

The Ocean Surface Microlayer and Biogeochemical Feedbacks in the Earth System

International Workshop from 1 – 3 July at Wissenschaftszentrum
Kiel | Fraunhoferstraße 13 | Kiel, Germany

Information and Abstracts



Welcome to the International Workshop “The Ocean Surface Microlayer and Biogeochemical Feedbacks in the Earth System” in Kiel, Germany

At the ocean surface important exchange processes between the water and the atmosphere take place. The exchange is controlled by physical, biological and chemical factors and, due to the complexity of the system, there are still many unknown links. This makes it difficult to entirely understand and predict the oceans role in the climate system. The three-day workshop brings together 40 national and international experts to work on this issue, to highlight main gaps and to identify fundamental next steps.

The workshop is organized as part of the Future Ocean semester topic “Ocean Interfaces – From Nanoscales to Global Impact”, focusing on processes at the ocean-atmosphere interface and aiming to investigate and better constrain its role for the earth system. As environmental change modulates biogeochemical feedbacks, the effect of warming, acidification and eutrophication will be critically discussed. The results of the workshop will be summarized in a white paper.



Anja Engel

GEOMAR Helmholtz Centre
for Ocean Research Kiel
aengel@geomar.de



Hermann Bange

GEOMAR Helmholtz Centre
for Ocean Research Kiel
hbange@geomar.de



Gernot Friedrichs

Institute of Physical
Chemistry, Kiel University
friedrichs@phc.uni-kiel.de



Anke Schneider

Scientific Coordination
Semester Topic
“Ocean Interfaces”
schneider@phc.uni-kiel.de

*We welcome you to Kiel and
wish, for all of us, inspiring and
creative days together!*

LIST OF PARTICIPANTS

1. **Alexander Soloviev** / Nova Southeastern University (USA), soloviev@nova.edu
2. **Alexandra Dabrowski** / Kiel University (GER), dabrowski@phc.uni-kiel.de
3. **Anja Engel** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), aengel@geomar.de
4. **Anke Schneider** / Kiel University (GER), schneider@phc.uni-kiel.de
5. **Annette Kock** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), akock@geomar.de
6. **Bernd Jähne** / University of Heidelberg, (GER), bernd.jaehne@iwr.uni-heidelberg.de
7. **Birgit Quack** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), bquack@geomar.de
8. **Birthe Zäncker** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), bzaencker@geomar.de
9. **Brian Ward** / National University of Ireland (IRL), bward@nuigalway.ie
10. **Caroline Leck** / Stockholm University (SWE), lina@misu.su.se
11. **Cayla Dean** / Nova Southeastern University (USA), cd821@nova.edu
12. **Christa Marandino** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), cmarandino@geomar.de
13. **Christian Stolle** / Leibniz-Institute for Baltic Sea Research Warnemünde (GER), christian.stolle@io-warnemuende.de
14. **Christoph Garbe** / University of Heidelberg (GER), christoph.garbe@iwr.uni-heidelberg.de

15. **Detlef Schulz-Bull** / Leibniz Institute for Baltic Sea Research Warnemünde (GER), detlef.schulz-bull@io-warnemuende.de
16. **Domenico Velotto** / German Aerospace Center (GER), domenico.velotto@dlr.de
17. **Doug Wallace** / Dalhousie University (CAN), douglas.wallace@dal.ca
18. **Emilie Brévière** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), ebreviere@geomar.de
19. **Enno Bahlmann** / University of Hamburg (GER), enno.bahlmann@zmaw.de
20. **Gernot Friedrichs** / Kiel University (GER), friedrichs@phc.uni-kiel.de
21. **Helmke Hepach** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), hhepach@geomar.de
22. **Hermann Bange** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), hbange@geomar.de
23. **Ina Tegen** / Leibniz-Institute for Tropospheric Research (GER), ina.tegen@tropos.de
24. **Inga Hense** / University of Hamburg (GER), hyjv001@uni-hamburg.de
25. **Jonathan Williams** / Max Planck Institute for Chemistry (GER), jonathan.williams@mpic.de
26. **Kerstin Krall** / University of Heidelberg (GER), kerstin.krall@iup.uni-heidelberg.de
27. **Kristian Laß** / Kiel University (GER), lass@phc.uni-kiel.de
28. **Luisa Galgani** / Scripps Institution of Oceanography, UC San Diego (USA), luisa.galgani@icloud.com
29. **Manuela van Pinxteren** / Leibniz-Institute for Tropospheric Research (GER), manuela@tropos.de

30. **Markus Schartau** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), mschartau@geomar.de
31. **Michael Cunliffe** / The Marine Biological Association of the UK (GBR), micnli@mba.ac.uk
32. **Norbert Hertkorn** / Helmholtz Centre München (GER), hertkorn@helmholtz-muenchen.de
33. **Oliver Wurl** / University of Oldenburg, Institute for Chemistry and Biology of the Marine Environment (GER), oliver.wurl@uni-oldenburg.de
34. **Patricia Quinn** / National Oceanic and Atmospheric Administration (USA), patricia.k.quinn@noaa.gov
35. **Peter Liss** / University of East Anglia (GBR), p.liss@uea.ac.uk
36. **Robert Upstill-Goddard** / Newcastle University (GBR), rob.goddard@newcastle.ac.uk
37. **Rüdiger Röttgers** / Helmholtz Centre Geesthacht (GER), ruediger.roettgers@hzg.de
38. **Sonja Endres** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), sendres@geomar.de
39. **Stefan Barthel** / Leibniz-Institute for Tropospheric Research (GER), barthel@tropos.de
40. **Susannah Burrows** / Pacific Northwest National Laboratory (USA), susannah.burrows@pnnl.gov
41. **Timothy Bates** / National Oceanic and Atmospheric Administration (USA), tim.bates@noaa.gov
42. **Tim Fischer** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), tfischer@geomar.de
43. **Tobias Hahn** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), thahn@geomar.de

AGENDA

WEDNESDAY, JULY 1ST 2015

- 15:00-15:30** *Arrival & Registration*
- 15:30-16:00** Welcome, short intro & road map / Gernot Friedrichs, Anja Engel and Hermann Bange
- 16:00-19:00** *Poster session & Icebreaker*

THURSDAY, JULY 2ND 2015

Session 1: Sea Surface Microlayer Characteristics – Physical, Biological, Chemical

- 08:00-09:00** ▶ “Physical, chemical and biological characteristics of the sea-surface microlayer – a whistle-stop tour of the state-of-the-art” / **Michael Cunliffe**
- ▶ “The role of the sea-surface microlayer in ocean-atmosphere interaction” / **Christian Stolle**

Session 2: Gas Exchange Processes

- 09:00-10:00** ▶ “The potential role of the sea-surface microlayer in gas exchange across the air-sea interface” / **Peter Liss**
- ▶ “The sea-surface microlayer’s influence on air-sea gas transfer” / **Kerstin Krall**
- 10:00-10:30** *Coffee break*

Session 3: Aerosols – Production and Emission

- 10:30-11:30** ▶ “Marine aerosol particles: production, composition and connection to the surface ocean” / **Manuela van Pinxteren**
- ▶ “Possible links between marine microorganisms, cloud-albedo and sea ice-melt in the Arctic?” / **Caroline Leck**

11:30-12:45 *Lunch break*

Session 4: Advanced Methods & Remote Sensing

- 12:45-13:45** ▶ “Advanced methods & remote sensing” / **Christoph Garbe**
- ▶ “Influence of the surface microlayer on validation of optical satellite remote sensing” / **Rüdiger Röttgers**

Session 5: Interactions in a Changing Climate / Anthropogenic Forcing

- 13:45-14:45** ▶ “Interactions in a changing climate / anthropogenic forcing” / **Douglas Wallace**
- ▶ “Do ocean-derived CCN play a role in the biological regulation of climate?” / **Patricia Quinn**

14:45-15:15 *Coffee break*

Session 6: Modelling of Processes Across the Sea Surface Microlayer

- 15:15-16:15** ▶ “OCEANFILMS: Modelling organic enrichment in submicron sea spray aerosol from ocean surface films”
/ **Susannah M. Burrows**
- ▶ “Model aspects of organic matter accumulation in the surface microlayer” / **Markus Schartau**
- 16:15-17:00** *Coffee break/Cake*
- 17:00-18:00** ▶ **Public Lecture “The BIG Questions”**: “Ocean Interfaces – From nanoscales to global impact: The case of the oceans’ plankton”
/ **Peter Liss**
- 18:30** *Bus leaves in front of the Wissenschaftszentrum for having dinner at the restaurant “Fördeblick” (Kanalstrasse 85, 24159 Kiel)*
- 22:30** *Bus leaves in front of the restaurant and takes you back downtown*

FRIDAY, JULY 3RD 2015

- 08:00-08:15** *Summary of day 2*
- 08:15-10:45** *Breakout groups*
- 10:45-11:15** *Coffee break*
- 11:15-12:00** *Presentation of results*
- 12:00-13:00** *First steps in preparing the white paper / End of workshop*



ABSTRACTS OF ORAL PRESENTATIONS

Physical, chemical and biological characteristics of the sea-surface microlayer – a whistle-stop tour of the state-of-the art



Michael Cunliffe

Marine Biological Association of the United Kingdom, Plymouth, United Kingdom; Plymouth University, Marine Institute, Marine Biology and Ecology Research Centre, United Kingdom University of East Anglia; Department of Environmental Sciences, Norwich, United Kingdom

Covering more than 70% of the Earth's surface, the sea surface microlayer (SML) is the boundary layer interface between the ocean and the atmosphere. Key to understanding the functional significance of the SML in Earth system processes is a comprehensive view of the SML's physical, chemical and biological characteristics. I will outline the SML paradigm and combine the physical, chemical and biological characteristics that define both structure and function. For example, biogenic molecules such as carbohydrates, lipids and proteinaceous material are enriched in the SML, forming a physicochemical gradient that is separate from underlying water and that influences gas transfer velocity. I will make the case that, in order to look to the future and address the limitations of the past, an advanced approach to understanding the ocean-atmosphere interface will be best achieved through multidisciplinary science.

The role of the sea-surface microlayer in ocean-atmosphere interaction

Christian Stolle

Leibniz-Institute for Baltic Sea Research,
Warnemünde, Germany



The air-water interface has attracted scientists from diverse disciplines for almost a century. This long-lasting interest unravelled the distinct physical, chemical and biological features of the sea-surface microlayer; causing an increasing awareness to study its functional role in ocean-atmosphere interaction. However, research on sea-surface microlayers faces several challenges, e.g. high spatial and temporal variability, which complicates the general understanding of the importance of the sea-surface microlayer in air-sea exchange processes. This talk will address some issues which should be considered in the future for a successful implementation of the sea-surface microlayer into an integrated picture of ocean-atmosphere interaction.



The potential role of the sea-surface microlayer in gas exchange across the air-sea interface

Peter S. Liss and M.T. Johnson

University of East Anglia, Centre for Ocean and Atmospheric Sciences (COAS), School of Environmental Sciences, Norwich, United Kingdom

It is instructive to think about the exchange of gases across the air-sea interface in terms of the resistance of the boundary layers in both the seawater and atmospheric interfacial regions. For any particular gas one or other resistance is generally dominant. However, the 2-film or later models imply a layer of differing properties from the underlying seawater (the sea-surface microlayer?) or overlying air. Here we concentrate on the seawater side of the interface (which in any case controls the exchange of most of the biogeochemically interesting gases, e.g. CO_2 , CH_4 , N_2O , DMS, organo-halogens, etc.).

With respect to the sea surface microlayer several questions arise with respect to exchange of these and similar gases, including:

1. Can gas concentration differences between the surface and underlying water be detected from measurements at sea?
2. How do the 'film' thicknesses implied by models of gas exchange relate to those measured by existing sea surface microlayer sampling devices?
3. Can the sea-surface microlayer affect the transfer rate (as quantified by the transfer velocity) of gases across the air-sea interface?
4. If the answer to 3. is positive, what components/properties of the microlayer bring about the effect?
5. If 4., what are the roles of natural and man-introduced organic materials?

The sea-surface microlayer's influence on air-sea gas transfer

Kerstin Krall

University of Heidelberg,
Institute of Environmental Physics,
Heidelberg, Germany



The exchange of gases across the air-water interface is described using the gas transfer velocity. Empirical models, which include the wind speed and the tracer's diffusivity to calculate the transfer velocity are state of the art. These simple, wind speed - gas transfer relationships work well for getting rough estimates of the gas transfer velocity, but they fail to catch the intricate interactions between the physico-chemical processes at play. Transfer velocities measured within the framework of the SOPRAN project at the Aeolotron wind-wave tank in Heidelberg during two extensive campaigns, including one with natural sea water, as well as during field experiments using active thermography in the Baltic Sea indicate, that the variability of the transfer velocity at a given wind speed is very large. Future air-sea gas exchange models must take the water surface characteristics such as the degree of coverage with surface active materials and a Schmidt number exponent varying between $2/3$ and $1/2$ into account.

Marine aerosol particles: production, composition and connection to the surface ocean

Manuela van Pinxteren

Leibniz-Institute for Tropospheric Research (TROPOS), Leipzig, Germany

Aerosol particles in the marine boundary layer are often complex mixtures of locally generated primary particles (from sea spray), locally generated from gas to particle conversion so called secondary particles (sulfate from oxidation of dimethylsulfide), and primary and secondary particles transported from distant sources. The chemical composition and the origin of fine particles ($< 1 \mu\text{m}$ in diameter) over the oceans are still largely unknown however very important as the nature of aerosol particles determines their direct (e.g. scattering and absorbing global radiation) and indirect effects (impact on cloud formation) on the climate system.

This presentation will introduce current knowledge on the production and chemical composition of marine aerosol particles and highlight present findings of field and laboratory campaigns. The high organic enrichment of marine aerosol particles and the connection to the sea surface microlayer will be shown. One focus will be on the relation of organic aerosol composition to surface ocean biological activity including different aspects. Finally an outlook with future needs in marine aerosol investigation will be given.





Possible links between marine microorganisms, cloud-albedo and sea ice-melt in the Arctic?

Caroline Leck

Stockholm University, Department of Meteorology, Stockholm, Sweden

One proposed influence on cloud albedo over remote marine areas is that dimethyl sulfide (DMS) produced by marine phytoplankton is oxidized in the atmosphere to sulfuric acid, aiding the nucleating of particles that grow to cloud nucleation nuclei (CCN). Observations from the Arctic question the key role attributed to DMS. In the emerging picture of the Arctic atmosphere, DMS concentration will determine the mass of the particles by producing material for their growth. But it is the number of airborne marine gels that will primarily influence the number of CCN and the resulting optical properties of the cloud droplets? Indeed, research during the past two decades – reviewed recently suggest this is also valid for other regions as well. Does this rule out a link between marine microorganisms and climate, especially on a regional scale? From that perspective, the Arctic observations discussed here could provide a more nuanced link between marine biology, cloud properties and climate.



Advanced methods & remote sensing

Christoph Garbe

University of Heidelberg,
Image Processing and Modeling,
Heidelberg, Germany

Measuring properties of the dynamic ocean surface microlayer and biogeochemical feedbacks is challenging. Recently, advances have been made in non-invasive techniques, which have compelling properties. Laboratory studies have significantly increased our understanding, but particularly with respect to in-situ measurements, advanced measurement techniques are required. For understanding exchange mechanisms and dependencies of processes on meso and global scales, earth observations from satellites are a convincing tool. However, satellite observations are limited in coastal regions, but also in the tropics where a strong cloud cover dominates. Still, new instruments and data processing approaches have pushed the envelope also in these regimes.

In this presentation, I will give an overview on the state-of-the art of advanced measurement methods and remote sensing, highlighting recent developments and unresolved questions.

Influence of the surface microlayer on validation of optical satellite remote sensing

Rüdiger Röttgers

Helmholtz Centre Geesthacht,
Remote Sensing, Geesthacht, Germany



Satellite optical remote sensing is based on sunlight “reflected” by the ocean. This reflectance is influenced by the optical properties of the water (i.e. light absorption and scattering) and direct reflections at the atmosphere/ocean interface. Optical influences of the relatively thin surface microlayer (SML) on the ocean’s surface reflectance are expected to be very low. However, validation of remote sensing products (like chlorophyll concentration) from optical satellites demands accurate determinations of the pigment concentrations and the inherent optical properties of seawater. Measurements of the light absorption and scattering properties are often influenced by higher concentration of particles and dissolved matter in the SML, if the SML is not avoided during sampling, as it is often the case with simple sampling methods. To evaluate the effects, the difference in these optical properties between the microlayer and the water beneath it were investigated. Besides the earlier observed higher absorption by chromophoric dissolved organic matter (CDOM), higher concentrations of particles and a higher and spectrally different particulate absorption are observed in the SML that show characteristic spectral features of specific particles like phytoplankton and soot from atmospheric deposit. The results can as well be used to investigate particles dynamics in the microlayer.

Interactions in a changing climate / Anthropogenic forcing

Douglas Wallace

Dalhousie University, Oceanography Department, Halifax, Canada



The sea-surface microlayer is the frontline which both separates and connects the forces and processes of the global ocean and atmosphere as these vast reservoirs adjust to the changes in environmental forcing associated with human activity. Almost all material transfer and much of the energy transfer associated with this adjustment is impacted directly by processes operating exactly at this frontline. The characteristics of the microlayer and hence the nature of processes operating there are, themselves, subject to change as a result of the changing forcing. The presentation will focus largely, but not exclusively, on external forcing changes that impact the ocean away from estuaries, especially forcing changes mediated via the atmosphere. Internal ocean processes, which have the potential to contribute significantly to changes of the microlayer via ecosystem feedbacks (including microbial community change), will not be addressed in detail.

Potential forcing changes and their impacts on the microlayer will be discussed according to general classes (and geographic region):

Physical: temperature, wind/wave, radiation (including fog occurrence), rainfall

Multi-phase: ice-cover, dust/aerosol input and output

Chemical: CO₂/acidification, ozone, DOM input, freshwater/salinity



Do ocean-derived CCN play a role in the biological regulation of climate?

Patricia Quinn

National Oceanic and Atmospheric Administration, Washington, USA

The general consensus through the 1980s and 1990s was that non-sea salt sulfate (nss SO_4^{2-}) derived from dimethylsulfide (DMS) made up the majority of the cloud condensation nuclei (CCN) in the remote marine boundary layer (MBL). Furthermore, a biological regulation of climate was proposed whereby an increase in DMS-derived CCN would lead to an increase in cloud albedo. The resulting changes in surface temperature and radiation would then initiate a climate feedback that would alter DMS emissions from phytoplankton. Although the role of nss SO_4^{2-} as CCN in the MBL is still recognized today, the evidence for a climate feedback loop is lacking. In the intervening years, field and laboratory studies have revealed a source of primary organic aerosol that is emitted to the atmosphere along with inorganic sea salt during the wind-driven production of sea spray aerosol. In addition, there is evidence that secondary organic aerosol in the MBL is derived from the sea-to-air flux of gas phase organic species. Surface seawater processes and properties that control the magnitude and composition of organics that are emitted to the atmosphere are not well understood. Climate ramifications of the emission of sea spray organics have been suggested but not confirmed. This presentation will consider current evidence and explore whether or not ocean-derived CCN play a role in the biological regulation of climate, particularly under conditions of a changing climate.



OCEANFILMS: Modelling organic enrichment in submicron sea spray aerosol from ocean surface films

Susannah M. Burrows¹, O. Ogunro², A. A. Frossard^{3,4}, L. M. Russell³, P. J. Rasch¹, S. M. Elliott⁵, R. Walker⁶, E. Gobrogge⁶, F. Li⁷, and H. Wang⁷

1 – Pacific Northwest National Laboratory, Atmospheric Science and Global Change Division, Richland, USA – **2** – New Mexico

Institute of Mining and Technology, Ocean and Atmospheric Chemistry, Department of Chemistry, Socorro, USA – **3** – University of California, Scripps Institution of Oceanography, San Diego, La Jolla, USA – **4** – Now at: University of California-Berkeley, Berkeley, USA – **5** – Los Alamos National Laboratory, Climate Ocean Sea Ice Modeling team, Computational Physics and Methods group, Los Alamos, USA – **6** – Montana State University, Department of Chemistry and Biochemistry, Bozeman, USA – **7** – Pacific Northwest National Laboratory, Environmental and Molecular Sciences Laboratory, Richland, USA

Ocean surface films determine the organic fractionation of submicron sea spray aerosol. Because the organic fraction of sea spray can affect cloud droplet concentration, with implications for cloud albedo and climate, it would be desirable to represent the organic fractionation of sea spray in climate models. However, reducing the complexities of marine chemistry to a level of detail appropriate for inclusion into global models is a challenge. Early parameterizations derived empirical relationships between aerosol composition and ocean chlorophyll from observations at a few sites, and then extrapolated these globally. However, field and laboratory measurements have increasingly shown that the relationship between ocean chlorophyll and the organic fraction of fresh sea spray differs between ocean ecosystems, and over time, requiring a more mechanistic representation. We have recently developed a novel approach to this problem in the OCEANFILMS parameterization, which partitions the ocean organic matter into a small number of mac-

romolecular classes. Each macromolecular class is assumed to be in equilibrium at the air-water interface following the Langmuir adsorption isotherm, and is assigned a Langmuir adsorption constant and other chemical properties based on laboratory studies of selected model molecules. The coating of bubble surfaces is then used to calculate the submicron organic fraction of the emitted spray. Seasonal and geographic patterns in organic fractions are driven by two major groups of macromolecules: a lipid-like class that is associated with primary production, and a semi-labile group of polysaccharide-like and protein-like molecules that can be transported to oligotrophic regions by ocean currents. In an initial evaluation, the model agrees reasonably well with observed organic mass fractions of "clean" and "generated" marine aerosol on ships and at coastal stations. This approach may help to resolve apparent discrepancies between observations of aerosol composition in different ocean regions. In recent experiments, we have shown that soluble polysaccharides can interact with surfactant monolayers. Representing this effect can dramatically increase the modeled polysaccharide fraction of the sea spray aerosol, improving agreement with observations. Recent developments, limitations of the approach and open research questions will be discussed. flux of gas phase organic species. Surface seawater processes and properties that control the magnitude and composition of organics that are emitted to the atmosphere are not well understood. Climate ramifications of the emission of sea spray organics have been suggested but not confirmed. This presentation will consider current evidence and explore whether or not ocean-derived CCN play a role in the biological regulation of climate, particularly under conditions of a changing climate.

Model aspects of organic matter accumulation in the surface microlayer

Markus Schartau

GEOMAR Helmholtz Centre for Ocean Research Kiel, Biogeochemical Modelling, Kiel, Germany

Many ocean field studies of the ocean's surface interface have documented an accumulation of organic matter (OM) within the surface microlayer (SML). At present, it remains unclear whether OM enrichment in the SML has to be resolved in biogeochemical climate models for improved estimates of primary organic aerosols emissions over ocean regions or of air-sea gas exchange. Mechanisms of OM formation, transport, as well as physicochemical processes within the upper millimeters are not well understood. To begin with, our first approach was to couple a dynamical model of plankton primary production (upper meters) to a reaction/adsorption-diffusion model of the SML (upper 103 μm), mainly to get an idea of relevant time-scales of OM supply from biological production. The productivity model resolves the unbalanced assimilation of nitrogen and carbon by phytoplankton. The phytoplankton's release of dissolved, extracellular OM (e.g. polysaccharides) acts as source of surface-active OM. This dissolved OM is also assumed to act as precursor for the formation of gel-particles like transparent exopolymer particles (TEP) in the model. The SML sub-model describes mass flux of surface-active OM from the productive layer towards the mass boundary layer of the SML. An OM saturation concentration is prescribed for the SML's mass boundary, which means that a continuous diffusive supply rate from below induces a gradual thickening of the saturated layer up to proximity of the viscous boundary layer. Model solutions turned out to be very sensitive to values chosen for diffusion and adsorption rates of OM. To further elucidate possible accumulation rates but also the variational range of enrichment factors (EF) an extensive compilation of data from literature (Surandokht Nikzad, personal communication) was analysed. Probability densities of EF values reveal modes near 40% of enrichment (EF=1.4) with only few high EF values of four and more (4x higher concentrations in SML than below). Different distributions of EF are found for organic nitrogen and carbon. Wind effects on EF are noticeable. Altogether, results of the EF meta-analysis exhibit less OM enrich-



ment than expected when devising the SML model. Instead of extending the SML adsorption-diffusion model approach I would now suggest to put more effort on resolving size-spectra of gas bubbles in the upper water column. With respect to the emission of primary organic aerosols, the consideration of the integral of OM adsorbed at all surfaces of bubbles seems more promising than an explicit SML model.

POSTER ABSTRACTS

Surfactant associated bacteria in the sea surface microlayer: Case studies in the Straits of Florida and the Gulf of Mexico

B. Hamilton¹, C. Dean¹, N. Kurata¹, K. Vella¹, Alexander Soloviev^{1,2}, B. Haus², A. Tartar³, M. Shivji¹, S. Matt⁴, W. Perrie⁵, S. Lehner⁶, and B. Zhang⁷

1 – Nova Southeastern University, Oceanographic Center, Dania Beach, USA – **2** – University of Miami, Rosenstiel School of Marine and Atmospheric Science, Miami, USA – **3** – Nova Southeastern University, Division of Math, Science and Technology, Fort Lauderdale, USA – **4** – Stennis Space Center, Naval Research Laboratory, MS, USA – **5** – Bedford Institute of Oceanography, Fisheries and Oceans Canada, Nova Scotia, Canada – **6** – German Aerospace Center (DLR) Remote Sensing Technology Institute, Bremen, Germany – **7** – Nanjing University of Information Science and Technology, Nanjing, China

Several genera of bacteria residing in the sea surface microlayer and in the near-surface layer of the ocean have been found to be involved in the production and decay of surfactants. Under low wind speed conditions, surfactants can suppress short gravity capillary waves at the sea surface and form natural sea slicks. These features can be observed with both airborne and satellite-based synthetic aperture radar (SAR). Using a new microlayer sampling method, a series of experiments have been conducted in the Straits of Florida and the Gulf of Mexico in 2013 to establish a connection between the presence of surfactant-associated bacteria in the upper layer of the ocean and sea slicks. In a number of cases, sampling coincided with TerraSAR-X and RADARSAT-2 satellite overpasses to obtain SAR

images of each study site. Samples collected from slick and non-slick conditions have been analyzed using DNA techniques to determine presence of surfactant associated bacteria both in the sea surface microlayer and water column below. Previous work has shown that the sea surface microlayer plays a role in air-sea gas exchange, sea surface temperature, climate-active aerosol production, biochemical cycling, as well as the dampening of ocean capillary waves. Determining the effect of surfactant-associated bacteria on the state of the sea surface may help provide a more complete global picture of biophysical processes at the air-sea interface and uptake of greenhouse gases by the ocean.

Influence of wind speed on the accumulation of organic matter in the surface microlayer during the Aeolotron experiment (2014)

Anja Engel¹, C. Sun^{1,2}, and M. Sperling¹

1 – GEOMAR Helmholtz Centre for Ocean Research Kiel – 2 – South China Sea Institute of Oceanology, Guangzhou, China

The sea surface microlayer (SML) is suggested to affect a variety of exchange processes between the ocean and the atmosphere. We investigated how SML formation, composition and stability are related to seawater biogeochemistry, microbial activity and physical factors during an experiment conducted with natural Atlantic water at the Aeolotron facility in Heidelberg. We show first data suggesting that heterotrophic as well as autotrophic microbial activity provide organic matter for SML formation. Accumulation of particulate components like transparent exopolymer particles (TEP) and bacteria in the SML decreased at higher wind speed, while dissolved organic carbon concentrations increased. Entrainment of bubbles was identified as a process enhancing accumulation of bacteria as well as of small TEP (<10 µm) in the SML. More detailed organic compound analysis is currently conducted to better understand differences in the observed accumulation patterns, and the role of an organic SML for gas exchange and primary aerosol emission.

A new estimate of global methane and nitrous oxide emissions from the MEMENTO database

Annette Kock and H. W. Bange

GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, Kiel, Germany

Oceanic emissions constitute a substantial source to the atmospheric budget of nitrous oxide and a minor source for methane. Although measurements of both gases have been conducted for more than fifty years, existing emission estimates are still associated with high uncertainties due to the large spatial and temporal variability of both gases in the ocean. Based on available surface measurements from the MEMENTO (MarinE MethanE and NiTrous Oxide) database, we are developing a routine to compute global maps of methane and nitrous oxide distributions. These maps will help to identify regions of high surface methane and nitrous oxide as well as regions of high spatial and temporal variability. We will use our global concentration maps to calculate the first global emission estimate for methane and an updated emission estimate for nitrous oxide.

Influence of surfactants on the spatio-temporal structures of the water-side mass boundary layer

C. Kräuter¹ and Bernd Jähne^{1,2}

1 – University of Heidelberg, Institute of Environmental Physics, Heidelberg, Germany – ckraeute@iup.uni-heidelberg.de – **2** – University of Heidelberg, Heidelberg Collaboratory for Image Processing at IWR, Heidelberg, Germany

A novel two dimensional boundary layer visualization technique has been developed [Kräuter et al., 2014]. The main idea of the technique is to transform a concentration gradient into a steep change in pH and to visualize in this way a controllable fraction of the thickness of the mass boundary layer. This setup has been installed at the large annular wind-wave facility at the Institute of Environmental Physics in Heidelberg, the Aeolotron. Experiments with clean fresh water and different con-

centrations of a soluble surface active material (Triton X-100) have been conducted. The start of microscale breaking is shifted to higher wind speeds if a surface film is added to the water, which leads to a delayed transition of the Schmidt number exponent from $2/3$ to $1/2$ with increasing wind speed. Surface films additionally reduce the occurrence of microscale breaking.

References:

Kräuter, C., D. Trofimova, D. Kiefhaber, N. Krahl, and B. Jähne (2014), *High resolution 2-D fluorescence imaging of the mass boundary layer thickness at free water surfaces*, J. Eur. Opt. Soc., 9, 14016, doi:10.2971/jeos.2014.14016.

Exploring the influence of the SML on air-sea gas transfer by active thermography

J. Kunz¹, K. Krall¹, and Bernd Jähne^{1,2}

1 – University of Heidelberg, Institute of Environmental Physics, Heidelberg, Germany – jakob.kunz@iup.uni-heidelberg.de – **2** – University of Heidelberg, Heidelberg Collaboratory for Image Processing at IWR, Heidelberg, Germany

Active thermography has been used for almost 30 years to explore air-sea gas transfer both in laboratory and field experiments [Jähne et al., 1989]. In November 2014 this technique was used in air-sea gas exchange measurements using natural seawater from the North Atlantic with various degrees of contamination by natural surface films at the Heidelberg Aeolotron, within the BMBF project SOPRAN (Surface Ocean Processes in the Anthropocene). An improved setup with a much more homogeneous heated patch was used. With this improvement it was possible to acquire significantly more accurate heat transfer measurements. Preliminary results will be presented.

Surfactants and waves

Brian Ward

National University of Ireland, Galway, Ireland

Surface waves propagating from clean waters into areas covered by a flexible surface cover, e.g. an oil slick will become (a) heavily damped due to frictional forces. The air-sea momentum fluxes that force then oceanic mean flows (b) depend on the waves and hence these will also be affected by the surface cover. In the wave damping process the waves exert a stress on the surface cover, hence (c) inducing mean flows that bring about changes in the surface cover properties, which will in turn impact on (a) the wave damping. Very few studies have considered the full coupling between the waves, the momentum fluxes, and the mean flow, and experimental evidence to validate components of such theories is lacking. Our scientific interests are to determine-how surfactants damp waves-how surfactants impact on the air-sea fluxes-how much of the lost wave momentum will lead to increased mean flow-how the near surface turbulence and effective viscosity are affected.

The effects of the rain on the sea surface microlayer as seen with CO₂ eddy covariance flux measurements in the Indian Ocean

A. Zavarsky, T. Steinhoff , and Christa Marandino

GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, Kiel, Germany

Rain has been shown to alter the physics at the air-sea interface with subsequent effects on gas exchange. Recently, it has been shown sea surface reductions in salinity, total alkalinity, and dissolved inorganic carbon due to rain may enhance the sink of CO₂ in high precipitation regions by driving the delta $p\text{CO}_2$ to higher values. It is possible that under low/moderate wind and high rain events, this feature may be persistent for a significant time, but is, however, undetectable when computing fluxes using the bulk method. Here we present results from the SPACES and OASIS cruises in the Indian Ocean from July-August 2014, during the summer Indian

monsoon. Direct measurements of CO₂ fluxes were made using the eddy covariance method concurrently with rainfall. A clear discrepancy is observed between bulk fluxes and EC fluxes, which are directly related to large rain events. This is the first direct measurement of this effect in the open ocean and it illustrates that rain may cause a larger sink for CO₂ (up to a factor of 6) than previously thought. Future modeling efforts of the near surface using this data will be conducted to gain more insight into the influence of rain on air-sea CO₂ exchange.

Recent advances in microlayer monitoring and surface reactivity studies using sum-frequency generation spectroscopy

Kristian Laß¹, J. Kleber¹, H. Bange³, and G. Friedrichs^{1,2}

1 – Kiel University, Institute for Physical Chemistry, Kiel, Germany

– 2 – KMS Kiel Marine Science-Centre for Interdisciplinary Marine

Science, Kiel, Germany – **3** – GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, Kiel, Germany

Accumulation of surface-active material at the air-water interface gives rise to very thin organic layers, sometimes down to monomolecular thickness. This “surface nanolayer” modulates trace gas exchange and alters the properties of marine aqueous aerosols as well.

To date, the picture of the nanolayer with respect to composition, structure, and reactivity is still incomplete. Due to its small vertical dimension and the small amount of material, this surfactant layer is challenging to separate and analyse. A way out is the application of second-order nonlinear laser spectroscopic methods, which allow a direct surface-specific and background-free optical investigation. In recent years, we have introduced the use of vibrational sum frequency generation (VSFG) spectroscopy to gain insight into natural and artificial organic monolayers at the air-water interface (Limnol. Oceanogr.: Methods 8 [2010] 216).

This contribution will outline the application of VSFG spectroscopy for sea surface nanolayer analysis. Spectra are interpreted in terms of layer composition and surfactant classes such as soluble and non-soluble (“wet” and “dry”) components (J. Geophys. Res. 116 [2011] C08042/1). Furthermore, the ozonolysis of monolayers of unsaturated fatty acids serves as model system for natural aging processes

of surfactant layers at the sea surface (J. Phys. Chem. A 117 (2013) 7863). Finally, a VSFG time series study of the sea surface nanolayer at the western Baltic Sea near-shore sampling station “Boknis Eck Time Series Station” will be presented (Biogeosciences 10 (2013) 5325-5334). This series indicates that high organic material content in the microlayer does not necessarily correlate with high nanolayer abundance.

Volatile organic compounds in the surface microlayer

Enno Bahlmann

University of Hamburg, Department of Geosciences,
Hamburg, Germany

The air sea exchange of volatile organic compounds (VOCs) is commonly computed from the concentration difference between the surface ocean and the overlying atmosphere. The sea surface microlayer may modulate the air sea exchange of VOCs either by affecting the physical transport processes across the interface or acting as an additional source for VOCs. Here we report concentrations of different VOCs in the surface microlayer and discuss possible implications for the air sea gas exchange.

The Peruvian upwelling as a source for iodine in the tropical East Pacific troposphere

**Helmke Hepach¹, B. Quack¹, A. Engel¹, S. Fuhlbrügge¹, E. Atlas²,
A. Bracher³, S. Raimund¹, S. Flöter¹, L. Galgani^{1,4}, and K. Krüger⁵**

1 – GEOMAR Helmholtz Centre for Ocean Research Kiel, Marine Biogeochemistry, Kiel, Germany – **2** – University of Miami, Rosenstiel School of Marine and Atmospheric Science (RSMAS), USA – **3** – University of Bremen, Institute of Environmental Physics, Bremen, Germany – **4** –

University of California, Scripps Institution of Oceanography, San Diego, USA – 5 – University of Oslo, Department of Geosciences, Oslo, Norway

Iodinated compounds such as methyl iodide (CH_3I), chloroiodomethane (CH_2ClI) and diiodomethane (CH_2I_2) are produced naturally in the oceans. While CH_2ClI and CH_2I_2 are predominantly produced by biological processes, CH_3I has been hypothesized to have additional photochemical sources. Once these compounds are produced in the ocean, they are released to the troposphere where they take part in numerous chemical processes such as the formation of aerosols and ultrafine particles, as well as ozone destruction. CH_3I may even be transported into the stratosphere in small amounts in the tropical ocean due to tropical deep convection.

The first measurements of these iodinated compounds in the Peruvian upwelling were conducted during the M91 cruise in December 2012 onboard the RV Meteor. Considering the very short life times of especially CH_2I_2 and CH_2ClI (a few minutes to hours), notably high concentrations of up to 35, 32 and 58 pmol L^{-1} were observed for CH_3I , CH_2I_2 and CH_2ClI in certain regions of the upwelling. A relationship was found between measurements of total combined carbohydrates and in particular uronic acids in the sea surface microlayer (SML) with the abundance of the iodocarbons, implying the involvement of DOM constituents from the SML in the production of these compounds. High oceanic iodocarbons finally result in elevated atmospheric mixing ratios of CH_3I (up to 3.2 ppt), CH_2I (up to 3.3 ppt, mostly only during night time) and CH_2ClI (up to 2.5 ppt, higher during night time).

Cyanobacteria surface mats

Inga Hense

University of Hamburg, IHF, Center for Earth System Research and Sustainability, Hamburg, Germany

Cyanobacteria surface mats significantly affect the exchange processes between ocean and atmosphere. These mats additionally alter the light absorption, the planetary albedo and the wind drag. Recent model results with an idealized coupled biogeochemical ocean model indicate potentially pronounced effects on ocean physics with an increase of sea surface temperatures, a subsurface cooling leading to enhanced stratification as well as modified ocean circulation patterns. The strength of these changes depends on the choice of model parameters. Large uncertainties

exist, because observations are sparse and even the most fundamental aspects of functional dependencies of the processes involved and parameter values are unknown. Since the abundance of surface floating cyanobacteria is expected to increase in future, more effort should be invested to study the surface mats at the air-sea interface.

Organic composition of the sea-surface microlayer in the Central Arctic under enhanced sea ice melting

Luisa Galgani^{1,2}, J. Piontek¹, and A. Engel¹

1 – GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany – **2** – Alfred Wegener Institute, Helmholtz Centre for Polar and Marine Research, Bremerhaven, Germany

The sea-surface microlayer (SML) is the layer at the immediate air-water interface which mediates the emission of sea-spray aerosols (SSA) to the atmosphere. Organic SSA are supposed to mainly originate from plankton-derived organic compounds accumulating in the SML at times of high biological productivity. During the Arctic sea-ice historical minimum in summer 2012, we sampled the SML and underlying seawater in the Central Arctic Ocean (82° to 89°N - 30° to 130°E). Samples were collected from sea-ice melt ponds, at the ice edge and in the open ocean. Organic carbon, polysaccharidic and proteinaceous gel particles, amino acids and bacterial abundances were determined, revealing a higher percentage of semi-labile dissolved organic matter (DOM) in the first phase of sea ice melting, which decreased towards higher salinity and higher carbon concentration. Abundance and concentration of proteinaceous marine gels in the SML were higher with respect to the polysaccharidic fraction, overall contributing to a larger percentage of organic carbon in surface waters. In the submicron fraction (0.4 – 1.0 µm) relevant for the accumulation mode of SSA, gels represented ~80% of total volume concentration in the SML with proteinaceous particles being 1.6 times more abundant than polysaccharidic ones (median value), thus suggesting relevant microbial processes on source and composition of DOM likely to be affected by the retreat of sea ice. These changes are expected to influence SSA organic composition, therefore establishing additional feedbacks on global carbon cycling and climate in the future Arctic Ocean.

Surfactant control of gas transfer velocity along an offshore coastal transect: results from a laboratory gas exchange tank

R. Pereira, K. Schneider-Zapp, and Robert Upstill-Goddard

Newcastle University, School of Marine Science and Technology, Newcastle upon Tyne, United Kingdom – *ryan.pereira@ncl.ac.uk*, *klaus.schneider-zapp@ncl.ac.uk*

We measured total surfactant activity (SA; Triton T-X-100 equivalent) in the surface microlayer (SML) and subsurface water (SSW) seasonally (2012-2013) along a 20 km offshore transect in the coastal North Sea, and evaluated corresponding values of the gas transfer velocity (k_{660} ; cm hr^{-1}) using a custom-designed, fully automated, laboratory air-sea gas exchange tank [Schneider-Zapp et al., 2014]. Spatial SA variability exceeded its temporal variability. Overall SA varied five-fold between all samples (0.08 - 0.38 mg l^{-1} T-X-100 equivalent) and was highest in the SML during summer. SML enrichment factors relative to SSW were ~ 1.05 - 1.9, excepting two values (0.75; 0.89: February 2013). The range in k_{660} was 6.8 - 22.2 cm hr^{-1} . High SML SA correlated to k_{660} suppression ~13-60 % relative to clean laboratory water (18.2 Ohm Milli-Q), highlighting strong spatio-temporal gradients in gas exchange due to varying surfactant in these coastal waters. CDOM absorbance (200-450 nm) broadly followed the distribution of SA but there was no clear relationship between CDOM and either SA in the SML or k_{660} derived from our gas exchange experiments. Chlorophyll-a showed similarly weak relationships with SA and k_{660} , which must to some extent reflect SA of varying composition and provenance, including terrestrial inputs. Strong spatio-temporal gradients in k_{660} due to SA, as observed here, should be taken account of when evaluating marine trace gas sources and sinks.

References:

Schneider-Zapp K., Salter M.E. and Upstill-Goddard, R.C. (2014). An automated gas exchange tank for determining gas transfer velocities in natural seawater samples. *Ocean Science* 10, 587-600.

Biofilm-like properties of the sea surface

C. Stolle¹, C. V. Thuoc², P. T. Thu², X. Mari³, and Oliver Wurl^{1#}

1 – Leibniz Institute for Baltic Sea Research, Warnemünde, Germany –
2 – Institute of Marine Environment and Resources, VAST, Haiphong City, Vietnam – **3** – Aix-Marseille Université, Université de Toulon, CNRS/INSU, IRD, MIO, UM 110, Marseille, France – **#** – Present address: University Oldenburg, Institute for Chemistry and Biology of the Marine Environment, Germany

Because the sea surface controls various interactions between the ocean and the atmosphere, it has a profound function for marine biogeochemistry and climate regulation. The ocean adsorbs and emits climate-relevant gases, heat, and particles, and its surface is the gateway for their exchange. Characterizing and understanding the processes at the sea surface are essential in determining how the ocean and the atmosphere interact and respond to environmental changes on a global scale. In slicks (wave-damped areas through the accumulation of surface-active organic material), we found up to 40 times more transparent exopolymeric particles (TEP), the foundation of any biofilm, compared to the underlying bulk water at multiple stations in the North Pacific, South China Sea, and Baltic Sea. Compared to non-slick samples, the community composition of bacteria in slicks was increasingly different from bulk water communities, indicating that the TEP-matrix creates specific environments for its inhabitants. Moreover, slicks were characterized by a large microbial biomass, another shared feature with conventional biofilms on solid surfaces. We, therefore, conclude that slicks can feature biofilm-like properties with the excessive accumulation of particles and microbes embedded in a TEP matrix.

Spatial variability of natural surfactant in the Atlantic Ocean

B. Sabbaghzadeh¹, Robert Upstill-Goddard¹, P. Nightingale², and R. Beale²

1 – Newcastle University, School of Marine Science and Technology, Newcastle upon Tyne, United Kingdom – **2** – Plymouth Marine Laboratory, Plymouth, United Kingdom – *b.sabbaghzadeh@ncl.ac.uk, pdn@pml.ac.uk, rbea@pml.ac.uk*

During Atlantic Meridional Transect cruise AMT24 total surfactant activity (SA: mg l⁻¹; Triton-X-100 equivalent) was measured daily in the sea surface microlayer (SML: Garret screen) and in the water column to 500m (CTD rosette and “non-toxic” seawater supply). Polarographic SA analysis (Metrohm 797 VA Computrace) used a hanging mercury drop electrode. We found the SML to be significantly enriched in SA relative to underlying water. SA ranged between 0.05 and 0.7 mg l⁻¹ (Triton-X-100 equivalent) in the SML and between 0.0 and 0.2 mg l⁻¹ (Triton-X-100 equivalent) in the underlying water (2 m depth). In both the SML and in the underlying water SA was higher in the Atlantic northern hemisphere than in the Atlantic southern hemisphere, on average by a factor of around four. However, SML enrichment factors (EFs) for SA were not significantly different between the two hemispheres. These data will be used in conjunction with estimates of the gas transfer velocity (k_{600} ; results currently being worked up) made daily on AMT 24 using a custom-built gas exchange tank (Schneider-Zapp et al., 2014), to examine the variability in k_{600} related to SA variability across contrasting biogeochemical regimes (RAGNARRoC Consortium: NERC GHG programme).

References:

Schneider-Zapp K., Salter M.E. and Upstill-Goddard, R.C. (2014). *An automated gas exchange tank for determining gas transfer velocities in natural seawater samples*. Ocean Science 10, 587-600.

Microbial control of bromocarbons in the surface ocean

Sonja Endres, H. Hepach, C. Marandino, B. Quack, and A. Engel

GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany

Oceanic bromocarbons are highly reactive volatile organic compounds and may contribute up to 40% of stratospheric ozone depletion in mid latitudes. High sea-air fluxes of bromocarbons in the tropical regions have been related to biological cycling in the surface ocean, mainly by phytoplankton and bacteria, but the underlying processes and magnitude of the biogenic sources and sinks are poorly known. In order to understand temporal and spatial fluctuations of oceanic bromocarbon emissions, we studied microbial production and removal processes in the surface ocean during a research cruise with RV SONNE (OASIS, Port Louis/Mauritius to Malé/Maledives) to the tropical Indian Ocean. Water samples were incubated with ^{13}C -labelled bromoform substrate to determine bromocarbon consumption rates. Oxygen consumption was monitored to estimate the heterotrophic activity. Attained rates are compared to observational data of bacterial abundance, bromoform (CHBr_3) and dibromomethane (CH_2Br_2) as well as organic matter concentrations in the water.

Regional modelling of the emission of primary marine organic material during 4 Atlantic transect cruises

Stefan Barthel, S. Huang, M. van Pinxteren, L. Poulain, R. Wolke, and I. Tegen

Leibniz-Institute for Tropospheric Research, Leipzig, Germany

In the past years global and regional modelling studies on the emission of primary marine organic material to the atmosphere mainly focused on the comparison to measurements by coastal stations in the mid and high latitudes (ex.: Vignati et al. 2010, Gantt et al. 2012, Westervelt et al. 2012). A validation in the tropics and subtropics is still missing. The data collected during the Atlantic transect cruises of the research vessel Polarstern from Bremerhaven (GER) to Cap town (RSA) or Punta Arenas (CHI) within the OCEANNET-project provides a basis for such eval-

uation. Furthermore the availability of aerosol data from the northern and southern hemisphere as well as from different geographical zones provide additional opportunities for the model validation. This poster will show the modelling results on primary marine organic material using the regional modelling system COSMO-MUSCAT compared to the measurements from an AMS and a Digital filter sampler onboard the Polarstern.

Source of organic matter in freshly emitted sea spray aerosol

Timothy Bates and P. Quinn

National Oceanic and Atmospheric Administration, Washington, USA

Breaking waves on the ocean surface generate air bubbles that scavenge organic matter from the surrounding seawater. When injected into the atmosphere, these bubbles burst, yielding sea spray aerosol (SSA) enriched in organic matter relative to seawater. Downwind of plankton blooms, the organic carbon content of SSA is weakly correlated with satellite-derived measurements of chlorophyll *a* levels, a measure of phytoplankton biomass. This correlation is currently used in large-scale models to calculate the organic enrichment in SSA. During the Western Atlantic Climate Study Cruises (WACS - August 2012 and WACSII - May-June 2014), we generated and measured freshly emitted SSA in high chlorophyll waters associated with plankton blooms in the North Atlantic and in the low chlorophyll waters of the Sargasso Sea. We found that the organic carbon content of freshly emitted SSA was similar in all regions sampled, despite significant differences in seawater chlorophyll levels. These observations revealed an unrecognized ocean carbon source that is not directly associated with chlorophyll and local biological activity but is available for incorporation into SSA. Further in situ measurements of surface sea water and nascent SSA properties are needed to confirm these results and to constrain and develop realistic parameterizations of the emission of the organic fraction of SSA to the atmosphere. In the absence of such a parametrization, the most accurate approach may be to calculate the size-dependent number flux of SSA as a function of wind speed and apply an average organic carbon enrichment factor based on the data presented here and distributed as a function of particle size using previously published size distributions for nascent SSA.

Bias of oceanic N₂O emission estimates caused by multi-day near-surface stratification in the Peruvian upwelling regime

Tim Fischer, A. Kock, D.L. Arévalo-Martínez, M. Dengler, P. Brandt, and H.W. Bange

GEOMAR Helmholtz Centre for Ocean Research Kiel, Germany

Upper ocean observations off Peru are used to study air-sea gas exchange in coastal upwelling regions. Observations include high-resolution nitrous oxide (N₂O) profiles in the topmost 10 meters far from ship's influence, ship based N₂O profiles and transects, and ship and glider based hydrography.

In the topmost meters of the water column, distinct vertical N₂O gradients were observed, with systematic concentration reduction towards the surface. This means that N₂O emission estimates are biased high, when based on measurements a few meters below the surface. The vertical N₂O gradients are associated with periods of persistent strong stratification in the near-surface layer of longer than 24 hours up to several days. The persistent stratification exists during low wind situations and inhibits mixing and gas transport from deeper layers to the surface, while the wind is still sufficient to cause N₂O depletion at the surface. The multi-day stratification seems to be a necessary condition for substantial vertical gas gradients, as diurnal thermocline stratification periods could only explain minor depletions. The water column between 10cm and 1 m was found near homogeneous in N₂O, indicating effective mixing by surface waves.

High field NMR spectroscopy and FTICR mass spectrometry: Powerful discovery tools for the molecular level characterization of (marine) dissolved organic matter

Norbert Hertkorn¹, M. Harir¹, B. P. Koch², B. Michalke¹, and Ph. Schmitt-Kopplin¹

1 – Helmholtz Centre München, German Research Center for Environmental Health, Research Unit Analytical Biogeochemistry, Neuherberg, Germany – **2** – Alfred Wegener Institute, Bremerhaven, Germany

Non-targeted molecular level characterization of complex biogeochemical materials by means of comprehensive information-rich detection has revealed the

fundamental molecular diversity of any natural organic matter (NOM: of freshwater, soil, marine, atmospheric and extraterrestrial origin).

Here, high-field NMR spectroscopy (nuclear magnetic resonance) offers isotope-specific and unsurpassed information about short-range atomic order, which is absolutely indispensable for any de novo structural analysis. In very complex mixtures, NMR is the most suitable profiling tool with an optimum combination of quantification and structural significance. High-field FTICR mass spectrometry (Fourier-transform ion cyclotron mass spectrometry) combines ultrahigh resolution with excellent sensitivity and significance of information about molecular ions related to unambiguous molecular formulas and possible fragmentation patterns for molecular identification. FTICR allows assignment of thousands of molecular formulas out of complex mixtures. Recently, network analysis has decisively enlarged the coverage of molecular formula assignment from FTMS spectra. High-performance separation: validates mass spectrometry against NMR spectroscopy. Electrophoretic and chromatographic fractionation on nano-, micro-, analytical- and preparative scale, fast TOF mass spectrometry (mass resolution $> 6 \cdot 10^4$) for combining high-performance separation with real time mass spectrometry, and ion mobility mass spectrometry (to differentiate isomeric compounds) are available. Mathematical data analysis of these expansive and correlated but highly complementary data is of ever growing importance to enable extraction of significant molecular information from complex unknowns.

This conceptual poster will show already published data (Hertkorn et al., 2013) in a single comprehensive display to show what kind of information is available on molecular level detail of an organic matter isolated from the open Atlantic Ocean. Specifically, solid phase extracted marine dissolved organic matter (PPL; SPE-DOM) were isolated from four different depths in the open South Atlantic Ocean off the Angola coast. Sampling was performed at depths of 5 m (Angola current; near surface photic zone), 48 m (Angola current; fluorescence maximum), 200 m (still above Antarctic Intermediate Water AAIW; upper mesopelagic zone) and 5446 m (North Atlantic Deep Water NADW; abyssopelagic, ~30 m above seafloor) and produced SPE-DOM with near 40% carbon yield and beneficial properties for NMR and FTICR/MS characterization.

The study demonstrates that the exhaustive characterization of complex unknowns in marine DOM will enable a meaningful classification of individual marine biogeosignatures. Future in-depth functional biodiversity studies with a clear understanding of DOM structure and function might eventually lead to a novel, unified perception of biodiversity and biogeochemistry.

References:

Hertkorn, N. et al., *Biogeosciences* 10 (2013) 1583-1624.

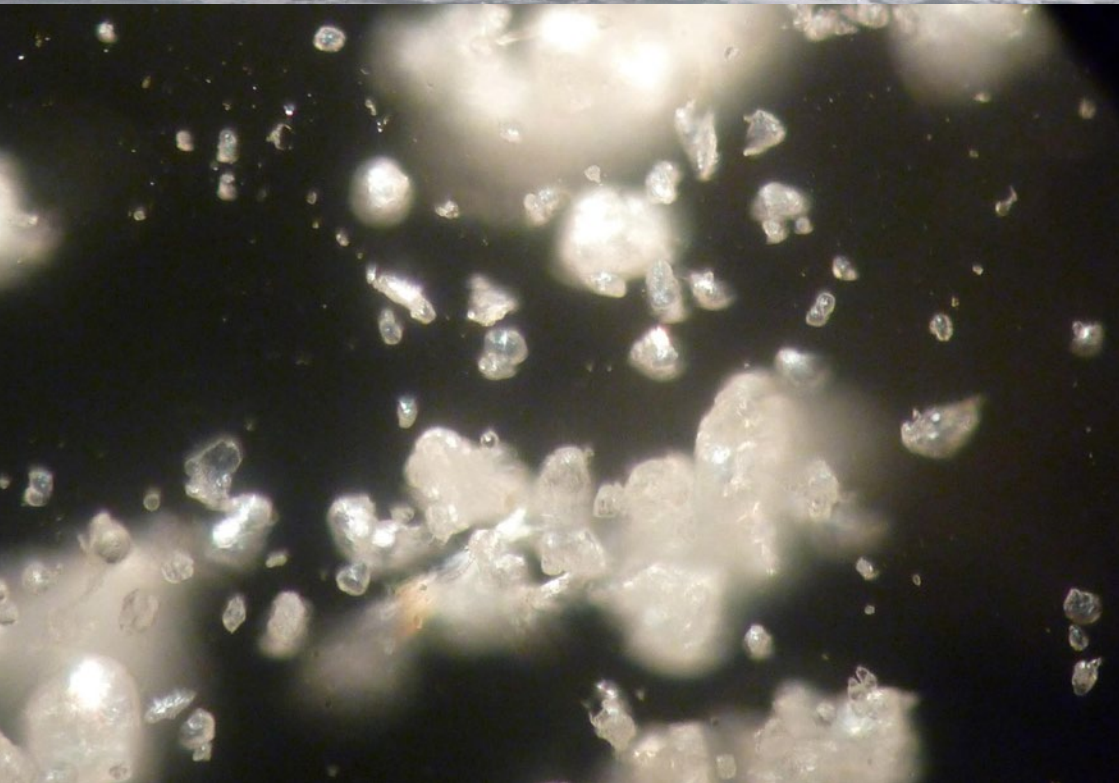
Towards operational near real time oil spill detection service using polarimetric TerraSAR-X Images

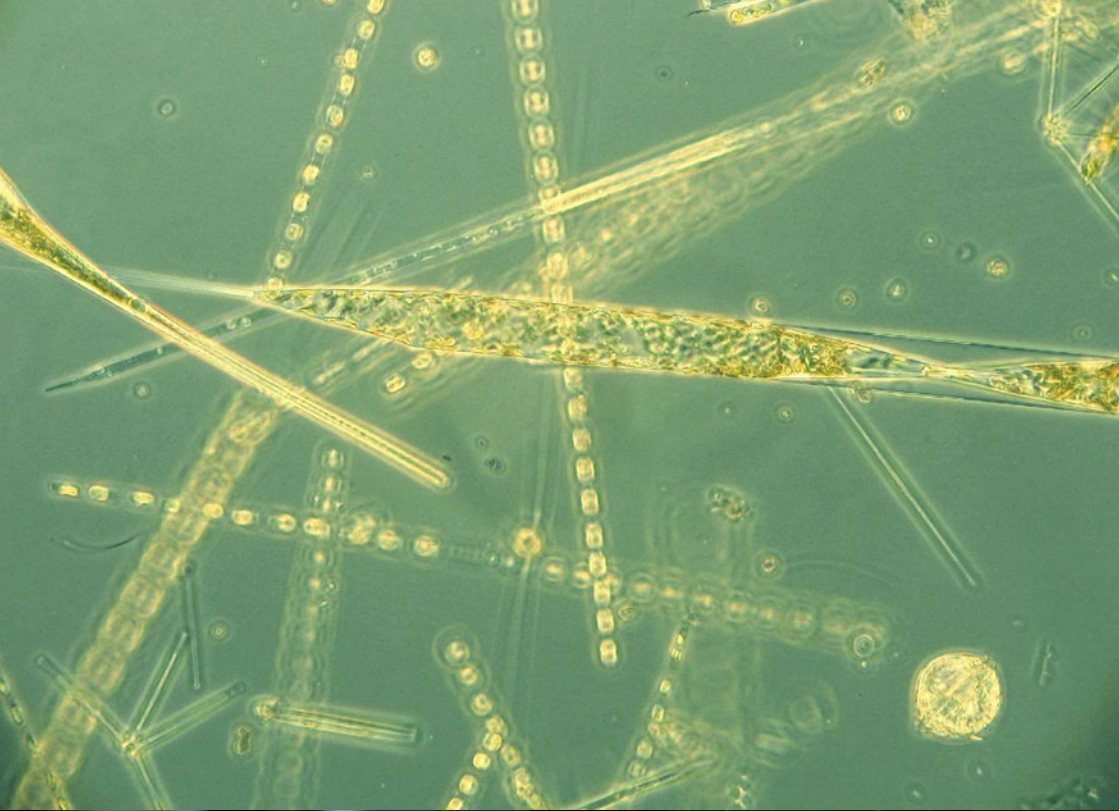
S. Singha, Domenico Velotto, and S. Lehner

German Aerospace Center, Earth Observation Center, Remote Sensing Technology Institute, SAR Signal Processing, Maritime Security Lab, Bremen, Germany

Exploitation of polarimetric features for oil spill detection is relatively new and until recently those properties were not exploited for operational services. This paper describes the development of a Near Real Time (NRT) oil spill detection processing chain using coherent dual-polarimetric (co-polarized channels, i.e. HH-VV) TerraSAR-X images. Proposed methodology introduces for the first time a combination of traditional and polarimetric features for object-based oil spill and look-alike (algae, weather induced phenomenon etc.) discrimination. A total number of 35 feature parameters were extracted from 225 oil spill and 26 look-alikes. Extracted features are then used for training and validation of a decision tree classifier. Initial performance estimation was carried out for the proposed methodology on a large dataset acquired over well-known platform location in order to evaluate its suitability for NRT operational service.

Notes





SEMESTER TOPIC

Ocean Interfaces – From nanoscales to global impact

The Cluster of Excellence “The Future Ocean” sets a primary focus nearly each semester on a different Marine Science topic. This helps to better coordinate various outreach activities as well as topical scientific conferences and workshops. This summer semester, the Future Ocean semester topic “Ocean Interfaces” highlights and challenges the question how nano- and microscale processes taking place at interfaces (in a broad sense) impact mesoscale and in the end global (biogeochemical) cycles. Why should we care – as a society facing global warming and environmental pollution – about very specific basic natural science problems? From a scientific perspective, the semester topic sets a focus both on technical aspects of modern analytical techniques as well as biogeochemical feedbacks such as warming, acidification and eutrophication triggered by key processes mediated by interfaces.

The semester topic initiates with the organization of a conference session at the European Geosciences Union General Assembly in Vienna. In the summer term 2015, a series of lectures, workshops and side events on the topic ‘Ocean Interfaces’ will take place and the semester topic will finish with the co-organization of the SOLAS Open Science Conference (Surface Ocean Lower Atmosphere Study) as a suitable international platform to discuss aspects of ocean-atmosphere coupling.

www.futureocean.org/ocean-interfaces

Gernot Friedrichs

Institute of Physical Chemistry, Kiel University
friedrichs@phc.uni-kiel.de

Hermann Bange

GEOMAR Helmholtz Centre for Ocean Research Kiel
hbange@geomar.de

Anke Schneider

Scientific Coordination Semester Topic “Ocean Interfaces”
schneider@phc.uni-kiel.de