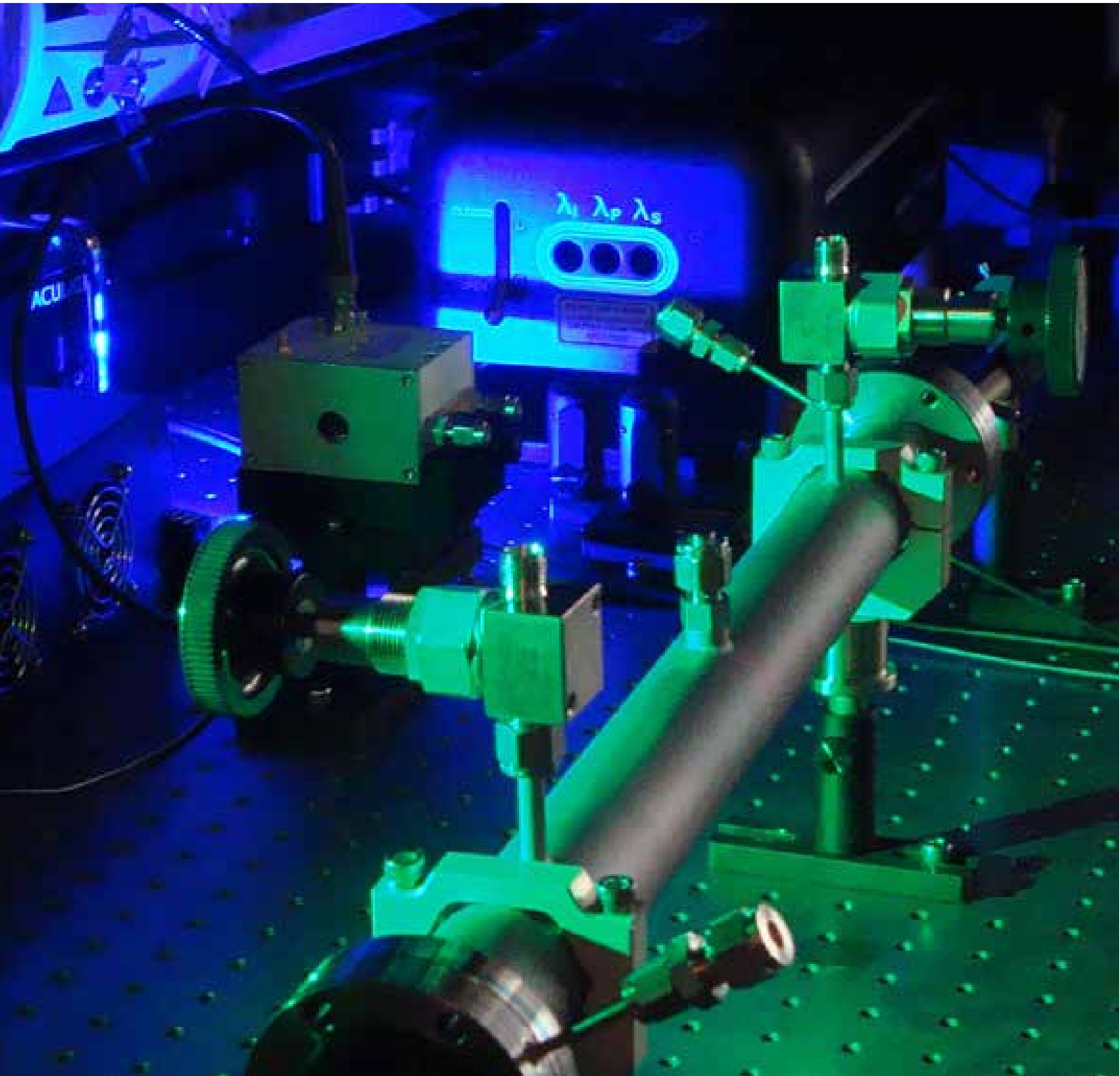
Marine Applications and Perspectives of Cavity Enhanced Optical Detection Schemes

Workshop from 20. – 21. April at Kiel University
Leibnizstraße 1, Room 105 | Kiel, Germany

Information and Abstracts



LIST OF PARTICIPANTS

1. **Damian L. Arevalo-Martinez** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), darevalo@geomar.de
2. **Hermann Bange** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), hbange@geomar.de
3. **Meike Becker** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), mbecker@geomar.de
4. **Petar Bliznakov** / HEKAtech GmbH, Wegberg (GER), p.bliznakov@blisotec.de
5. **Stefan Bücker** / Leibniz Institute for Baltic Sea Research Warnemünde (GER), stefan.buecker@io-warnemuende.de
6. **Peer Fietzek** / GEOMAR Helmholtz Centre for Ocean Research Kiel/ Contros Systems and Solutions GmbH (GER), pfietzek@geomar.de
7. **Gernot Friedrichs** / Kiel University (GER), friedrichs@phc.uni-kiel.de
8. **Michael Glockzien** / Leibniz Institute for Baltic Sea Research Warnemünde (GER), michael.glockzin@io-warnemuende.de
9. **Kuan Huang** / Duke University / Picarro Inc. (USA), kuan.huang@duke.edu
10. **Jan Kaiser** / University of East Anglia (UK), j.kaiser@uea.ac.uk
11. **Arne Körtzinger** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), akoertzinger@geomar.de
12. **Jost V. Lavric** / Max-Planck-Institute for Biogeochemistry Jena (GER), jlavric@bgc-jena.mpg.de
13. **Sinikka Lennartz** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), slennartz@geomar.de
14. **Hans-Peter Loock** / Queens University (CA), peter.loock@chem.queensu.ca

15. **Damien Maher** / Southern Cross University (AUS), damien.maher@scu.edu.au
16. **Christa A. Marandino** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), cmarandino@geomar.de
17. **Anna Michel** / Woods Hole Oceanographic Institution (USA), amichel@whoi.edu
18. **Eric J. Morgan** / Max-Planck-Institute for Biogeochemistry Jena (GER), emorgan@bgc-jena.mpg.de
19. **Malte Nordmann Winther** / Niels Bohr Institute (DK), ndc549@alumni.ku.dk
20. **Inga Piller** / Kiel University (GER), piller@phc.uni-kiel.de
21. **Gregor Rehder** / Leibniz Institute for Baltic Sea Research Warnemünde (GER), gregor.rehder@io-warnemuende.de
22. **Grant A.D. Ritchie** / University of Oxford (UK), grant.ritchie@chem.ox.ac.uk
23. **Tim Rixen** / Leibniz Center for Tropical Marine Ecology (GER), tim.rixen@zmt-bremen.de
24. **Ibrahim Sadiek** / Kiel University (GER), sadiek@phc.uni-kiel.de
25. **Anke Schneider** / GEOMAR Helmholtz Centre for Ocean Research Kiel (GER), aschneider@geomar.de
26. **Sally Walker** / Dalhousie University (CA), sallywalker@Dal.Ca
27. **Scott Wankel** / Woods Hole Oceanographic Institution (USA), sdwankel@whoi.edu
28. **Jan Werner** / Leibniz Institute for Baltic Sea Research Warnemünde (GER), jan.werner@io-warnemuende.de

AGENDA

MONDAY, 20 APRIL 2015

09:30 – 09:45 Welcome and Introduction

Session: Perspectives and Emerging Marine Applications 1

09:45 – 10:50
- "New developments and applications of cavity enhanced spectroscopies: from optical physics to healthcare" / **Grant A.D. Ritchie** (highlight talk)
- "Advances in evanescent-wave and saturated absorption cavity ringdown spectroscopy (ew-CRDS & sat-CRDS) for environmental applications"/ **Ibrahim Sadiek**

Session: Field performance

10:50 – 11:10
- "Improving N_2O and CO measurements in the surface ocean: application of OA-ICOS"/ **Damian L. Arevalo-Martinez**

11:10 – 11:30 *Coffee break*

11:30 – 13:00
- "Ground-Based and Shipboard Measurements of Atmospheric Greenhouse Gases in the Benguela Region, Using the CRDS and OA-ICOS Techniques"/ **Eric J. Morgan**
- "Automated trace gas monitoring on a ship of opportunity – Results from the Baltic and a note on equilibrator requirements" / **Gregor Rehder**
- "Use of cavity ring-down spectrometry to investigate aquatic carbon cycling from microbial to ecosystem scales" / **Damien Maher**
- "Equilibrator-based measurements of dissolved nitrous oxide in the surface ocean using an integrated cavity output laser absorption spectrometer"/ **Jan Kaiser**

13:00 – 14:15	*Lunch in Mensa*

Session: Isotopes

14:15 – 15:30

- "Oxygen isotope measurements in natural seawater using cavity ring-down spectroscopy (CRDS): a comparison of methods" / **Sally Walker**
- "An Ultra-high precision, High-frequency Dissolved Inorganic Carbon Analyzer based on Dual Isotope Dilution and Cavity Ring-Down Spectroscopy"/ **Kuan Huang**
- "The seasonality of $\delta^{13}C(CO_2)$ in the North Atlantic as derived from underway measurements onboard a Voluntary Observing Ship (VOS)"/ **Meike Becker**

15:30 – 16:00 *Coffee break*

16:00 – 18:00 **Poster session**

19:00 – *Joint Dinner at Restaurant"Längengrad"*

TUESDAY, 21 APRIL 2015

	Session: Perspectives and Emerging Marine Applications 2
08:30 – 10:15	▸ "Chemical sensing with optical waveguide cavities"/ **Hans-Peter Loock** (highlight talk) ▸ "Water isotopes and trace gas measurements using Cavity Ring Down Spectroscopy"/ **Malte Nordmann Winther** ▸ "Emerging applications of laser spectroscopy in deep-sea biogeochemistry"/ **Scott Wankel** ▸ "Can we use CRDS for direct measurements of open ocean air-sea exchange using the eddy covariance technique?" / **Christa A. Marandino**
10:15 – 10:45	*Coffee break*
10:45 – 11:30	General Discussion: a) Summary b) Perspectives c) Outline of Review Paper
	Session: Preparation of review paper
11:30 – 12:30	Breakout groups on different chapters / aspects of review paper
12:30 – 13:30	*Lunch in Mensa*
13:30 – 14:30	Breakout groups on different chapters / aspects of review paper
14:30 – 15:30	Report of workgroups / synthesis work / final discussion /closing remarks
16:00 –	*Labtour*

POSTERS

1. **"Underway N_2O measurements in the eastern tropical South Pacific"**, D.L. Arévalo-Martínez, A. Kock and H. W. Bange

2. **"Sea-to-air fluxes of N_2O and CO_2 in the Benguela upwelling system"**, D.L. Arévalo-Martínez, T. Steinhoff, J. Werner, A. Körtzinger, G. Rehder and H.W. Bange

3. **"Implementation of Saturated Cavity Ringdown Spectroscopy: First Results and Working Limits "**, I. Sadiek, and G. Friedrichs

4. **"Monitoring of adsorbed polar substances at the quartz-air interface using ew-CRDS"**, I. Piller and G. Friedrichs

5. **"The seasonality of $\delta^{13}C(CO_2)$ in the North Atlantic as derived from underway measurements onboard a Voluntary Observing Ship (VOS)"**, M. Becker

6. **"Measurements of marine OCS and CO_2 with OA-ICOS in the Indian Ocean: Advantages & Caveats"**, S.T. Lennartz, M. von Hobe, D.L. Arevalo-Martinez, T. Steinhoff, K. Krüger and C.A. Marandino

7. **"Laser-based Underwater Sensor for the Measurement of Methane Partial Pressure"**, P. Fietzek, M. Schmidt, P. Linke and C. Frank

8. **"The BALTIC VOS: Continuous Greenhouse Gas measurements within the European ICOS-network"**, G. Rehder, B. Schneider, J. Werner, W. Gülzow, M. Glockzin and B. Sadkowiak

9. **“Multiple trace gas patterns in upwelling-influenced surface waters offshore Namibia in Austral winter”**, J. Werner, D.L. Arévalo-Martínez, M. Glockzin, N. Nunez, W. Gülzow, H. Bange, D. Quadfasel and G. Rehder

10. **“Surface water distribution and air-sea fluxes of nitrous oxide and methane in shelf seas and the open ocean”**, J. Kaiser

11. **“New directions for biogeochemical laser applications in the deep-sea”**, S. Wankel and A. Michel

12. **“Continuous water vapor isotope measurements across the North Atlantic”**, M. Nordmann Winther

13. **“Photoacoustic spectroscopy in liquids using a fiber vibration sensor”**, H.P. Loock

14. **“A newly developed gas extraction system”**, P. Bliznakov

New developments and applications of cavity enhanced spectroscopies: from optical physics to healthcare

Grant A.D. Ritchie
Department of Chemistry, Physical & Theoretical Chemistry Laboratory, University of Oxford, Oxford, United Kingdom

In this talk I will present recent work from my laboratory in which optical feedback cavity enhanced absorption spectroscopy (OF-CEAS) in the mid-infrared has been conducted using both quantum cascade lasers (QCLs) and interband cascade lasers (ICLs). OF-CEAS is traditionally conducted within V-shaped cavities so that only intracavity light is able to feedback to the laser and thereby cause injection seeding; in the case of QCLs we show, both experimentally and theoretically, that OF-CEAS can be realised within a linear cavity configuration with high power sources while maintaining high sensitivity. In addition, I will discuss two practical applications of cavity enhanced spectroscopy in the areas of physiology and healthcare. In the former case, I will introduce a real time breath analyser developed for the measurement of oxygen consumption on a breath-to-breath basis, while in the latter, I will detail the uses of breath acetone monitoring for diabetes and lifestyle management.

Advances in evanescent-wave and saturated-absorption cavity ringdown spectroscopy (ew-CRDS & sat-CRDS) for environmental applications

Ibrahim Sadiek

Institute for Physical Chemistry, Kiel University, Kiel, Germany

Cavity ringdown spectroscopy is well-established to detect trace gases by measuring the change of the monoexponential ringdown time attributable to the additional optical loss of an absorbing gaseous species present in the sample cavity. Since a monoexponential behavior of the decay of the light intensity is crucial to extract reliable ringdown times, the majority of CRDS implementations are operated in the linear absorption regime. However, at high intra-cavity photon densities, which are readily achieved with narrow linewidth continuous wave (cw) laser sources, deviation from the monoexponential behavior is observed due to the absorption saturation. A new approach of CRDS taking advantage instead of avoiding these saturation effects, sat-CRDS, has been recently developed by Giusfredi et al. [Phys Rev Lett 104 (2010) 110801]. It allows one to measure the gas absorption and the cavity loss simultaneously, hence making scanning of the detection laser frequency over the absorption line dispensable. Moreover, this approach overcomes the fluctuations in the empty cavity decay rate, which often are the main limiting factor for achieving the ultimate sensitivity by the conventional CRD method. In the first part of this talk, the setup and implementation of sat-CRDS will be presented using a high power tunable cw-IR-OPO laser as the light source. The fundamental theory as well as the technical working limits of sat-CRDS will be discussed. The new technique holds potential for further enhancing the sensitivity of CRD based spectrometers with the aim to detect organohalogens in the marine environment at ambient ppt mixing ratio levels.

In a second part of the talk, advances in the setup and the implementation of an evanescent-wave CRDS for interface measurements will be highlighted. During the past years, different cavity designs have been developed containing a reflecting surface within the ringdown cavity. Upon total internal reflection (TIR) of the light at this surface, an evanescent wave is formed that penetrates into the overlying sample. The attenuation of this wave can be sensitively measured by CRDS and yields quantitative and qualitative information about the adsorbed species on the TIR surface. The presented novel ew-cw-CRD spectrometer allows us to observe vibrational overtone absorption bands in the near-infrared region between 1600-1700 nm. Monolayer sensitivity has already been achieved and Brunauer-Emmett-Teller (BET) type adsorption isotherms of selected compounds could be measured. However, so-called etaloning effects complicated the collection of high quality spectra. Providing that a further improvement of the detection sensitivity is successful, the method holds potential to directly monitor the difficult to measure heterogeneous chemistry taking place at surfaces submerged into liquid water.

Improving N_2O and CO measurements in the surface ocean: application of OA-ICOS

Damian L. Arévalo-Martínez

GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

Nitrous oxide (N_2O) and carbon monoxide (CO) are atmospheric trace gases which significantly influence Earth's climate through their role as greenhouse gases. In addition, N_2O is currently considered to be main ozone-depleting substance of the 21st century. Despite its importance, N_2O and CO emission estimates from vast areas of the ocean are associated with large uncertainties mainly due to the lack of adequate temporal and spatial resolution. By making use of a novel technique based upon off-axis integrated cavity output spectroscopy (OA-ICOS) in combination with custom equilibration systems, we developed a method which allows measuring along-track N_2O and CO in surface waters and the overlying atmosphere. Performance tests demonstrated the high stability of the analytic system, with low optimal integration times of 2 and 4 min for N_2O and CO respectively, as well as detection limits <40 ppt and precision better than 0.3 ppb $Hz^{-1/2}$. Comparison of our method and well-established discrete methods for dissolved N_2O and atmospheric CO evidenced a reliable operation of the setup in the field. The applicability of the system for continuous measurements both in research ships and vessels of opportunity is discussed in light of the results obtained during different deployments carried out in the tropical and North Atlantic.

Ground-Based and Shipboard Measurements of Atmospheric Greenhouse Gases in the Benguela Region, Using the CRDS and OA-ICOS Techniques

E.J. Morgan

Max Planck Institute for Biogeochemistry, Jena, Germany

During August 2013, a Picarro cavity ring-down spectrometer (CRDS) was installed on the FS Meteor for the purpose of making continuous atmospheric measurements of CO_2 and CH_4 in the Benguela current region. The instrument generally performed well but cavity pressure was affected by vessel motion. These measurements represented a complement to ongoing atmospheric measurements at the Namib Desert Atmospheric Observatory in Gobabeb, Namibia. At this site, semi-automated, continuous measurements of carbon dioxide, methane, nitrous oxide, carbon monoxide, and basic meteorology are made at a height of 21 m a.g.l., 50 km from the coast at the northern border of the Namib Sand Sea. Carbon dioxide and methane are measured with an early-model cavity ring-down spectrometer (CRDS); nitrous oxide and carbon monoxide are measured with an off-axis integrated cavity output spectrometer (OA-ICOS). The compatibility of the shipboard and ground-based measurements is discussed. Instrument-specific water corrections are employed for all instruments in lieu of drying. The performance and measurement uncertainties are discussed in detail. As the station is located in a remote desert environment, there are some particular challenges, namely fine dust, high diurnal temperature variability, and minimal infrastructure. The gas handling system and calibration scheme were tailored to best fit the conditions of the site. The CRDS and DFCA provide data of acceptable quality when base requirements for operation are met, specifically adequate temperature control in the laboratory and regular supply of electricity. In the case of the OA-ICOS instrument, performance is significantly improved through the implementation of a drift correction through frequent measurements of a working tank.

Automated trace gas monitoring on a ship of opportunity – Results from the Baltic and a note on equilibrator requirements

Gregor Rehder

Leibniz Institute for Baltic Sea Research Warnemünde, Warnemünde, Germany

With the growing maturity of CRDS and oa-ICOS instruments, the continuous measurement of trace gases other than CO_2 in surface waters has become possible. We were the first to report the permanent installation of a Los Gatos GGA for the measurement of surface pCO_2 and CH_4 on a voluntary observing ship (VOS) as an amendment to an already installed LICOR-based equilibration system on the ferry M/S Finnmaid, traversing the Baltic Sea between Lübeck and Helsinki approximately every 2 days (Gülzow et al., 2011). As a German contribution to ICOS (Integrated Carbon Observation System), the extension of the system to additionally monitor N_2O and the stable isotopic signature of carbon dioxide ($\delta^{13}C_{CO2}$) is currently in preparation.

We present the almost continuous record of surface water pCO_2 and dissolved CH_4 along the cruise track for the last three years, and highlight some of the reoccurring annual patterns. We also provide examples of the use of the data for regional process studies from recent publications (Gülzow et al., 2013, Schneider et al., 2014), including the identification and quantification of primary production in the central Baltic Sea and the impact of the River Neva runoff on surface methane concentrations.

Finally, we will draw attention on new challenges for equilibrator design resulting from the lower response time and higher contamination sensitivity of less soluble gases (e.g. CH_4, CO), as well as the larger volume of oa-ICOS sensors in particular.

Field use of cavity enhanced optical spectroscopy – some insights from coastal and estuarine studies in Australia

Damien Maher
Southern Cross University, Lismore, Australia

One of the major benefits of cavity enhanced optical spectroscopy techniques is the ability to measure trace gas concentrations, along with isotopologue and isotopomer concentrations (for some gases) at high temporal resolution in the field. I will present data from a range of in situ field and laboratory experiments collected using several different commercially available cavity ring down spectrometers. I will explain some of the problems and solutions we have encountered, and present a wish list for future cavity enhanced optical spectroscopy developments.

Surface water distribution and air-sea fluxes of nitrous oxide and methane in shelf seas and the open ocean

Jan Kaiser
University of East Anglia, Norwich, United Kingdom

In recent years, improvements in spectroscopic technology have revolutionised atmospheric trace gas research. In particular, cavity-based optical absorption analysers allow determination of gas concentrations with high frequency, repeatability, reproducibility and long-term stability. These qualities make them particularly suitable for autonomous measurements on voluntary observing ships (VOS). Here, we present results from deployments of such analysers on research ships, as a first step towards VOS installations.

Los Gatos off-axis ICOS (Integrated Cavity Output Spectroscopy) analysers were used to measure trace gas concentrations in ocean surface waters during research cruises between 2010 and 2013. The analysers were coupled to an equilibrator fed by the scientific seawater supply in the ship's laboratories. The equilibrator measurements were alternated with regular measurements of marine air and calibrated standard gases.

For the deployments, a CO_2/CH_4 and an N_2O/CO analyser were successfully operated in series, off of a single equilibrator feed. While such a configuration would be ideal for VOS installations as part of the ICOS observational network, it has an inherent weakness, that is, if one of the analysers develops a fault or leak, the measurements of the second analyser will also be affected. An independent or parallelised arrangement may therefore be preferable.

Short-term uncertainty for N_2O mole fractions at an acquisition rate of 1 Hz was better than 0.2 nmol mol^{-1}. The same value was achieved for duplicate measurements of a standard gas analysed within 1 hour of each other. The response time to concentration changes in water was 2 to 3 min, depending on the headspace flow rate. Response times for CH_4 were significantly longer due to the lower solubility of this gas, which results in a time-averaged response to changes in oceanic concentrations.

I will also show some unexpected scientific results. For example, the oceans are generally believed to be net sources of N_2O. However, we found surprisingly large oceanic areas with N_2O undersaturations, implying that they acted as sinks for this greenhouse gas. In contrast, tidal fronts and weakly stratified coastal areas appear to be strong N_2O sources, presumably due to denitrification associated with high particulate concentrations and/or sediments.

Oxygen isotope measurements in natural seawater using cavity ring-down spectroscopy (CRDS): a comparison of methods

Sally Walker
Dalhousie University, Halifax, Canada

The recent advent of cavity ring-down spectroscopy (CRDS) provides a cost effective and mobile approach to measure the oxygen isotope ($\delta^{18}O$) ratio of a water molecule. However, when analyzing ocean samples, the influence of salt on CRDS instrument performance, precision and accuracy, and the comparability to calibration methods developed for isotope ratio mass spectrometry (IRMS) require investigation. To address these issues, we conducted two comparisons relating CRDS and IRMS $\delta^{18}O$ measurements in natural marine environments. First, we conducted an inter-laboratory comparison of $\delta^{18}O$ measurements over a wide range of salinities (0 – 34.9), using two CRDS and two IRMS instruments from four independent labs. Secondly, we compared $\delta^{18}O$ values measured in Northeast Atlantic Deep Water (NEADW) collected during the 2013, 2012, 2009, and 1995 occupations of the AR7W repeat hydrography transect across the Labrador Sea. In this comparison, seawater samples were measured by both the CRDS and IRMS techniques, depending on the year analyzed. Results from this study conclude that: (1) the CRDS instrument standard deviation for the analysis of seawater (salinity range 0 – 34.9) can be 0.05 ‰, (2) the accuracy for CRDS ocean-based $\delta^{18}O$ measurements are comparable to the analytical precision of the instrument (0.05), and (3) ocean-based CRDS $\delta^{18}O$ measurements are inter-comparable with measurements by IRMS to within +/- 0.08 ‰ (pooled standard deviation), and can therefore be compared directly with historical $\delta^{18}O$ data. Finally, we discuss problems and potential solutions, including effects on analytical data quality, associated with salt build-up with current CRDS analyzers.

An Ultra-high precision, High-frequency Dissolved Inorganic Carbon Analyzer based on Dual Isotope Dilution and Cavity Ring-Down Spectroscopy

Kuan Huang

Duke University, Durham, USA / Picarro Inc., Santa Clara, USA

Dissolved inorganic carbon concentration ([DIC]) is one of the most important properties of the carbonate system in the ocean. High-precision, high-resolution [DIC] measurements are desired for studying the key processes in the global carbon cycle, e.g. the oceanic uptake of anthropogenic CO_2, net community production, etc. We present a novel method for continuous and automated shipboard measurements of dissolved inorganic carbon concentration ([DIC]) in surface water. The method is based on the techniques of Dual Isotope Dilution and Cavity Ring-Down Spectroscopy (DID-CRDS), and consists of two major modules for continuous measurements of $\delta^{13}C$ of DIC and δD of water, respectively. In our new method, seawater is continuously sampled and mixed with a flow of $NaH^{13}CO_3$ solution that is also enriched in deuterated water (D_2O). Half of the mixed flow is acidified and sent through a membrane contactor, where CO_2 derived from the acidified solution is stripped by a CO_2-free carrier gas. $^{13}C/^{12}C$ of the CO_2 ($\delta^{13}C_{spiked\_sample}$) is then measured by a carbon isotope CRDS. The other half of the mixture is run through an expanded polytetrauoroethylene (ePTFE) membrane tube, where water vapor diffusing across the membrane is carried by dry air to a water isotope CRDS for measurement of its D/H ratios. The D/H of the water in the mixture allows accurate estimates of the mixing ratio of the sample and the spike. [DIC] of the sample can then be calculated is from the mixing ratio, [DI^{13}C] of the spike, and $\delta^{13}C_{spiked\_sample}$. The system is temperature-controlled to stabilize fractionation of water isotopes across the membrane. The precision of δDspiked_sample, and thus the mixing ratio, is <0.02%. In the laboratory, the overall precision of the method is <0.02% (±0.4 μmol kg^{-1} when [DIC] = 2000 μmol kg^{-1}). A shipboard test was conducted in the Delaware Bay and Estuary, where large variability (1300-2000 μmol kg^{-1}) and rapid change (up to 5 μmol kg^{-1} min^{-1}) in [DIC] were observed. A precision of <0.03% was achieved during the field deployment. Results from the DID-CRDS showed good agreement with independent measurements of discrete samples using the standard coulometry- and NDIR-based methods.

The seasonality of $\delta^{13}C(CO_2)$ in the North Atlantic as derived from underway measurements onboard a Voluntary Observing Ship (VOS)

Meike Becker
GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

The understanding of the seasonal cycle of carbon-related processes in the surface North Atlantic Ocean can be improved by using stable carbon isotope observations. By installing a seagoing Cavity Ringdown Spectrometer (CRDS) interfaced to an equilibration-based pCO_2 measurement system onboard a Voluntary Observing Ship (VOS) it now becomes possible to autonomously acquire data for the stable carbon isotope ratio of carbon dioxide ($\delta^{13}C(CO_2)$) in the surface ocean with high spatial and temporal resolution.
Here we present two and a half years of sea surface $\delta^{13}C(CO_2)$-measurements in the subpolar North Atlantic. A commercially available CRDS was installed on a VOS that runs continuously between Liverpool, UK and Halifax, CA. The quality and limitation of the data is explored. Also we show the different seasonalities in the eastern and western part of the North Atlantic.

Chemical sensing with optical waveguide cavities

Hans-Peter Loock

Dept. of Chemistry, Queen's University, Kingston, Canada

While cavity-enhanced spectroscopy is typically used to increase the sensitivity of gas phase absorption measurements, it is straightforward to perform such measurements also in liquids.

I will give a brief review on cavity-enhanced detection methods that can be applied to liquids and focus, in particular, on cavities that are made from waveguides such as fiber loops, silicon micro-resonators and fiber Fabry-Perot cavities. In our group we have exploited the sensitivity of optical resonators for measurements of optical absorption, refractive index, pressure, and strain.

Optical loss can be easily and inexpensively measured using fiber ring cavities made from loops of multimode silica fibers. The refractive index of liquids and microextraction films can be determined from the resonance frequency shift of micro-ring resonators made form e.g. silicon nanowires. Finally, Fiber Fabry-Perot cavities made from two identical fiber-Bragg gratings can be interrogated either using cavity ring-down spectroscopy or cavity frequency shifts and serve as sensitive strain sensors that can find applications in photoacoustic absorption spectroscopy in strongly scattering liquid media.

Water isotopes and trace gas measurements using Cavity Ring Down Spectroscopy

Malte Nordmann Winther
Centre for Ice and Climate, Niels Bohr Institute,
University of Copenhagen, Copenhagen, Denmark

At the Centre for Ice and Climate we drill and analyze deep ice cores with the purpose of gaining a better understanding of the past climate changes and thereby advance our understanding of the present and future climate changes. Through our recent instrument development in collaboration with Picarro Inc. we endeavour to perform measurements of both present and past water isotopes and trace gases using cavity ring down spectroscopy.
Because of the annual snow precipitation and accumulation on the ice caps on Greenland and Antarctica, greenhouse gases and water isotopes are trapped in the ice for approximately 130.000 years and 800.000 years, respectively. By drilling and obtaining deep ice cores, we are able to perform high resolution and precision measurements of both the past greenhouse gases and the water isotopes in the ice. In our laboratory we have four generations of water isotope measuring Picarro instruments, with which we endeavour to perform measurements of both $\delta^{18}O$, $\delta^{17}O$ and δD of the water isotopes in the ice cores. Likewise we perform high resolution measurements of Methane (CH_4) using a custom made small cavity Picarro CRDS analyzer.
Nitrous oxide (N_2O) is another very important trace gas. We are collaborating with Picarro on developing a mid-IR analyzer to measure N_2O concentration and isotopomers. So far we perform high resolution continuous position dependent $\delta^{15}N$ measurements of the denitrifying N_2O cycle, and thereby survey the site preference dependency on the bacterial N_2O producer. Furthermore we use our water vapor Picarro analyzer to perform shipboard measurements of water vapor between Denmark and Greenland.
We present results from our online water isotope and CH_4 measurements of discrete ice core samples, position dependent $\delta^{15}N$ measurements of the denitrifying N_2O cycle and preliminary results from our recent water vapor polar expedition.

Emerging applications of laser spectroscopy in deep-sea biogeochemistry

Scott D. Wankel

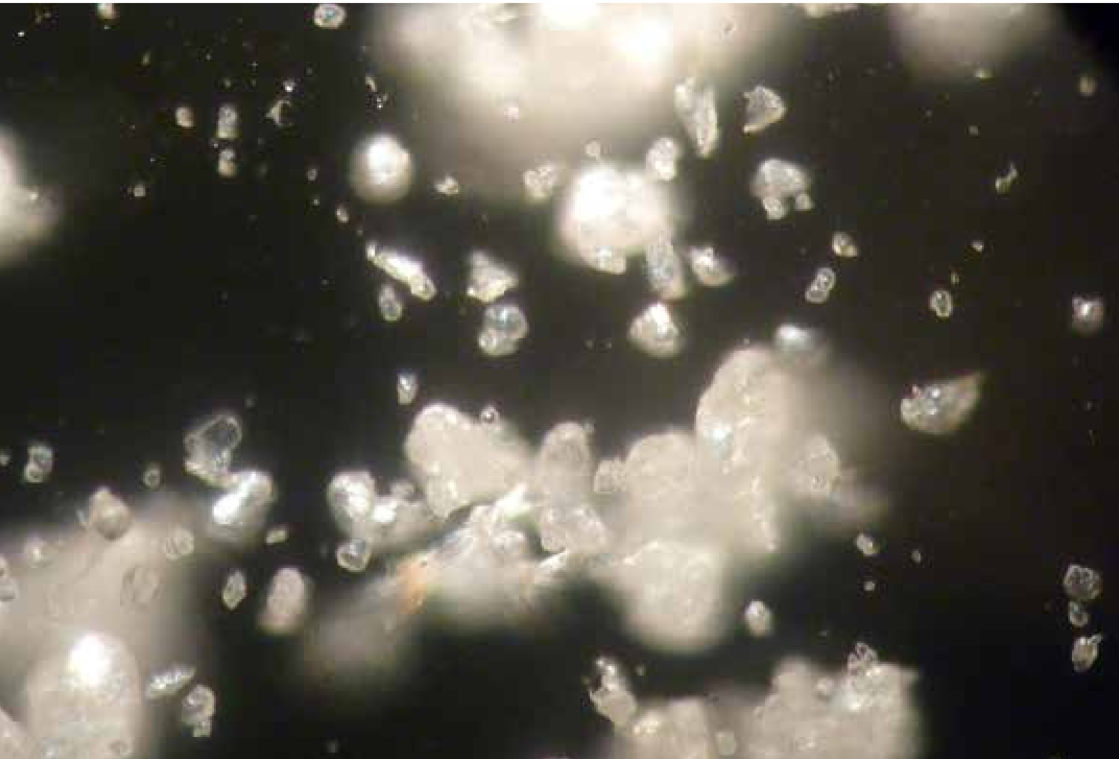
Woods Hole Oceanographic Institution, Woods Hole, USA

The deep ocean plays an important, yet largely understudied and unconstrained, role in many important global biogeochemical cycles. Recent advances in the application of in situ sensor technologies have begun providing unprecedented levels of sensitivity and temporal and spatial resolution, offering new insights on deep-sea biogeochemical cycling and opening doors to new questions on the nature of many of these enigmatic environments. Here we will highlight recent advances in the deployment of an in situ laser spectroscopy platform (using off-axis integrated cavity output spectroscopy, OA-ICOS). Specifically, we have coupled a dual laser (for CH_4 and CO_2) platform together with a high-pressure, flow-through membrane-inlet dissolved gas extractor, an in-line acidification module and a bubble collection strategy to enable novel measurements of carbon isotopic composition under high pressure, deep-sea conditions. We will briefly discuss key features of the system, ongoing technical challenges and results from deployments to a hydrocarbon seep in Monterey Bay (California, USA) and an active submarine volcano in the Caribbean Sea (Grenada).

Can we use CRDS for direct measurements of open ocean air-sea exchange using the eddy covariance technique?

Christa A. Marandino
GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

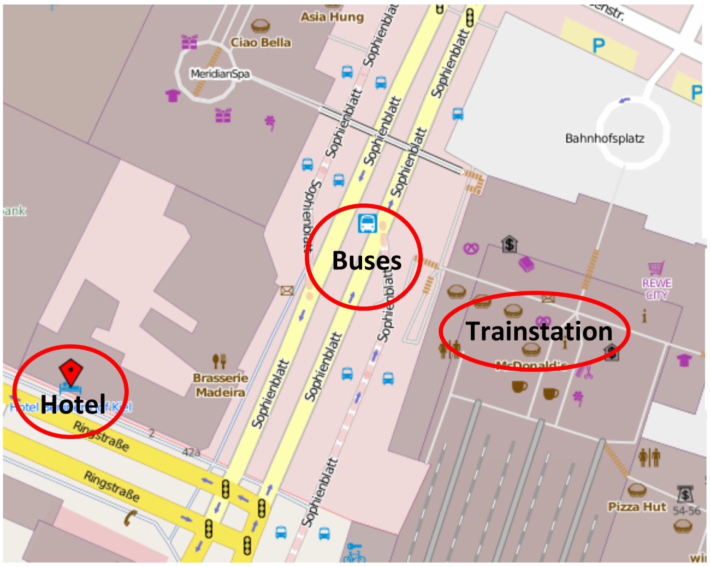
The eddy covariance technique (EC) is the most direct method of measuring air-sea fluxes. Direct measurements can provide flux values without the approximations inherent in the bulk flux calculation method, which often lead to large discrepancies and uncertainties in flux estimations. In addition, EC is a powerful tool for studying processes that influence air-sea exchange. Unfortunately, the technique is under-utilized, because of the many challenges associated with it. EC requires making fast, sensitive measurements of the fluctuations in vertical wind speed concurrently with the fluctuations in the concentration of the trace gas of interest (i.e. sampling atmospheric turbulent motions for trace gases). In the last decade, technological advancements in trace gas detection have made it feasible to perform this technique in the open ocean for DMS, CO_2, and oxygenated volatile organics. However, there are still many problems to overcome, namely the effects of the ship's motion and infrastructure on the measured winds. More importantly, trace gas detectors are still not optimized for shipboard EC measurements. Many are too large, require too much power, and air conditioning to be placed close to the front of the ship, where conditions are ideal for sampling turbulent motions. Long sampling lines and the effects of hampered pumping capabilities make measurements suboptimal. The good news is that many instruments now have the time response and sensitivity needed to measure a variety of trace gases. Cavity ring down spectrometers (CRDS) are one such class of instruments. EC using these instruments has been successfully performed on land, but the question remains: can they be used at sea where gas levels are often lower and conditions more challenging? This workshop would be the ideal place to explore how the CRDS class of instruments can be implemented for shipboard EC measurements in the not-so-distant future.



Some information on locations and buses in Kiel

From hotel to workshop

To get from the hotel “Berliner Hof” to the workshop you can take the bus Nr. 61, 62 or 81. From “Hauptbahnhof” (right next to the hotel – see first map) you go to “Leibnizstraße” (right next to the workshop building – see second map). For bus times, you find some examples below.



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Daten von OpenStreetMap - Veröffentlicht unter ODbL

Kiel Hauptbahnhof **Kiel Leibnizstraße**	20.04.2015	08:44 ab 09:05 an
Kiel Hauptbahnhof **Kiel Leibnizstraße**	20.04.2015	08:54 ab 09:15 an
Kiel Hauptbahnhof **Kiel Leibnizstraße**	20.04.2015	08:55 ab 09:21 an

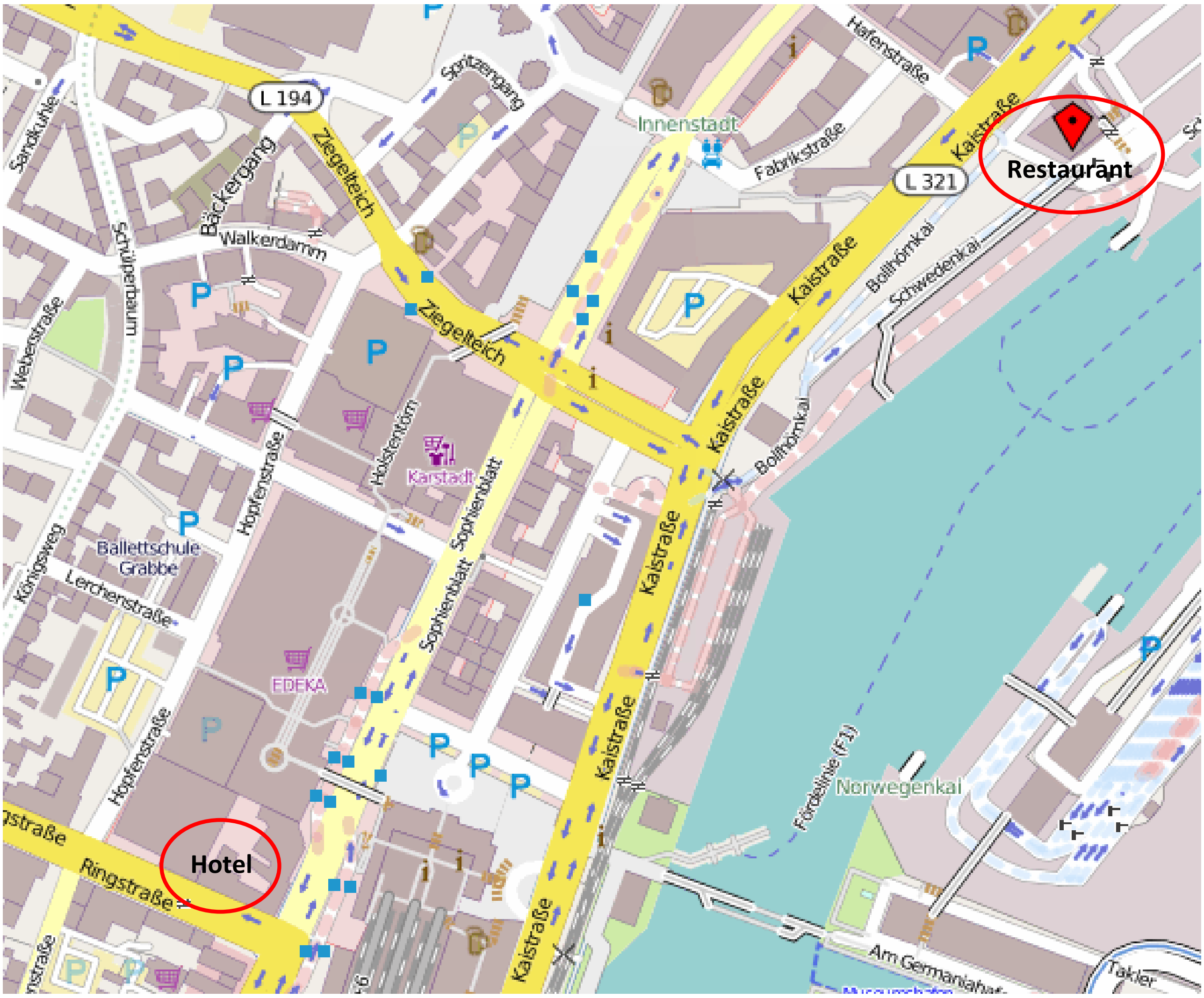
08:44 ab	Kiel Hauptbahnhof
Bus 62 Richtung Kiel Woltersweg	behindertengerechtes Fahrzeug, 0431 2203-2203
09:05 an	Kiel Leibnizstraße
08:54 ab	Kiel Hauptbahnhof
Bus 61 Richtung Kiel Rungholtplatz	behindertengerechtes Fahrzeug, 0431 2203-2203
09:15 an	Kiel Leibnizstraße
08:55 ab	Kiel Hauptbahnhof
Bus 81 Richtung Kiel Botanischer Garten	behindertengerechtes Fahrzeug, 0431 2203-2203
09:21 an	Kiel Leibnizstraße

… and back:

18:03 ab 20.04.2015	Kiel Leibnizstraße
Bus 81 Richtung Kiel Rungholtplatz	behindertengerechtes Fahrzeug, 0431 2203-2203
18:26 an	Kiel Hauptbahnhof
18:10 ab	Kiel Leibnizstraße
Bus 61 Richtung Kiel Aalborgring	behindertengerechtes Fahrzeug, 0431 2203-2203
18:31 an	Kiel Hauptbahnhof

From hotel to restaurant

You can easily walk from the hotel „Berliner Hof" to the restaurant "Längengrad". It takes about 10-15 min.



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From the airport to Kiel and back

At the airport Hamburg, outside Terminal 1 busses leave to Kiel. You can take the "Kielius" (Green/yellow coaches – only cash or you can book tickets in advance on https://www.kielius-onlinebuchung.de/index.php/tarife.html). One-way = Einzelfahrschein Erwachsener; Return = Rückfahrschein Erwachsener.

Timetables can be found here: http://www.bahn.de/autokraft/view/angebot/kielius/en-time-table.shtml

Or you can take the “KielExx” (Minivans – with reservation only – unless you are lucky and there is still a free seat). Prices and tickets on:
http://www.vineta.net/downloads/KielExx%20Fahrplan+Preise%20ab%2014.12.2014_V2.pdf

Another way to get to Kiel is by train. You have to change trains at the main station for that (it takes a bit longer than the bus).

In Kiel the airport bus stops in front of the train station or at the ZOB (close to the train station – see map), from there you can walk in 5 min to the hotel “Berliner Hof”. If you take the KielEXX, they will bring you directly to the hotel.

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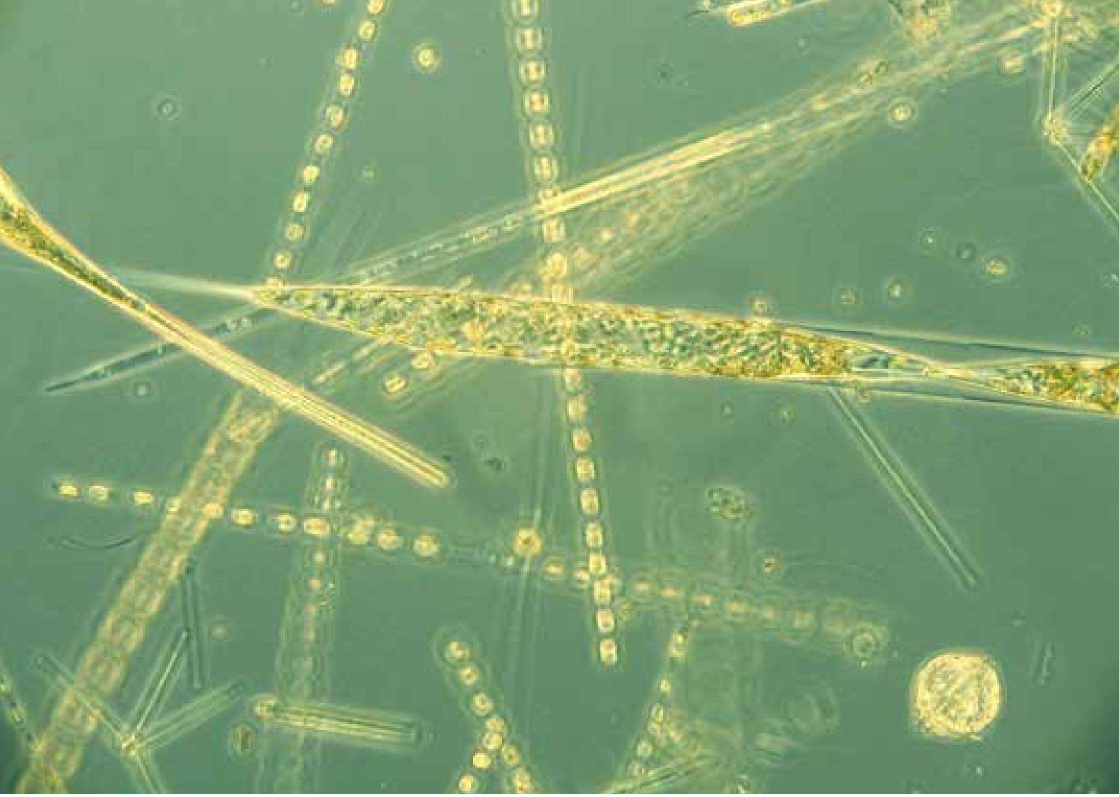

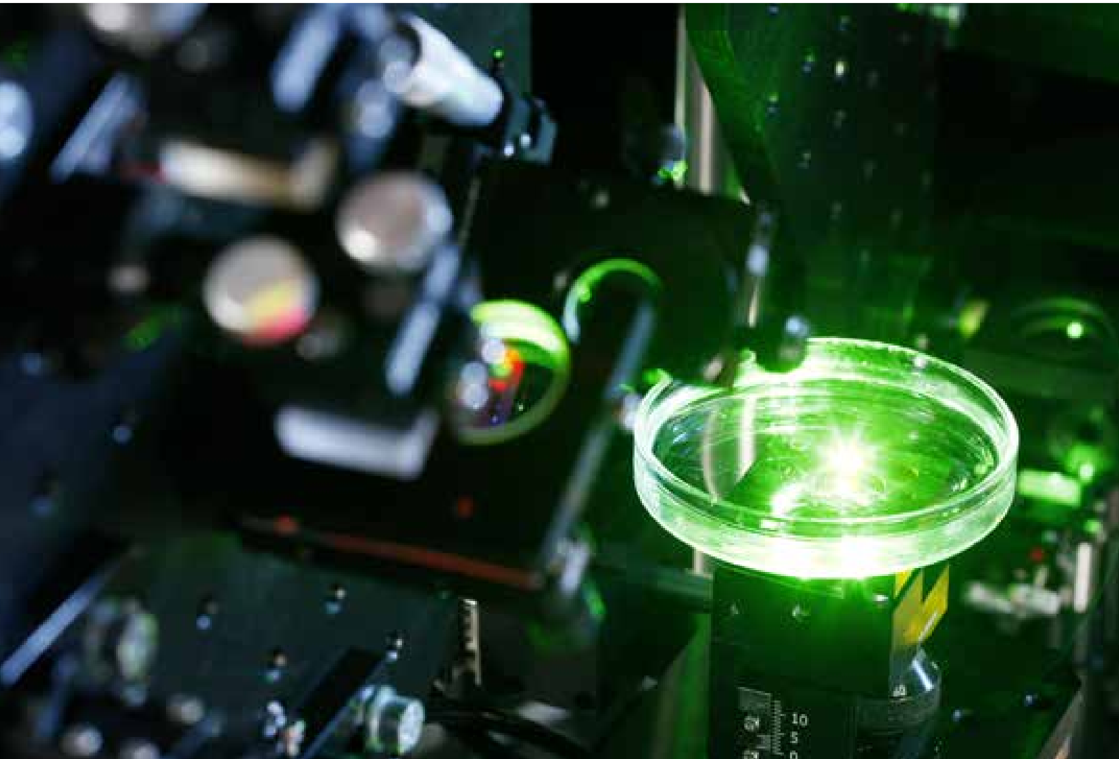

Ocean Interfaces – From nanoscales to global impact

The 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.

Organisation:

Prof. Gernot Friedrichs, Institute of Physical Chemistry, Kiel University
Prof. Hermann Bange, GEOMAR Helmholtz Center for Ocean Research Kiel
Dr. Anke Schneider, Scientific Coordination of the Semester Topic

C A U
Christian-Albrechts-Universität zu Kiel
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