters that will eventually upwell in the euphotic zone. In the absence of N₂ fixing organisms export production will be reduced and denitrification will in turn diminish. However, If N₂ fixers are overlaying denitrified waters than export production will not be reduced. Because of stoichiometric constrains more N is going to be lost than gained from the remineralization of organic matter. This in turn stimulates again N₂ fixers activity in a vicious cycle that leads to net N inventory losses. To break the vicious cycle and minimize changes in the N inventory N inputs need to be spatially decoupled from N losses. In contrast with common understanding we find that factors such as iron limitation of diazotrophs promote N inventory stabilizing negative feedbacks and allow the maintenance of nutrient's Redfield proportions.

22. A box model to simulate N₂O and CH₄ concentrations in the mixed layer at Boknis Eck, SW Baltic Sea

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The Time Series Station Boknis Eck (SW Baltic Sea) reflects conditions often found in shallow coastal areas and is representative for the Southwestern Baltic Sea. Boknis Eck has been sampled monthly for the trace gases N₂O (since 2005) and CH₄ (since 2006) in the water column. Based on the time series of these trace gas measurements and further parameters such as oxygen concentration, temperature and wind speed, a simple box model was developed to simulate trace gas concentrations in the mixed layer.

The model includes air-sea gas exchange, upward mixing in the water column and production processes specific to each gas. Production and flux rate parameterisations were either taken from literature or estimated with a least-square optimisation. The model reproduced the pronounced seasonal cycle of N₂O concentrations including short-term high production peaks after the breakdown of summer stratification very well. It also reproduced CH₄ concentrations in an acceptable range of uncertainty, but performance was overall better for N₂O. For both gases, the major source was the production below the mixed layer, either in the sediment as in the case for methane or in the subsurface layer as in the case of N₂O. The main sink for both gases was the emission to the atmosphere, which is significant given the climatic relevance of both gases.

23. Distributions and fluxes of nitrous oxide in lower reaches of the Yellow River and its estuary: Impact of water-sediment regulation

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The Yellow River is the second largest river in China and is famous for its high sediment load worldwide. Water-sediment regulation scheme has been carried out since 2002, in order to avoid the dry-up of water flow in lower reaches. By artificially releasing a large amount of water from different reservoirs in a short time, the great discharge scoured through the channel and took most of the sediments deposited away, which not only shifted the seasonal patterns of water and nutrients transport, but also has a great influence on N₂O production and emission. Up to 55.9% of annual N₂O input was transported to Bohai Sea during the regulation event in 2009, while the water discharge within the month accounted for only 26.9% of total annual runoff.

24. Can simple model parameterizations be used to predict ocean isoprene concentrations and emissions over varied biogeochemical regimes in the eastern Atlantic Ocean?

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Isoprene is a volatile hydrocarbon abundantly emitted by terrestrial ecosystems and known, globally, to be a precursor of ozone and secondary organic aerosols. Marine isoprene has been hypothesized to be important for regional remote marine boundary layer cloud formation, but measurements of oceanic isoprene concentrations and emissions are sparse. Nonetheless, several attempts to model isoprene concentrations in the surface ocean have been published. Here we investigate if oceanic isoprene concentrations and emissions can be predicted using simple model parameterizations based, mainly, on chlorophyll for the source and wind speed for the sink. We compare surface ocean isoprene concentrations measured over the varied biogeochemical regimes of the eastern Atlantic Ocean (Polarstern Cruise, Nov 2008, Bremerhaven to Cape Town) to those calculated using a simple model. The aim of this study is to improve predictive tools for a range of climate active trace gases under present and future scenarios.

25. Investigation of dust impact on optical water properties using Glider measurements

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During atmospheric storms Saharan dust is transported from land surface to the Atlantic Ocean. The dust is deposited in the water column and can potentially enhance the biological productivity by its fertilization properties. The dust particles in the water interact with the solar radiation and change the optical water properties.

Until recent the impact of deposited dust on optical water properties was only studied in laboratory experiments. Now the impact is investigated using a multi-disciplinary approach, including measurements in marine oceanic environments. Glider optical measurements obtained during March to May 2010 appear to be sensitive to dust deposition in the water column. The glider-derived turbidity was analyzed in connection with ground-based AERONET- and remotely-sensed aerosol optical depths. The mass concentrations measured at the Cape Verde Atmospheric Observatory at Sao Vicente and modeled dry depositions of dust were included in the study.

During the Glider observation period, different dust storms were identified by analysis of AERONET- as well as MODIS-derived aerosol optical depths. There were indications for the correlation of glider-derived turbidity and aerosol optical depths. One dust storm between 27 and 30 March 2010 was recognized where the turbidity increased during the dust event. The interpretation of turbidity enhancement by dust deposition was supported by the measured chlorophyll-a concentration because the concentration remained unchanged during the turbidity event. Using a dust transport model, dust deposition into the surface ocean layer could be verified for the observed dust storm. It also confirmed the irregular deposition of Saharan dust in the study area. After around two days the deposited dust was sunken to the depth of the chlorophyll-a maximum. With backward trajectories and remote sensing data it was possible to identify the source areas of the observed dust, which originated from southern and western Saharan sources.

26. Release of volatile organic compounds from the Mediterranean Sea and the Black Sea

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The main aim of this work was to study the distribution and the sea/air exchange of marine derived volatile organic compounds (VOCs), especially CHBr_3 , CH_3I and DMS in the Black Sea and the Mediterranean Sea.

During a transit across the Mediterranean Sea in November 2013 surface water samples were taken for analysis of VOCs and various biological parameters. In the Black Sea, in addition to measurements along a transect also discrete water samples, from the surface and the depth with maximal chlorophyll a concentration were analysed to further investigate the regulating factors for production, decomposition and export of volatile organic compounds in the marine environment. Furthermore, the vertical distribution of VOCs in the water column was measured at selected locations. Additionally to water samples, air samples were collected to estimate the sea/air fluxes of these trace gases.

The cruise MSM33 gave a great opportunity to study distribution and behaviour of VOCs in this rather scarcely investigated region. Data collected during this cruise will be a vital contribution to the global database of oceanic trace gas measurements.

27. Bromoform in the open ocean

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A 1D water-column model is applied to simulate vertical bromoform distribution in the oligotrophic North East Atlantic. The model results show that abiotic degradation alone is insufficient to reproduce observed profiles. A good representation is only achieved when an additional, biological, degradation process is included. Degradation during remineralisation of detritus and degradation by ammonium oxidizing bacteria are tested. Here, the additional degradation by nitrifiers leads to profiles that match the observations. The OGCM MPIOM/HAMOCC is used to simulate CHBr_3 at the global scale. Surface concentrations are very similar when considering either one of the biological sink processes and reproduce observed surface bromoform concentrations well. Largest differences occur in polar regions, which are not well captured by the model, because production within sea ice is not considered and uptake from the atmosphere is a significant source. Overall, in most regions the ocean is a bromoform source to the atmosphere.

28. Bacterial uptake of iodomethane - elucidating degradation rates and involved organisms

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Within SOPRAN theme 1, we aim a better understanding of key processes controlling the distribution and fluxes of iodomethane (CH₃I), a strong source of highly reactive iodine oxide radicals in the atmosphere. In previous studies, several sources (mainly photoautotrophic organisms) and sinks (e.g. hydrolytic cleavage) have been identified and associated rates determined. Yet, knowledge about bacterial degradation remains enigmatic. Our previously determined uptake rates (50 – 600 pmol h⁻¹ L⁻¹) - using ¹⁴C-labelled CH₃I – were unexpectedly high regarding CH₃I *in situ* concentrations (5-30 pmol L⁻¹) and published production rates (< 10 pmol h⁻¹ L⁻¹).

Therefore, the goal of the present study was to re-evaluate bacterial CH₃I-degradation rates. Natural seawater from the Southern Baltic Sea was inoculated with excess CH₃I (5 nM) and changes in concentration were monitored over time and compared to autoclaved samples. In order to identify stimulated bacteria in these incubations, we applied 16S rRNA fingerprints. Our experiments revealed that biological loss rates of CH₃I were 0.02 d⁻¹, which is consistent with the few studies available. Abiotic loss rates were 0.014 d⁻¹, suggesting that bacterial degradation of CH₃I is comparably low. Nevertheless, stimulated bacteria were phylogenetically related to *Leisingera* sp., which are known monohalomethane-degraders. Currently, we analyse functional enzymes involved in monohalomethane degradation to deepen our knowledge about this slow but consistent degradation of CH₃I.

29. Glyoxal and Methylglyoxal in Atlantic Sea Surface Microlayers and in marine Aerosol Particles

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The oceans are recently discussed to be an important source for glyoxal and methylglyoxal in the atmosphere, however, to date there are few available marine field data of these compounds. We present measurements of the two carbonyls in the marine environment during a transatlantic Polarstern cruise (2011). Both compounds were detected in the sea surface microlayer in the nanomol-range and are significantly enriched (factor of 4) compared to the underline water, implying photochemical production. On aerosol particles glyoxal and methylglyoxal were strongly connected to each other, suggesting similar

formation mechanisms. The correlation with particulate oxalate supports the idea of a secondary formation of oxalic acid via glyoxal and methylglyoxal. A slight correlation of the two carbonyls in the sea surface microlayer and in the aerosol particles was found at co-located sampling areas. In summary, these results give first insights towards interaction processes of these alpha dicarbonyls between ocean and atmosphere.

Reference:

M. van Pinxteren and H. Herrmann, *Glyoxal and Methylglyoxal in Atlantic Seawater and marine Aerosol Particles: Method development and first application during the Polarstern cruise ANT XXVII/4*. Atmos. Chem. Phys. 13, 11791-11802 (2013).

30. Contrasting behavior of Cd, Fe and Mn in the Eastern Tropical Atlantic compared to the Eastern Tropical Pacific

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The cycling of trace metals and their bioavailability play a vital role for the marine productivity. At the moment we are synthesizing previous trace metal work in SOPRAN, where a main focus has been on the role of desert dust for biogeochemical cycles in waters off Cape Verde and in the Eastern Tropical Atlantic Ocean compared to the less dust influenced Eastern Tropical Pacific Ocean (M90). In cooperation with Ulf Riebesell and Linn Hoffmann we designed a trace metal clean dust collection system and placed it in a remote area on the lee side of the Cape Verdean Island, Sao Vicente. With this dust and open ocean seawater collected in this region we will perform controlled laboratory dust solubility experiments. Second, we are currently participating in incubation experiments at Gran Canary to investigate possible phytoplankton-trace metal interactions in response to atmospheric perturbation (dust & CO₂).

Furthermore, we will present data collected in two different regions. In the Eastern Tropical North Atlantic (ETNA) Ocean atmospheric dust is the main source of Mn to surface waters (Wuttig et al., in prep., 2013). However this study provides clear evidence that equatorial upwelling and sediment resuspension are important Mn sources in this region. In contrast to findings from the Eastern Tropical Pacific (ETP), where unexpected high surface concentrations were observed, no secondary Mn(II) maximum was found in the ETNA. This could have been introduced by a combination of lateral transport of Mn rich waters from the coastal margins and reduction of Mn-oxides.

While Aeolian sources were predominantly influencing Mn and also Fe cycling in the ETNA, Cd was not controlled by dust deposition. These trace metals exhibited contrasting distribution patterns. For the biologically relevant elements, Fe and Mn, atmospheric depositions masked a classical nutrient type profile, while Cd was depleted at the surface and concentrations steadily increased with depth. Cd was highly correlated to phosphate. The Cd/P ratio was mainly controlled by P with elevated concentrations at depth resulting in strongly differing ratios in surface and subsurface layers.

31. The effect of ocean acidification on Dimethylsulfoxide (DMSO)

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DMSO is ubiquitous in the global oceans and is a large biogenic sulfur pool. Because DMSO is a precursor of dimethylsulfide (DMS), it indirectly affects the Earth's climate. DMS, emitted from the ocean, is important for the atmospheric sulfur oxidation cascade, which can result in the formation of aerosols impacting the radiative budget. Ocean acidification (OA) has a pronounced effect on the physiology of phytoplankton species, some of which are important for DMSO production. Previous OA experiments showed that elevated carbon dioxide (CO₂) decreased oceanic biogenic sulfur concentrations, which lead to fewer emissions of sulfur to the atmosphere. During a mesocosm experiment conducted in a Swedish fjord in spring 2011, we investigated for the first time the effect of increasing CO₂ on oceanic DMSO. With increasing CO₂ the dissolved DMSO (DMSOd) concentration decreased while particulate DMSO was unaffected by OA. On average, highest DMSOd concentrations and highest cell

abundances of the phytoplankton taxa cryptophytes and *Synechococcus* were observed when nitrate concentrations range between 2 and 3 $\mu\text{mol L}^{-1}$. Further on, these algae taxa correlated with DMSOd. Thus, DMSOd was controlled by a complex interplay of cryptophytes and *Synechococcus* influenced by nutrient availability and OA. Due to OA less DMSOd is available for bacterial reduction to DMS in the surface ocean and subsequent for sulfur air-sea exchange.

32. Future emission scenarios of halogenated substances

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Very short lived halogenated substances from the oceans containing bromine and iodine compounds, contribute to the atmospheric halogen budget, where they are involved in ozone depletion and aerosol formation. Oceanic regions characterized by high biological activity are often associated with increased halocarbon abundance e.g. of bromoform (CHBr_3) and dibromomethane (CH_2Br_2), representing the main contributors to atmospheric organic bromine. Apart from biological production, photochemical pathways play an important role for the formation of methyl iodide (CH_3I), the most abundant organic iodine in the marine atmosphere. In the tropics, rapid uplift of surface air can transport these short-lived compounds (lifetime < 0.5 years) into the upper troposphere lower stratosphere (UTLS). Tropical oceans, close to regions of strong atmospheric convection, might therefore contribute large amounts of halocarbons to the UTLS.

Based on the sea-to-air flux maps from Ziska et al. (2013), emissions of iodo- and bromocarbons from different oceanic upwelling systems, the Mauritanian and the equatorial upwelling in the Atlantic, as well as the Peruvian upwelling in the Pacific (SOPRAN relevant regions), will be presented and compared.

We use the input parameter sea surface temperature, salinity, pressure and wind speed from different CMIP5 (the Coupled Model Intercomparison Project Phase 5) models as well as from two Representative Concentration Pathways (RCP) scenarios (2.6 and 8.5) for calculating future emissions (2010-2100). Further, the temporal variability and the global

relevance of these halogenated fluxes in the SOPRAN regions are investigated for the past and future.

Additionally, we will analyze the physical driving factors which control the distribution of the future sea-to-air fluxes.

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