



# **6<sup>th</sup> SOPRAN Annual Meeting**

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## **Abstracts**

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## Content

1. Underway N <sub>2</sub> O/CO/CO <sub>2</sub> measurements in the eastern tropical South Pacific Ocean during M90, M91 and M93 .....	1
2. Tidal controls on trace gas dynamics in a subtropical seagrass meadow of Ria Formosa lagoon (southern Portugal) .....	1
3. Study of different primary marine aerosol emission schemes with COSMOMUSCAT .....	2
4. Turbulence in the upper-ocean mixed layer .....	2
5. First results on selected parameters of the SOPRAN CO <sub>2</sub> enrichment study 2011: Pteropods, particle sinking velocities and sedimentation .....	3
6. Ocean acidification effects on pteropod larval and adult stages at „in-situ“ conditions during a mesocosm experiment .....	4
7. Title .....	4
8. Nitrous Oxide Fluxes in the Eastern Tropical Atlantic Ocean .....	5
9. Trace metal fractional solubility in marine aerosols at CVAO .....	5
10. Radar Backscatter Measurements on FINO-2 .....	6
11. Bacteria mediated alteration of the gelatinous surface microlayer .....	6
12. The sea-surface microlayer during the R/V Meteor Cruise M91: Measurements and satellite detection of surface films.....	7
13. Sahara dust impact on solar radiation at Cape-Verde: A synergy of in-situ radiation and AOD measurements.....	8
14. Contributions to tropical VLSL emissions from the equatorial Atlantic upwelling region .....	8
15. MEMENTO (Marine Methane and Nitrous Oxide database).....	9
16. Atmospheric signatures of air-sea exchanges of CO <sub>2</sub> , O <sub>2</sub> /N <sub>2</sub> , CH <sub>4</sub> , CO, and N <sub>2</sub> O recorded at the Cape Verde Atmospheric Observatory (CVAO) .....	9
17. Partitioning of the transfer resistance between air and water .....	10
18. Gas Exchange at Hurricane Wind Speeds.....	11
19. DOAS Measurements of Reactive Halogen Species .....	11
20. Dimethylsulphide (DMS) emissions from the West Pacific Ocean: a potential marine source for the stratospheric sulphur layer .....	12
21. SOPRAN II and SOPRAN III Activities of the Max Planck Institute in Mainz .....	13
22. Chemical Characterization of Aerosol Particles at the CVAO - interesting new observations..	13
23. Physical properties of mineral dust and measurements of dust concentration.....	14
24. Wave and Heat Exchange Measurements in the Southern Pacific .....	14
25. Collection and analysis of data that describe the accumulation of organic matter in the surface microlayer .....	15

26.	Improved analyses and synthesis of dust impact on radiative transfer, optical properties and phytoplankton development in cooperation with other subprojects .....	16
27.	Results of SOPRAN II in relation to the impacts of Saharan dust on optical water properties, phytoplankton development and satellite derived products .....	16
28.	Bromoform in the central Baltic Sea during a cyanobacterial bloom .....	17
29.	Sensitivities of biogeochemical flux estimates to variations in model parameters at Baltic Sea monitoring site <i>BY15 Gotland Deep</i> .....	18
30.	SOPRAN data archive and website .....	19
31.	Plankton blooms at elevated atmospheric carbon dioxide levels: the SOPRAN Bergen 2011 mesocosm study.....	19
32.	Seasonal variability of iodomethane (CH <sub>3</sub> I) production in the surface ocean .....	20
33.	Upwelling velocities inferred from helium isotopes .....	21
34.	Global modelling of methyl iodide production in the open ocean .....	21
35.	Bacterial turnover of iodomethane in Baltic and North Sea surface waters .....	22
36.	Oceanic VLSL contribution to stratospheric ozone .....	23
37.	Organic carbon and aliphatic amines in marine particles: exchange processes between ocean and atmosphere .....	23
38.	A case study on modeling the dissolution of hematite under urban and non-urban conditions with SPACCIM.....	24
39.	Impacts of dust depositions and ocean acidification on trace metal cycling and bioavailability . .....	25
40.	Cycling of organic Fe-binding ligands in a 3D biogeochemical model .....	25
41.	Uncertainties in future marine N <sub>2</sub> O emissions in the eastern tropical Pacific.....	26
42.	Sulphur compounds, methane, and phytoplankton: interactions along a north-south transit in the western Pacific Ocean.....	27

## **1. Underway N<sub>2</sub>O/CO/CO<sub>2</sub> measurements in the eastern tropical South Pacific Ocean during M90, M91 and M93**

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Dissolved N<sub>2</sub>O, CO and CO<sub>2</sub> were measured in the surface ocean layer in the eastern tropical South Pacific Ocean during the Meteor cruises M90 (Cristobal-Callao, October/November 2012) and in the upwelling off Peru during M91 (Callao-Callao, December 2012) and M93 (Callao-Cristobal, February/March 2013). First (preliminary) results are presented.

## **2. Tidal controls on trace gas dynamics in a subtropical seagrass meadow of Ria Formosa lagoon (southern Portugal)**

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Coastal zones are important source regions for a variety of trace gases including halocarbons and sulphur bearing species. While salt-marshes, macroalgae and phytoplankton communities have been intensively studied, little is known about trace gas fluxes in seagrass meadows. Here we report results of a newly developed dynamic flux chamber system that can be deployed in intertidal areas over full tidal cycles allowing for high time resolved measurements. The trace gases measured in this study included CO<sub>2</sub>, methane and a variety of hydrocarbons, halocarbons and sulphur bearing compounds. In contrast to most previous studies our data indicate significant enhanced fluxes during tidal immersion relative to periods of air exposure. In particular for methane, we observed short emission peaks with the incoming tide just arriving at the sampling site. We suggest an overall strong effect of the advective pore water flow across the water sediment interface on the trace gas fluxes at the sediment interface. As most emission estimates from tidally influenced coastal areas rely on measurements carried out during low tide our results may have significant implications for budgeting trace gases in coastal areas.

### **3. Study of different primary marine aerosol emission schemes with COSMOMUSCAT**

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Primary marine aerosol (PMA), consisting of sea salt and organic enrichment, is one of the major natural aerosol types. Because it is the dominating aerosol in marine air in many regions it can have a major influence on cloud properties and solar radiative fluxes over the oceans. Due to heterogeneous reactions PMA impacts on atmospheric chemical reactions involving gases and aerosols and can thus influence on coastal air quality. Up to now PMA has been included as tracer in many different global and regional aerosol models. The high diversities in the model results were likely related to differences in the different particle-size dependent surface production parameterizations. Therefore PMA emission schemes need to be carefully evaluated before PMA should be used for further large-scale model studies. For this reason we compared different source functions in the MUSCAT aerosoltransport model, which is online-coupled to the COSMO meteorology model. The results of these model studies are compared to EMEP and AERONET data, as well as to observations data of the Cape Verde intensive campaign in the framework of the BMBF SOPRAN project. We find that a temperature dependence of the source flux is required to obtain reasonable agreements between model results and observations at both the tropical and the European sites. In addition, two different parameterizations for the organic enrichment in PMA are compared.

### **4. 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 and therefore have to be parameterized in coarse ocean models to simulate realistic air-sea gas exchanges (e.g. Oschlies (2002)). Linear stability analysis is used to construct an analytical closure for submesoscale eddy fluxes in the surface mixed layer which can be easily implemented in an ocean general circulation model with coarser resolution. The linearized Navier Stokes equations using

unstable mixed layer situations as basic state yield unstable wave solutions. The fastest growing mode of this eigenvalue problem is taken as representation for the vertical structure of the submesoscale eddy fluxes -- i.e. in terms of diapycnal diffusivity and eddy streamfunction. Maximum growth rate and corresponding wave number of the fastest growing mode yield the magnitude of the diapycnal diffusivity and eddy streamfunction. Highly resolved simulation of mixed layer type scenarios are used to investigate the parameterization for a wide range of dynamical regimes that may occur. By comparing the diagnosed eddy fluxes with their parameterized counterpart the proposed parameterization is validated and it turns out that vertical structure and magnitude of the eddy fluxes are well captured.

## **5. First results on selected parameters of the SOPRAN CO<sub>2</sub> enrichment study 2011: Pteropods, particle sinking velocities and sedimentation**

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Anthropogenic carbon emissions lead to acidification of the marine realm. The consequences of ocean acidification on a natural pelagic plankton community were investigated in the KOSMOS system deployed in Bergen (Norway). CO<sub>2</sub> induced changes were detrimental on pteropod larvae abundances and caused shell dissolution in adult individuals. These results show, for the first time, that ocean acidification negatively affects pteropods living in their natural community. Particle sinking velocities showed an increase in low CO<sub>2</sub> treatments towards the end of the experiments while there was no clear effect during the initial period. Observed differences largely corresponded with the abundance of calcifying phytoplankton (*Emiliana huxleyi*). Particle export was further investigated by quantifying the total mass of sedimented material. Material export was largest in low CO<sub>2</sub> treatments and gradually decreasing towards higher CO<sub>2</sub> levels. Our investigations show that ocean acidification has the potential to affect natural pelagic ecosystems on various levels.

## 6. Ocean acidification effects on pteropod larval and adult stages at „in-situ“ conditions during a mesocosm experiment

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Present anthropogenic CO<sub>2</sub> emissions are causing acidification of the world's surface oceans. There is increasing experimental evidence that CO<sub>2</sub> induced changes in seawater carbonate chemistry negatively affects the development of calcifying planktonic metazoa. Pteropods, shelled euthecosomate mollusks, are key species in epipelagic food webs as consumers and prey for various marine organisms. Contributing significantly to organic matter and biogenic calcium carbonate export, pteropods are relevant for global biogeochemical cycles. The Bergen 2011 KOSMOS study was investigating ocean acidification effects on a North Atlantic plankton community from physiology to food chain ecology. 9 mesocosms with a volume of each 80 m<sup>3</sup> enclosed the natural plankton community including the boreal-temperate pteropod species *Limacina retroversa* for a period of 40 days. Mortality of pteropod larval and adult stages was significantly correlated to increased CO<sub>2</sub> levels. Shell corrosion was observed at increased CO<sub>2</sub> levels, but not in the control mesocosms. With prospect on the high sensitivity already to moderate CO<sub>2</sub> concentrations as expected within this century, pteropods are highly endangered if CO<sub>2</sub> emissions are not mitigated. The disappearance of pteropods from the marine ecosystem could have considerable consequences for commercially important fisheries as well as biologically mediated ocean carbon sequestration. This is the first time that CO<sub>2</sub> effects could be investigated at "in-situ" conditions and for an extended time period on these fragile organisms.

## 7. Title

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*Abstract not available yet*

## 8. Nitrous Oxide Fluxes in the Eastern Tropical Atlantic Ocean

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The ocean contributes as a major net source to the atmospheric content of the potent greenhouse gas nitrous oxide ( $N_2O$ ). The Eastern Tropical Atlantic holds some of the sites expected to be locations of strong outgassing and/or high  $N_2O$  production: the Northwest African coastal upwelling, the equatorial upwelling in the Gulf of Guinea and the oxygen minimum zone (OMZ) off West Africa. In the course of projects SOPRAN, SFB754 and NORDATLANTIK,  $N_2O$  was sampled in these regions, in conjunction with hydrographic parameters, current velocity, oxygen and mixing. This allowed estimating vertical  $N_2O$  fluxes, particularly the upward flux through the thermocline into the mixed layer. Near surface  $N_2O$  supersaturation was detected in discrete and underway samples, and gave a handle on sea-to-air flux distribution. The estimated  $N_2O$  sea-to-air flux was found substantially higher than the estimated  $N_2O$  supply from below in the Northwest African upwelling and in the OMZ. The causes for this budget discrepancy are not completely clear and a matter of further research. A plausible candidate is surface slicks inhibiting air-sea gas exchange.

## 9. Trace metal fractional solubility in marine aerosols at CVAO

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Deposition of aerosol particles to the ocean is a useful pathway in providing micronutrients such as iron, manganese to the open oceans. Amongst other aspects, the critical parameter with respect to biological activities is the amount of soluble trace metal (fractional solubility) that is deposited to the ocean. Results of trace metal speciation measurements involving the analysis of soluble Fe (II) and Fe (III) and also the total fractional solubility of iron and manganese obtained from analysis of batch extracts of aerosol particles collected at the CVAO shall be presented. The fractional solubility was evaluated for different solvents with varying pH, including DI water (~ pH 5.5), acetate buffer (pH 4.6) and a pH 2 solvent of HCl. Results show strong increase in fractional solubility with decreasing pH. In general, most of the fractional iron observed was in the Fe (III) state. Soluble Fe (II) was mostly observed at lower pH. Solubility of iron was very low and was estimated to be less than 0.5% especially in DI water but increased to about less than 10% in pH 2 solvent. An inverse relationship between total and fractional soluble iron was observed with higher soluble iron observed

mostly during low total iron loading. Fractional solubility of Manganese was found to be higher than that of iron especially in DI water and buffer extracts.

## 10. Radar Backscatter Measurements on FINO-2

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Since September 2011, continuous and autonomous measurements of the radar backscattering from the sea surface are being performed on FINO-2 using the Multi<sup>3</sup>Scat of the University of Hamburg. The scatterometer is working at five microwave frequencies (1.0 GHz, 2.3 GHz, 5.3 GHz, 10.0 GHz, and 15.0 GHz, corresponding to L, S, C, X, and Ku band, respectively) and at all polarization combinations (HH, HV, VV, and VH). Great efforts have been spent to maximize the signal-to-noise ratio (SNR) by removing the phase noise, which may be of the same magnitude as the ocean backscatter, particularly at high radar frequencies and low wind speeds. In addition, and in order to complement the measured relative (i.e. uncalibrated) radar backscatter time series, synthetic aperture radar (SAR) images acquired by the radar sensors aboard the German TerraSAR-X and TanDEM-X satellites and the Canadian Radarsat-2 satellite are being used. Those images provide snapshots of the spatial variation of the radar backscatter at X band (TerraSAR-X) and C band (Radarsat-2) and, together with data from spaceborne scatterometers (Ku band; on QuikScat and OceanSat-2), enable us to put our time series in a greater (synoptical) context.

## 11. Bacteria mediated alteration of the gelatinous surface microlayer

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Within the SOPRAN II project, nine Kiel Off Shore Mesocosms for Ocean Simulations (KOSMOS) were deployed in the Raunefjord, southern Norway, in May 2011. The seawater enclosed in the mesocosms was manipulated for increasing levels of CO<sub>2</sub>. Our objectives were to examine the chemical composition and bacterial activity of the sea-surface microlayer (SML) and its dynamics in the future scenario of an acidified ocean. We focused on Transparent Exopolymer Particles (TEP) and Coomassie Stainable Particles (CSP),

marine gels of polysaccharidic and proteinaceous nature. We followed the variability of the SML as a result of phytoplankton blooms in the water column. TEP formation depended on phytoplankton exudation, more enhanced at high  $p\text{CO}_2$ . Bacterioplankton profited from the release of polysaccharides and bacteria-TEP aggregates accumulated in the SML most likely through physical upward transport, evident by increased bacterial abundance. CSP, besides being always more abundant, appeared in the SML concurrent with the decline in arabinose, a neutral sugar probably source-indicator for TEP. Moreover, increasing  $p\text{CO}_2$  negatively affected CSP formation and bacterioneuston growth, while stimulated TEP and bacterioplankton. We suggest that CSP might result after chemical alterations of TEP mediated by bacterioneuston. This process occurs in the SML, where CSP probably originate while TEP are scavenged from the water below.

## **12. The sea-surface microlayer during the R/V Meteor Cruise M91: Measurements and satellite detection of surface films**

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The Meteor cruise M91 took place from 1 to 26 December 2012 in the coastal upwelling region off Peru. One of the major aims of M91 was to characterize the sea-surface microlayer and to assess its effect for the exchange of climate-relevant trace gases across the ocean/atmosphere boundary layer. During M91 we have, therefore, focused on sea-surface microlayer composition in terms of DOM dynamics. For this purpose samples from the microlayer, from 20cm below the ocean surface as well as from CTD casts were taken as comparison. Our measurements include dissolved and total organic carbon (DOC and TOC), total nitrogen and total dissolved nitrogen (TN and TDN), chromophoric dissolved organic matter and fluorescent dissolved organic matter (CDOM and FDOM), total and dissolved combined carbohydrates, total and dissolved hydrolysable amino acids, bacterial cells number and phytoplankton cells number, and marine gels like TEP and CSP. Organic marine surface films reduce the surface roughness (i.e. they dampen the small-scale surface waves), which in turn results in a reduced radar backscattering from the ocean surface. This is why they can be detected by Synthetic Aperture Radar (SAR) sensors, if the wind speed is low to moderate, so that the surface films (slicks) are not disrupted. SAR images from the area under investigation, acquired by the German TerraSAR-X and TanDEM-X satellites during the research cruise M91, are therefore used to provide information about the spatial distribution of those slicks and about small-scale wind speed variations in the area of interest. In addition, spaceborne scatterometer data of the scatterometer aboard the Indian Oceansat-2 satellite are used to provide daily wind field information on larger scales (and at coarser resolution).

### **13. Sahara dust impact on solar radiation at Cape-Verde: A synergy of in-situ radiation and AOD measurements**

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Dust aerosols play an important role in the climate system. The incoming solar (shortwave) radiation is directly affected by the soil dust aerosols due to scatter and absorption, while on the other hand, the outgoing terrestrial (longwave) radiation is affected by scattering and re-emission. In particular, the mineral dust and aerosol alter the radiative forcing at the surface of the ocean by changing the atmospheric opacity, and hence affecting the Sea Surface Temperature (SST) by modifying the ocean heat budget. The primary goal of this work 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.

### **14. Contributions to tropical VSLs emissions from the equatorial Atlantic upwelling region**

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Very short lived halogenated substances (VSLs) such as methyl iodide ( $\text{CH}_3\text{I}$ ), dibromomethane ( $\text{CH}_2\text{Br}_2$ ) and bromoform ( $\text{CHBr}_3$ ) can be produced naturally in the oceans and take part in ozone chemistry both in the troposphere and the stratosphere. Tropical oceanic upwelling areas have been identified as source regions for these compounds but their global significance is still uncertain. Deep tropical convection can lift considerable amounts of VSLs into the stratosphere, underlining the importance of the tropical oceans. During the SOPRAN cruise MSM18/3 from June to July 2011 in the tropical equatorial Atlantic upwelling,  $\text{CH}_3\text{I}$ ,  $\text{CH}_2\text{Br}_2$  and  $\text{CHBr}_3$  were measured in sea surface water and the deeper water column. Biological and physical drivers of the formation of these VSLs as well as their transport within the ocean and to the atmosphere were investigated.

## 15. MEMENTO (Marine Methane and Nitrous Oxide database)

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**MEMENTO (Marine Methane and Nitrous Oxide)** is a result of a joint initiative between SOLAS (Surface Ocean Lower Atmosphere Study; [www.solas-int.org](http://www.solas-int.org)) and COST Action 735 (European CoOperation in the Field of Scientific and Technical Research; [www.cost-735.org](http://www.cost-735.org)) to improve our understanding of the oceanic distribution of methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O). During SOPRAN III, available N<sub>2</sub>O and CH<sub>4</sub> depth profiles and surface data will be archived and global N<sub>2</sub>O and CH<sub>4</sub> concentration and sea-to-air flux fields will be calculated to develop MEMENTO into a living and valuable tool for the scientific community. The database will be an important resource for the calculation of an oceanic emission estimate of N<sub>2</sub>O and CH<sub>4</sub> and will help to identify oceanic regions that need to be further investigated to improve the quality of the emission estimate.

## 16. Atmospheric signatures of air-sea exchanges of CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, and N<sub>2</sub>O recorded at the Cape Verde Atmospheric Observatory (CVAO)

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The Cape Verde Atmospheric Observatory (CVAO) located on Sao Vicente island (16°52' N, 24°52'W) in the north-eastern subtropical Atlantic was established in 2006. Since 2007 biweekly air flask samples have been taken on a 30m tower and analyzed for concentration and isotopic composition of long-lived trace gases and oxygen at the Max-Planck-Institute for Biogeochemistry in Jena, Germany. In October 2008 a system for quasi-continuous measurements of CO<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>O and SF<sub>6</sub> has been installed and operated since then, albeit with large data gaps caused by technical difficulties at the remote site. Here we present the observed records from CVAO and analyze the data on synoptic, seasonal and interannual time scales. CVAO is located in the North-Atlantic trade wind system in an area with a very stable marine boundary layer. Seasonal cycles and interannual variability reflect changes in atmospheric transport and sources and sinks of the trace gases in the northern hemisphere. However, sources and sinks closer to CVAO primarily cause synoptic concentration variations. Most air masses arriving at the station have passed over the coastal upwelling areas off the coast of Western Sahara and Mauritania which are

supersaturated in CO<sub>2</sub>, CH<sub>4</sub>, and partly in N<sub>2</sub>O, and undersaturated in oxygen. Small shifts in the wind trajectories therefore induce synoptic variations of the atmospheric concentrations depending on the travel time of the air mass over the upwelling region and which can be detected in the observations. Using backtrajectory analyses, we can place bounds on integrated air-sea fluxes in the upwelling area and relate them to in situ surface ocean measurements of biogeochemical gases. Based on the analysis we estimate the potential to detect longer-term changes in air-sea fluxes of biogeochemical gases from long term measurements at the Cape Verde station.

## 17. Partitioning of the transfer resistance between air and water

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A detailed experimental study of the partitioning of the transfer resistance between air and water-side was performed in the Heidelberg air-sea facility (*Aeolotron*). The transfer resistances of tracers with a wide range of solubilities were measured, including species with medium solubility and environmentally important tracers such as DMS and acetone. The resistance addition model of Liss and Slater (1974) was tested with a combined Schmidt number scaling. The air-sided (water-sided) part of the total resistance was determined using tracers controlled by only one side because of their either very high or low solubility. The total resistance is obtained by adding both parts. Computed and measured transfer resistances agree well. It is shown that the value of solubility for which the air and water-side transfer resistances are equal depends both on the friction velocity as well as on the coverage of the water surface with surfactants.

## 18. Gas Exchange at Hurricane Wind Speeds

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In a pilot study, air-sea gas transfer velocities of two different sparingly soluble tracers were measured in the unique high-speed wind-wave tank at Kyoto University, Japan. This tank is capable of producing hurricane strength wind speeds of up to 67 m/s. The measured transfer velocities spanned two orders of magnitude, lying between 11 cm/h and 1180 cm/h with the latter being the highest ever measured wind induced gas transfer velocity. They are more than a factor of 20 larger than the ones observed in the Aeolotron at the highest wind speed. The measured gas transfer velocities are in agreement with the only available dataset at hurricane wind speeds (McNeil & D'Asaro 2007). The disproportionately large increase of the transfer velocities found at highest wind speeds indicates a new regime of air-sea gas transfer, which is characterized by strong wave breaking, enhanced turbulence and bubble cloud entrainment. However, using only two tracers in the presented pilot experiment, the respective effects of enhanced turbulence due to breaking waves, additional surface and turbulence due to bubbles and spray as well as generally enlarged surface due to waves could not be separately quantified.

## 19. DOAS Measurements of Reactive Halogen Species

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Reactive halogen species (RHS) such as bromine oxide (BrO) or iodine oxide (IO) play a major role in the chemistry of ozone in both, the troposphere, and the stratosphere and possibly influence the ozone budget on a global scale. In order to estimate the amount of RHS release from marine sources DOAS measurements in three different upwelling regions (Mauritanian, African equatorial and Peruvian) as well as long-term-observations at the Cape Verde Atmospheric Observatory (CVAO) were performed within the SOPRAN Project (BMBF Förderkennzeichen 03F0611F). Based on the constantly measuring MAX-DOAS Setup on CVAO, in 2010 the HaloCaVe campaign with a set of DOAS instruments on the CVAO and RV Poseidon allowed for an intercomparison of various instruments on shore as well as for extending these observations to a larger area with the simultaneous ship-borne MAX-DOAS measurements during the DRIVE campaign from Gran Canaria to Cape Verde and back

along the mauretanic coast. These measurements again can be compared to results from other groups such as halocarbon precursors or aerosol data as well as they can be used together with data from RV Polarstern to obtain a global map of RHS. The recent SOPRAN cruise M91 on RV Meteor along the coast of Peru in December 2012 allows for first comparisons of both upwelling regions. First results from MAX-DOAS and CE-DOAS measurements will be presented.

## **20. Dimethylsulphide (DMS) emissions from the West Pacific Ocean: a potential marine source for the stratospheric sulphur layer**

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Sea surface and atmospheric measurements of dimethylsulphide (DMS) were performed during the TransBrom cruise in the West Pacific Ocean between Japan and Australia in October 2009. Air-sea DMS fluxes were computed between 0 and 30  $\mu\text{mol m}^{-2} \text{d}^{-1}$ , which are in agreement with those computed by the current climatology, and peak emissions of marine DMS into the atmosphere were found during the occurrence of tropical storm systems. Atmospheric variability in DMS, however, did not follow that of the computed fluxes and was more related to atmospheric transport processes. The computed emissions were used as input fields for the Lagrangian dispersion model FLEXPART, which was set up with actual meteorological fields from ERA-interim data and different chemical life times of DMS. A comparison with aircraft in-situ data from the adjacent HIPPO2 campaign revealed an overall good agreement between modeled versus observed DMS profiles over the tropical West Pacific ocean. Based on observed DMS emissions and the meteorological fields over the cruise track region, the model projected that up to 30 g S per month in the form of DMS can be transported above 17 km in this region. This surprisingly large DMS entrainment into the stratosphere is disproportionate to the regional extent of the cruise track area and mainly due to the high convective activity in this region as simulated by the transport model. Thus, we conclude that the considerably larger area of the tropical West Pacific Ocean can be an important source of sulphur to the stratospheric persistent sulphur layer, which has not been considered as yet.

## **21. SOPRAN II and SOPRAN III Activities of the Max Planck Institute in Mainz**

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*Abstract not available yet*

## **22. Chemical Characterization of Aerosol Particles at the CVAO - interesting new observations**

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Interannual variation of all aerosol parameters is higher than in European aerosols due to the high variability of dust transports from the Saharan desert to Cape Verde. The halogenide ions chloride and bromide were depleted in aerosols depending on the season and on the history of air mass. Bromide depletion reached often 100 % in summer samples indicating halogen activation. Lowest depletion was observed for halogenides in air masses with high dust loading during winters. A comparison of chlorophyll A concentration in oceanic water with ammonium and oxalate in aerosols delivers hints to marine sources of ammonium and oxalate. Nss-sulfate is highly correlated with oxalate in pure marine air masses indicating formation pathways coupled to photochemistry and biogenic oceanic emissions of precursors. Organic matter and elemental carbon have their annual maximum during winter time. The effects of long range transports with continental air masses from Africa during the Harmattan season are much stronger than the production of organic matter from oceanic emissions which increases in summer.

## **23. Physical properties of mineral dust and measurements of dust concentration**

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Mineral dust is one of the most important aerosol types under investigation. Their impact on clouds (e.g. serving as ice nuclei) and radiation can differ depending on their chemical composition and aging state. Furthermore, the understanding of the global dust cycle is still incomplete. The removal of mineral dust is essential for bioactivity in the ocean, since dust serves as a source of nutrients (e.g. iron) for oceanic microorganisms such as phytoplankton. Long-term observations of Saharan dust layers spreading over the Northeast Atlantic Ocean do however not exist so far. Physical properties of mineral dust, here the optical properties, shape and hygroscopicity, can differ from the properties of other aerosols, e.g. marine or most anthropogenic aerosols. These properties can be used for differentiating between aerosol concentrations from dust and other sources. However a thorough investigation of the magnitude of how the physical can differ is still missing. We will give an overview of the physical dust properties, how they affect measurements and the quantification of dust concentrations. The present work can help to improve measurement techniques, which are more robust and operate with lesser infrastructure. This could lead to a larger set of data from more stations without having a complex infrastructure.

## **24. Wave and Heat Exchange Measurements in the Southern Pacific**

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To improve our understanding of the dependency of air-sea gas exchange on wind waves, simultaneous and collocated measurements of (statistical) wave parameters and heat/gas exchange are needed. A number of (mostly optical) instruments was deployed to the SOPRAN M91 cruise on FS Meteor off the coast of Peru in December 2012. Heat transfer velocities were measured with the Active Controlled Flux Technique (ACFT), turbulent fluxes for CO<sub>2</sub>, heat, and momentum were measured by eddy covariance (EC), wave statistics (mean square slope, significant wave height, dominant wave frequency) were measured with the Reflective Stereo Slope Gauge (RSSG). In addition, an experimental instrument that can measure two-dimensional water surface topography and wavenumber spectra based on

stereo photography and the measurement of light polarization was tested during the cruise. Examples of the acquired images that illustrate the measurement principle are presented and the data processing techniques that are used to extract the physical parameters from the image sequences are described. An overview of the cruise stations at which measurements were taken will be given and first preliminary results will be presented.

## **25. Collection and analysis of data that describe the accumulation of organic matter in the surface microlayer**

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In the SOPRAN-II meeting, the effect of organic matter (OM) accumulation within the thin interfacial layer between atmosphere-ocean, called surface microlayer (SML), has been discussed. Yet, it is unclear whether the enrichment of OM in the SML has to be accounted for, when modeling the formation of primary organic aerosols over ocean areas. As a first step, we collected data from the literature and analyzed the enrichment factor (EF), which indicates the concentration measured in the SML relative to the concentration within the subsurface water (SSW). In a second step, we sorted the observed EF according to wind conditions, measurement techniques and region. For our first analysis, we have posed three Null-hypotheses: 1) the enrichment of OM in the SML is independent of environmental conditions like wind; 2) enrichment factors are invariant in space and time; 3) results of EF depend on the measurement technique applied. Our analysis shows that most EF are close to one, indicating little to no accumulation of OM in the SML. Elevated EF range between 2 and 5. For coastal areas we see a clear tendency towards elevated EF. We also find higher EF for windy conditions. No difference in EF is evident when comparing data of different measurement techniques. The effect of OM enrichment in the SML was found to be generally small, with few exceptions where EF increased by a factor of five. We here conclude that knowledge about the OM concentration within SSW provides sufficient information when parameterizing the formation of primary organic aerosol in atmosphere-chemistry models (e.g. with the Community Multi-scale Air Quality model, CMAQ).

## **26. Improved analyses and synthesis of dust impact on radiative transfer, optical properties and phytoplankton development in cooperation with other subprojects**

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The main topics in the third phase of SOPRAN are the relationship between direct dust- and iron input and absorbing and scattering phytoplankton blooms, the quantification of the dust impact on inherent and apparent optical properties and the derivation of relationships for the implementation in ecosystem models. Therefore, the satellite derived aerosol optical depths former used as rough approximation for the dust deposition will be replaced by the near surface mass concentration and dust deposition rates. Dust source areas derived from backward trajectory modeling and from satellite data will be compared with dust deposition at the atmospheric station and with the development of absorbing (Diatoms, Dinoflagellates) and scattering (Coccolithophoride) phytoplankton as a potential response. In the synthesis phase the influence of dust on the optical water properties for dust in atmosphere and dust in water will be combined. To capture concentrations of water constituents or optical water properties during dust events, in situ data of project partners will be included for model parameterization. Therefore, provided data like turbidity, chlorophyll-fluorescence, beam attenuation measurements and PAR from Gliders, Floats and Islandia will be evaluated.

## **27. Results of SOPRAN II in relation to the impacts of Saharan dust on optical water properties, phytoplankton development and satellite derived products**

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This poster summarizes investigations focused on the biological response to dust deposition, as well as on the quantification of dust impact on photosynthetically available radiation (PAR), on optical water properties and on satellite derived products. The main sources of nutrient supply in the area off Northwest Africa are coastal upwelling and Saharan dust deposition. Statistical analyses showed that alongshore wind stress and induced upwelling were most significantly responsible for surface chlorophyll-a (Chl-a) variability mainly in winter and spring with delay of up to 16 days. Only 5 % of the Chl-a variability was related to

the dust input. Only a few of the dust storms between 2000 and 2008 caused a biological response expressed by an increase of surface Chl-a. Time lags between 8 and 16 days were determined. The Chl-a concentration was increased up to 2.4 mg m<sup>-3</sup>. The derived relationship between PAR and dust aerosol optical depth (AOD<sub>dust</sub>) implied a decrease of nearly 1.2% in PAR per increase of about 0.1 in AOD<sub>dust</sub>. This means a reduction in PAR of about 32% for the strongest dust storms. Atmospheric dust modifies the amount and the spectral distribution of water light field. In the applied optical model the effect of dust on incident solar radiation was parameterized by radiation measurements. The reduction of PAR during observed dust storms were up to 19.3% in the upper water column. The impacts of spectral effects on PAR were different in oceanic and coastal regions. A compensation of the spectral effects at water depths of about 7 m was only observed in ocean regions because of different light attenuation in coastal areas. Dust deposited in the water column modifies the optical water properties. Laboratory measurements of absorption coefficients of different dust samples showed an increase to short-wavelength range. Dust in water reduces the euphotic depth more in the blue than in the red spectral range. The euphotic depth and PAR are decreased more in clear ocean water than in turbid coastal waters. Saharan dust impacts satellite derived ocean surface wind speeds. The influence depends mainly on the strength of dust storms, the microwave frequency and the wind speed. The impact is higher for stronger dust storms, higher frequencies and lower wind speeds.

## **28. Bromoform in the central Baltic Sea during a cyanobacterial bloom**

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The study was conducted with the aim to investigate the distribution of bromoform and its controlling factors in the central Baltic Sea during a cyanobacterial bloom in summer 2012. In order to identify and quantify the key processes of bromoform turnover, discrete water samples, from the surface and the chlorophyll a maximum, were taken for analysis of bromoform concentrations and its stable carbon isotopic ratio. Moreover, atmospheric bromoform mixing and isotope ratios were measured and the sea/air flux was calculated. Various biological parameters, including autotrophic biomass and community composition as well as microbial abundance and activity were analysed to determine source-sink relationships. Typical conditions for a summer phytoplankton bloom were observed, in which total autotrophic biomass ranged from about 1.5 to 6 µg Chl-a. Phototrophic cyanobacteria contributed about one third to autotrophic abundance. The concentration of bromoform in the water varied from 4.4 to 19.7 pmol L<sup>-1</sup> and the atmospheric mixing ratios ranged from 1.6 to

19.6 pptv. Bromoform in air was enriched in  $^{13}\text{C}$  ( $\delta^{13}\text{C}$ : -1.5 - -22 ‰) compared to sea water ( $\delta^{13}\text{C}$ : -10 - -27 ‰). The measurements obtained during this cruise provide a vital set of isotopic signatures of bromoform in the sea water and the marine air of the Baltic Sea region.

## **29. Sensitivities of biogeochemical flux estimates to variations in model parameters at Baltic Sea monitoring site *BY15 Gotland Deep***

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Our study describes a sensitivity analysis that allows the parameters of a one-dimensional ecosystem model (Kreuz et al., in prep.) to be ranked according to their specificity in determining biochemical key fluxes. Key fluxes of interest are annual total production, remineralization above the halocline, and export at 50 m at the Baltic Sea monitoring site *BY15 Gotland Deep*. The model resolves mass flux of carbon- (C), nitrogen- (N), and phosphorous- (P), while considering nitrogen fixation explicitly. Our first null hypothesis is that the variation of the value of every single model parameter affects each annual C-, N-, and P-budget simultaneously. Our second null hypothesis states that the variation of every parameter value induces changes at least in either of the annual C-, N-, P-budgets. Our analyses falsify both null hypotheses. Thirteen out of 36 parameters must be regarded redundant, as their variation neither alter annual key fluxes nor produce considerable time-shifts in model trajectories at the respective site. Only six parameters were found to induce substantial changes in annual C-, N-, and P-flux estimates. The assimilation efficiency of zooplankton turned out to be of vital importance, because the fraction of unassimilated dead algal cells is critical for the amount of organic matter exported out of the euphotic zone. Overall, our detailed specification of model sensitivities to parameter variations will facilitate the formulation of a well-posed inverse problem for the estimation of the air-sea flux of  $\text{CO}_2$ , given typical standing stock observations at the *Gotland Deep*.

## 30. SOPRAN data archive and website

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The main task of the PANGAEA group for the last phase of SOPRAN II and the next phase SOPRAN III is to provide a long term archive for project data and to support the project communication by maintaining the project's website. At present the project archive contains 195 SOPRAN related data sets. These data sets include e.g. physical oceanography, hydrochemistry, element concentrations and distributions. Geographically most of the recent data are located off Mauretania. During SOPRAN III a close cooperation between the data management at GEOMAR and PANGAEA will help to upload, archive and publish data in an easy way. The website has been reorganized end of 2012. The website now appears in a new layout. The information content has been taken from the former website with only slight changes. New features of the website are internal areas for discussion and document exchange. Personal accounts are necessary to access of these areas.

## 31. Plankton blooms at elevated atmospheric carbon dioxide levels: the SOPRAN Bergen 2011 mesocosm study

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Increasing levels of atmospheric carbon dioxide (CO<sub>2</sub>), caused by human activities such as the burning of fossil fuels are driving climate change, but also affect the oceans. Here, increasing levels of CO<sub>2</sub> are decreasing pH and carbonate saturation states, termed ocean acidification. Coccolithophores, marine calcifying phytoplankton, are key drivers of global carbon cycling, especially as calcium carbonate is known to act as ballast for the otherwise slowly sinking organic material, thus impacting export production. Calcification rates of several coccolithophores have been found to be negatively influenced by ocean acidification in various laboratory studies. Understanding how this might impact future ecosystem

functioning and element cycling is crucial. Here we report on a mesocosm CO<sub>2</sub> perturbation study in the framework of SOPRAN carried out in Bergen, Norway, at a time at which blooms of the coccolithophore *Emiliana huxleyi* occur naturally. We will present temporal biomass and nutrient dynamics and compare it to the dominant phytoplankton community composition, with a special focus on the success of *Emiliana huxleyi* at increasing levels of carbon dioxide.

## **32. Seasonal variability of iodomethane (CH<sub>3</sub>I) production in the surface ocean**

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Volatile iodocarbons, including CH<sub>3</sub>I, are major carriers of iodine from the ocean to the atmosphere. The transferred iodine participates in ozone destruction and aerosol formation in the troposphere. However, the production pathways of methyl iodide in the ocean still remain under debate. Experiments to investigate CH<sub>3</sub>I production were conducted over an annual cycle in the Kiel Fjord. The experiments involved 57 hour light and dark incubations of natural seawater. Samples incubated in the light had significantly higher daily production than samples kept in the dark. The daytime accumulation was not affected by filtration (0.2µm), suggestive of a photochemical pathway for CH<sub>3</sub>I production. A strong seasonal variation of methyl iodide in Kiel Fjord was correlated with solar radiation, sea surface temperature (SST) and sea surface salinity (SSS). However, methyl iodide loss during the night was larger in the samples that were incubated under daylight. As a result, the daily net production of methyl iodide over 24 h was low in the incubation flasks. There are two main possibilities for this additional loss pathway. One is bacterial degradation, the other is chemical oxidation by compounds that are produced during the day and which accelerate the degradation of CH<sub>3</sub>I during the night.

### 33. Upwelling velocities inferred from helium isotopes

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Oceanic upwelling velocities are too small (in the order of  $10^{-5}$  m/s) to be measured directly. We applied the recently developed helium method to infer these velocities indirectly by means of the mixed layer disequilibrium of the helium-3/helium-4 ratio. Study areas are the two 'SOPRAN' regions in the eastern equatorial Atlantic and off Mauritania. Near the coast, the helium derived upwelling velocities are in good agreement with Ekman theory. In the open ocean, the vertical Ekman velocities are smaller by about one order of magnitude compared to the onshore region. The helium method, on the other hand, points to a much stronger offshore upwelling at some locations, which we attribute to eddy activity. The sea surface temperature and ocean primary productivity rates are in qualitative agreement with the distribution of the helium inferred vertical velocities, both for the equatorial and the Mauritanian upwelling region. This underlines the importance of vertical advection for the heat and nutrient budget of the surface ocean.

### 34. Global modelling of methyl iodide production in the open ocean

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Methyl iodide ( $\text{CH}_3\text{I}$ ) is a volatile organic halogen compound that contributes significantly to the transport of iodine from the ocean to the atmosphere, where it plays an important role in tropospheric chemistry.  $\text{CH}_3\text{I}$  is naturally (and globally) produced ocean. The processes involved in the formation of  $\text{CH}_3\text{I}$ , however, are not fully understood. Suggested production pathways include production by phytoplankton and photochemical degradation of organic matter. Here, both the biological and photochemical production mechanisms are considered in a biogeochemical module that is coupled to a global three-dimensional ocean general circulation model (MPIOM-HAMOCC). In a series of sensitivity studies different production rates are tested towards the model's ability to represent observed concentrations. The simulated  $\text{CH}_3\text{I}$  concentrations agree well with observed values. The results indicate that the dominating source cannot be clearly identified, though many observations can be best

explained by photochemical production, specifically degradation of refractory dissolved organic carbon. Overall, the global annual  $\text{CH}_3\text{I}$  fluxes range between 70 and 260 Gg yr<sup>-1</sup>, i.e. The ocean is a net source of methyl iodide for the atmosphere, though in some regions in boreal winter fluxes are of opposite sign (from the atmosphere to the ocean).

### **35. Bacterial turnover of iodomethane in Baltic and North Sea surface waters**

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Iodomethane is a strong source of highly reactive halogen oxide radicals in the atmosphere. However, its oceanic emission budgets are still weakly understood, partly due to uncertainties about the equilibrium of production and decomposition processes. Several sources (mainly photoautotrophic organisms) and sinks (e.g. hydrolytic cleavage) have been identified, but knowledge about bacterial degradation is very limited. Therefore, our aim was to determine the bacterial uptake of iodomethane using <sup>14</sup>C-labelled substrates and to identify bacterial organisms to be stimulated in iodomethane enrichment experiments in Baltic and North Sea surface waters. To further link the uptake processes with the identity of involved species, we applied RNA-based stable isotope probing using <sup>13</sup>C-labelled iodomethane. The uptake rates of iodomethane ranged between 50 – 600 pmol h<sup>-1</sup> L<sup>-1</sup>, which was unexpectedly high regarding the *in situ* concentrations (5-30 pmol L<sup>-1</sup>). We found that only few bacterial taxa were stimulated upon the addition of iodomethane among which we identified members affiliated to *Methylophilaceae* in Baltic Sea and *Oleispira* in North Sea samples, respectively. However, RNA-SIP did not yet result in <sup>13</sup>C-enriched sequences, probably because of insufficient RNA labelling. Nevertheless, our results show that bacterioplankton is able to take up and probably degrade iodomethane, and future studies will concentrate to identify the involved species.

## **36. Oceanic VSLS contribution to stratospheric ozone**

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Halogenated very short-lived substances (VSLS) are expected to contribute significantly to stratospheric ozone chemistry. Coastal waters and upwelling regions in the tropical oceans have been identified as important source regions for the naturally produced VSLS. In this study we investigate VSLS emissions in the tropical Atlantic and West Pacific and their contribution to the stratospheric halogen loading. For this purpose we use the Lagrangian particle dispersion model FLEXPART, which simulates transport, small scale mixing, washout and photochemical decay. The transport simulations are based on VSLS sea-to-air flux obtained from the tropical East Atlantic in May/June 2010 (SOPRAN II, DRIVE cruise), from the tropical Western Pacific in October 2009 (WGL project TransBrom) and from the recent SHIVA Sonne expedition to the South-China Sea during November 2011 (EU project SHIVA). While relatively large brominated VSLS fluxes are found in the Mauritanian upwelling in the East Atlantic, the VSLS transport is most efficient in the Western Pacific atmosphere. We show based on the evaluations for the three tropical campaigns that the peak emissions of brominated VSLS together with strong convective transport leads to significant VSLS abundances which are comparable to available upper air measurements. For methyl iodide however, emission-based profiles are larger than observations, which suggests that existing measurements may not be representative and methyl iodide could have a larger impact on the stratospheric halogen loading than assumed so far.

## **37. Organic carbon and aliphatic amines in marine particles: exchange processes between ocean and atmosphere**

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In order to investigate exchange processes between air and sea, in two intensive campaigns at the Cape Verdes, seawater and marine aerosol was sampled and analyzed for the organic content. Chlorophyll A data near Sao Vicente showed low biological activity at the first campaign (May 2011) but higher biological activity in the second campaign (November 2011). For seawater analysis, higher dissolved organic carbon concentrations were found in

November 2011. Furthermore, enrichment of organic carbon in the sea surface microlayer – the direct interface between air and sea - was found up to an enrichment factor of 2. General aerosol composition regarding inorganic ions was similar in May and November, but the OC content was strongly increased in November. Also OC enrichment in aerosols compared to seawater increased in times of high biological activity by 30%. Besides organic sum parameters, aliphatic amines were investigated on aerosol particles and found in concentrations between 11 and 17 ng m<sup>-3</sup>. The concentrations of the amines were similar at the two campaigns; however their contribution to the DOC was higher at times of high biological activity. The results suggest that organic carbon on aerosols is connected to the biological activity within the ocean being an important source.

### **38.A case study on modeling the dissolution of hematite under urban and non-urban conditions with SPACCIM**

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Since aerosol iron contained in desert dust is known to be a nutrient enhancing biological activity in the world oceans, many investigations have been undertaken to identify the chemical speciation of iron that makes it bioavailable for phytoplankton. Several physical and chemical processes have been identified influencing the state of iron and it has been observed that the soluble form of iron, notably Fe(II), is most biologically available. Especially acidification of desert dust has been recognized as one of the leading processes that makes iron soluble and in this context it has been reported that high initial concentrations of sulphate are needed to transport substantial amounts of dissolved iron to the oceans. In this regard the difference that arises out of anthropogenic and natural acidification of iron is investigated in this work using the chemical transport model SPACCIM ("SPectral Aerosol Cloud Chemistry Interaction Model"). The focus will be on Hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>), that is in addition to Goethite ( $\alpha$ -FeOOH) one of the most common irons that is found in desert dust.

## **39. Impacts of dust depositions and ocean acidification on trace metal cycling and bioavailability**

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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. In this region we will perform controlled laboratory dust solubility experiments using dust collected in atmospheric samplers at CVOO and natural seawater from the Cape Verde region. Second, we will participate in the Gran Canaria mesocosm Experiment to investigate possible phytoplankton-trace metal interactions in response to atmospheric perturbation (dust & CO<sub>2</sub>). Furthermore, we will present temporal changes in the concentration of dissolved trace metals (Mn, Fe and Al) in trace metal clean mesocosms after two consecutive evapocondensed dust additions (mimicking wet depositions of 10 g m<sup>-2</sup>) to the northwestern Mediterranean, close to the coast of Corsica (DUNE2). In Wuttig et al. (2012), we focused on the similarities and differences between these 3 elements and their release from Saharan dust in this low nutrient low chlorophyll area and the subsequent processes of biouptake and scavenging.

## **40. Cycling of organic Fe-binding ligands in a 3D biogeochemical model**

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The abundance of organic Fe-binding ligands strongly influences the bioavailability and photochemical cycling of dissolved iron (DFe) as well as the reactive fraction of DFe available for particle adsorption, and thus its residence time. New insights into the sources and fate of these ligands have been gained over the last decade and patterns of spatial variability are beginning to emerge. Most biogeochemical models including DFe, however, fix organic ligands to an observed mean concentration. Here we show sensitivity studies with a global biogeochemical model including assumptions on the release of iron-binding ligands from either the remineralization of biogenic particles or directly from phytoplankton, combined with assumptions on their biological or photochemical degradation. We compare

the resulting ligand distributions with a compilation of ligand measurements. Despite the heterogenous nature of the compiled data that includes very different approaches to measure iron complexing capacity, some trends on deep ligand profiles and their interbasin variability begin to emerge. These trends are well reproduced by the model, provided the bacterial degradation time-scale of ligands is on the order of several hundred years. Closer to the surface, disagreements between model and observations show that a model with only bacterial degradation is missing important processes, such as photochemical degradation, siderophore production, and biological uptake. Taking these processes into account can improve model-data agreement both in the deep and surface ocean.

## **41. Uncertainties in future marine N<sub>2</sub>O emissions in the eastern tropical Pacific**

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Marine emissions of nitrous oxide (N<sub>2</sub>O) supply ~10-30% of the annual N<sub>2</sub>O flux to the atmosphere, affecting both climate and stratospheric ozone. Low oxygen regions of the eastern tropical Pacific (ETP) supply much of open ocean N<sub>2</sub>O, but the processes that control N<sub>2</sub>O production there are not well constrained. Future N<sub>2</sub>O emissions are particularly uncertain due to this region's sensitivity to future climate change (apparent based on previous short-term responses to ENSO events). Here we a) derive flux estimates of N<sub>2</sub>O from the ocean to the atmosphere, and b) identify the most major uncertainties in current and future N<sub>2</sub>O emissions using an Earth system climate model. We identify 3 factors that have the greatest potential to impact future N<sub>2</sub>O emissions: future oxygen concentrations, the oxygen concentration at which subsurface net N<sub>2</sub>O productions switches to net N<sub>2</sub>O consumption, and potentially, poorly constrained surface N<sub>2</sub>O production rates. Due to uncertainties in these factors, even the sign of future N<sub>2</sub>O change in the ETP is unclear.

## 42. Sulphur compounds, methane, and phytoplankton: interactions along a north-south transit in the western Pacific Ocean

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The concentrations of dimethylsulfide (DMS), dimethylsulphoniopropionate (DMSP), dimethylsulphoxide (DMSO), and methane (CH<sub>4</sub>), as well as various phytoplankton marker pigments in the surface ocean were measured along a north-south transit from Japan to Australia in October 2009. DMS, dissolved DMSP (DMSPd) and particulate DMSP (DMSPp) concentrations were generally low, while dissolved DMSO (DMSOd) and particulate DMSO (DMSOp) concentrations were comparably enhanced. Positive correlations were found between DMSO and DMSP as well as DMSP and DMSO with chlorophyll a, which suggests a similar source for both compounds. Similar phytoplankton groups were identified as being important for the DMSO and DMSP pool, thus, the same algae taxa might produce both DMSP and DMSO. In contrast, phytoplankton seemed to play only a minor role for the DMS distribution. The DMSPp:DMSOp ratios were very low and seem to be characteristic of oligotrophic tropical waters representing the extreme endpoint of the global DMSPp:DMSOp ratio vs. SST relationship. It is most likely that nutrient limitation and oxidative stress in the tropical West Pacific Ocean triggered enhanced DMSO production leading to an accumulation of DMSO in the sea surface. Positive correlations between DMSPd and CH<sub>4</sub>, as well as between DMSO (particulate and total) and CH<sub>4</sub>, were found along the transit. We conclude that both DMSP and DMSO serve as substrates for methanogenic bacteria in the western Pacific Ocean.