

# solas news

issue 14:: Summer2012:: www.solas-int.org



↑The SOLAS Summer School 2011 attendees at the Institut d'Etudes Scientifiques de Cargèse, Corsica

### Sharing SOLAS science

This issue of the Newsletter highlights the success of the SOLAS Summer Schools over the last eight years. One of the key aims of the SOLAS Summer School is to develop connections and communication between SOLAS scientists at an early stage in their careers whilst deepening their understanding of the wider field of air-sea science outside of their research area.

Within this issue, we follow the Summer School alumni, who attended the SOLAS Open Science Conference 2012, through their scientific careers and feature their current research foci. This exercise representatively demonstrates the accomplishments of former students and is a credit to all who have volunteered their valuable time toward making the Summer School a continued success.

In addition, we report on the outcomes of the SOLAS Open Science Conference held in May this year, in Cle Elum, Washington. Discussion sessions based on pressing topics with the SOLAS field are highlighted and, in combination

with updates from a number of SOLAS endorsed projects, eloquently illustrate the sustained momentum of SOLASs' Mid-Term Strategies.

Following on from the success of previous Summer Schools, we, in partnership with staff at Xiamen University, have begun the process for developing the next school which will be held in Xiamen, China, in August 2013. The first announcement poster can be found on the back page of this newsletter; so please display at your institute. Similarly, if you are a PhD student or an early career scientist, or know of someone who would be keen to attend the SOLAS Summer School 2013, application opens on 01 October 2013. Please visit http://mel.xmu.edu.cn/solassummerschool for more information. Any further announcements about the Summer School and all other SOLASrelated news are provided in our monthly e-bulletin. To subscribe to the e-bulletin and future newsletters, please email skontradowitz@geomar.de with your contact details.

### In this issue...

### **Scientific Contributions**

NanoSIMS reveals efficient transfer	
of fixed N <sub>2</sub> from Trichodesmium	
to large size phytoplankton	n(

Estimating global ocean carbon trends using in-situ pCO<sub>2</sub> observations

 $pCO_2$  observations pO4Dust deposition: the fate of

p06

p09

p14

p16

atmospheric new nutrients, interactions with organic matter and the impact on carbon export

The ocean has a gel-like skin made of proteins p07

Halogenated very short lived substances in the tropical western Pacific region

Iron solubility and dust mineralogy p10

AMOP: Activity of research dedicated to the Minimum of Oxygen in the Eastern Pacific p1

The characterisation and quantification of carbon cycle processes in the Gulf of Cádiz and the Strait of Gibraltar p12

Interfacial gas exchange in the sea-ice zone

Field measured atmospheric deposition fluxes over the Southern Ocean

Nitrous oxide in the tropical
Atlantic Ocean p18

High-resolution measurement of volatile organic compounds dissolved in seawater using proton transfer reaction-mass spectrometry (PTR-MS) p19

**plus...** 6 more scientific articles.

#### Including...

SOLAS Open Science Conference	p30
SOLAS Summer School	p35
SOLAS Special Reports	p40
Discussion Session Reports	p42
In Focus	p50
SOLAS Endorsed Projects	p53



#### **SOLAS Spain**

Highlights of recent research activities in Spain related to SOLAS:

(a) The Malaspina 2010-11 Expedition, funded mainly by the Spanish Ministry of Science and Innovation, the CSIC, the IEO, several universities and the BBVA Foundation, and coordinated by C.M. Duarte (IMEDEA-CSIC), completed its trip around the world's oceans (Dec 2010-Jul 2011). SOLAS activities aboard the R/V Hespérides and R/V Sarmiento de Gamboa included measurements of seawater O<sub>2</sub>, CO<sub>2</sub>, pH, alkalinity, NH<sub>3</sub>, DMS, total volatile carbon, organic semivolatiles, organic pollutants, plankton metabolism, N<sub>2</sub> fixation, aerosols, bioaerosols, atmospheric halogens, and isotopic ratios of atmospheric CO<sub>2</sub> and water vapour. For further details, please visit: http://www.expedicionmalaspina.es and contact Rafel Simó (rsimo@icm.csic.es) or Jordi Dachs (jordi.dachs@idaea.csic.es).

(b) A compilation of data from 36 cruises, conducted between 1997 and 2009 and funded within the framework of several national and international projects, has allowed a reconstruction of the seasonal and interannual variabilities of the air-sea CO<sub>2</sub> exchange in the Strait of Gibraltar (de la Paz et al. (2011) *Mar. Chem* 126:155-72; for further details contact Emma Huertas, ICMAN-CSIC, emma.huertas@icman.csic.es).

(c) A study of biomarkers in sediment cores from the Eastern Equatorial Pacific was conducted to investigate the role of phytoplankton composition in the regulation of air-sea CO<sub>2</sub> exchange over the last 40 k years. The study revealed that, during the last deglaciation, the retreat of Antarctic sea-ice and the consequent upwelling of CO<sub>2</sub>-rich water from the deep was more determinant tan the replacement of coccolithophores by diatoms for the simultaneous rise of atmospheric CO<sub>2</sub> (Calvo et al., (2011) Proc. Nat. Acad. Sci. USA, doi:10.1073/pnas.1009761108; for further details contact Eva Calvo, ICM-CSIC, ecalvo@icm.csic.es).

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Sophie Bonnet obtained her PhD in marine biogeochemistry from University of Paris VI, France, in 2005 and then worked for two years at University of Southern California. Since 2007, she is a permanent researcher at IRD in Marseille, France. Her research is focused on the role of marine nitrogen fixation in biogeochemical cycles.

# NanoSIMS reveals efficient transfer of fixed N<sub>2</sub> from Trichodesmium to large size phytoplankton

S. Bonnet

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Nitrogen (N), as an important constituent of proteins and nucleic acids, is essential for life. In the ocean, the availability of N is one of the most important factors controlling primary productivity (Falkowski et al., 1998). Biological N<sub>2</sub> fixation, i.e. the reduction of atmospheric N<sub>2</sub> gas to biologically available ammonium, constitutes one of the major sources of 'new' N for the surface ocean with a net input estimated at 100-200x10<sup>12</sup> g yr<sup>-1</sup> (Mahaffey et al., 2005). This process is performed by a limited group of prokaryotes that possess the nitrogenase operon (Zehr et al., 1998; 2001); the most studied diazotroph species is the cyanobacterium Trichodesmium. Important progress has been made over the last decade on N<sub>2</sub> fixation in marine environments, including the landmark discovery of unicellular diazotrophic organisms of pico- and nanoplanktonic size (Zehr et al., 2001; 2008), and new and unexpected ecological niches where diazotrophs are active, such as N-rich areas (Fernandez et al., 2011). Thus, we have gained a much better understanding of the magnitude and the ecological role of marine N2 fixation in global biogeochemical cycles. However, a critical question that has been little studied so far is how N, newly fixed by diazotrophs, enters oceanic food webs. In many studies, the importance of the input of 'new' N in surface waters by N<sub>2</sub> fixation is often assessed using Redfield ratios to evaluate the hypothetical carbon (C) production which would be sustained by this source of 'new' N. The actual quantity of this N, that supports autotrophic phytoplankton and can be transferred up the trophic chain and/ or exported from the euphotic zone, is unknown. This question has remained unanswered due to a lack of techniques which allow us to directly trace the passage of this element through different biological compartments.

In the framework of the VAHINE project (PI: S. Bonnet), we are currently using high-resolution, nanometre-scale, secondary ion mass-spectrometry (NanoSIMS) coupled to

flow cytometry cell sorting to trace the passage of <sup>15</sup>N derived from <sup>15</sup>N<sub>2</sub> fixation by diazotrophs into non-diazotrophic phytoplankton (Bonnet et al., In rev.). We have demonstrated for the first time that <sup>15</sup>N derived from <sup>15</sup>N<sub>2</sub> fixation by a bloom of Trichodesmium, a widespread diazotrophic marine cyanobacterium, is efficiently and rapidly transferred to non-diazotrophic phytoplankton, such as micro-phytoplankton (diatoms) and pico-phytoplankton (Synechococcus) (Fig.1). Under nitrate depleted conditions, the abundance of these phytoplankton populations increased by a factor of 6 to 11 in experiments with *Trichodesmium* compared to controls without Trichodesmium.

The fact that *Trichodesmium* fuels 'C-exporters' and directly induced a diatom bloom is an important new observation. A few previous studies had observed blooms of diatoms and dinoflagellates during and subsequent to *Trichodesmium* blooms (Devassy et al., 1978; Furnas et al., 1996) and showed that N derived from N<sub>2</sub> fixation can move into bulk plankton (Mulholland et al., 2004; Bryceson et al., 1981) but, the coupling of innovative technologies has allowed us to quantify, on a mixed planktonic ecosystem, which species assimilate the N released by *Trichodesmium*.

As diatoms are efficient at exporting C beyond the euphotic zone (Nelson et al., 1995) (vertical transfer), and constitute ideal prey for higher trophic levels (trophic transfer), this study provides new insights into our understanding of the role of N<sub>2</sub> fixation in potentially enhancing the biological C pump, directly by settling of micro-phytoplankton, or indirectly after transfer of recently fixed N to higher trophic levels. Obviously, further studies including a larger part of the planktonic food web (targeted primary and secondary producers, and components of the microbial loop) and export material are required to identify clearly the primary route of fixed N transfer in the planktonic ecosystem.

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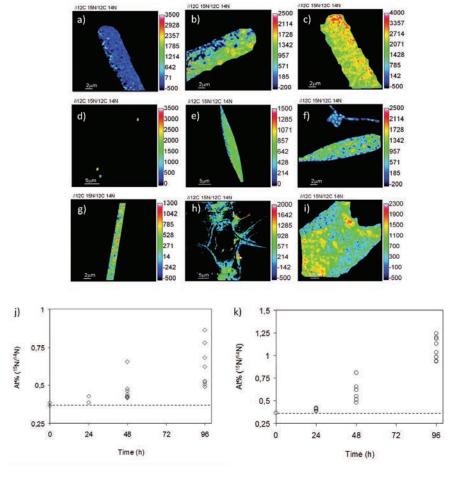
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↑ Figure 1: Summary of NanoSIMS analyses performed in the framework of the VAHINE project. NanoSIMS images of the <sup>15</sup>N/<sup>14</sup>N ratios (per mil) for individual filament of *Trichodesmium* (A), at T=0hrs, (B), at T=24 hrs, (C), at T=48 hrs, (D), individual cells of *Synechococcus* at T=96hrs, (E), and (F), *Cylindrotheca closterium* at T=96hrs, (G), *Leptocylindrus spp.* at T=96hrs, (H), *Chaetoceros spp.* at T=96hrs and (I), *Hemiaulus spp.* at T=96hrs. Summary of results obtained from NanoSIMS analyses, (J), Atom% of the <sup>15</sup>N/<sup>14</sup>N ratios for the five diatom species dominating the community as a function of incubation time, (K), Atom% of the <sup>15</sup>N/<sup>14</sup>N ratios for *Synechococcus* sorted by flow cytometry. The dashed line indicates the average value for phytoplankton in control treatments (not amended with <sup>15</sup>N<sub>2</sub>).



### **SOLAS Germany**

SOPRAN (Surface Ocean Processes in the Anthropocene, www.sopran.pangaea.de) is a German national contribution to SOLAS. Major field campaigns of SOPRAN during the last year include two mesocosm experiments on ocean acidification (Raunefjord, Norway, 2011 and off Tvärminne, Finland, 2012), a R/V Merian cruise to the equatorial Atlantic (2011) as well an air/sea gas exchange campaign in the Aeolotron wind/wave facility in Heidelberg in 2011. The ongoing activities and the proposal for a third phase of SOPRAN (Feb. 2013-Jan. 2016) have been successfully reviewed by an international review panel during the 5th SOPRAN Annual Meeting in Kiel in March 2012. SOPRAN is currently submitting the final proposal for SOPRAN III to the German BMBF.

As part of the EU 7th Framework programme SHIVA (Stratospheric Ozone: Halogen Impacts in a Varying Atmosphere; http://shiva.iup.uni-heidelberg.de/) a multi-platform campaign in the South China Sea took place in November 2011: In order to study the exchange of halocarbons between the ocean and the atmosphere a *RIV Sonne* cruise was conducted with concurrent aircraft and land-based measurements.

#### Science highlights

Lai et al. (2011) were able to show that the occurrence of atmospheric iodine containing species over the southwestern Atlantic Ocean is connected to oceanic emissions during phytoplankton blooms. (see: Lai, C., et al. (2011), *Geophys. Res. Lett.* 38:L20801)

The importance of organic surface films on the air-sea gas exchange was shown in two studies: A lab study revealed that the CO<sub>2</sub> uptake in the Baltic Sea could be reduced significantly by surfactants (Schmidt and Schneider, 2011). Based on measurements of the diapycnal flux and N<sub>2</sub>O profiles from the eastern tropical North Atlantic, Kock et al. (2012) calculated a N<sub>2</sub>O budget for mixed layer. Their results indicate that the N<sub>2</sub>O flux into the mixed layer can be balanced only when a surfactants-corrected (reduced) airsea transfer coefficient is applied. (see: Schmidt, R., and Schneider, B. (2011) Mar. Chem. 126:56-62; Kock, A., et al. (2012) Biogeosciences 9:957-64)

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#### **SOLAS Peru**

Driven by an initiative between the Instituto del Mar del Perú (IMARPE) and the State Key Laboratory of Marine Environmental Science, Xiamen University, a collaborative project, initiated in 2009, was developed in order to study the carbonate system and the "acidification" off the Peruvian upwelling system by a time series measurements of total CO<sub>2</sub>, pH and alkalinity in the central area, Callao. The preliminary results confirm the vulnerability of the area characterised by significant total CO<sub>2</sub> concentrations and low pH values.

Associated also with the SOLAS OMZs-EBUEs Mid-Term Strategy Initiative topics, in 2011, a collaborative project between IMARPE and SFB754II phase / GEOMAR was established in order to implement a time series measurements of nitrous oxide and methane and understand the impact of the oceanographic and OMZ variability in the role of this areas as source of these gases. The first results obtained from May and October 2011, show that most of the water column along the sampled transect was oversaturated with N2O, indicating N2O production within the sampled region. Maximum N<sub>2</sub>O concentrations appear directly related with the intensity and shallow distribution of the Oxygen Minimum Zone. In November 2012, staff from IMARPE will also participate in a German SOLAS cruise initiative, METEOR 91 / SFB754 / GEOMAR, which offers an unique opportunity to explore the dynamic of different greenhouse and others gases along the Peruvian upwelling system.

In October 2011, several Peruvian scientists from the Instituto del Mar del Perú (IMARPE) and the Instituto Geofísico del Perú (IGP) participated in the international conference "Ocean Deoxygenation and implications for marine biogeochemical cycles and ecosystems" Toulouse (24-26 October 2011; http://www.eur-oceans.eu/confoxygen). France. This EUR-OCEANS conference was an excellent opportunity to discuss about one of the relevant topics associated with the global climate change, "the ocean loss of oxygen and the "extension of the Oxygen Minimum Zones (OMZs)"; one of the main foci of the SOLAS OMZs-EBUEs Mid-Term Strategy Initiative. This meeting was also an opportunity to advance in the initiative AMOP (Activity of Reserch associated with the OMZ off Perú), a French project in collaboration with Perú and with the participation of scientists from Germany, Ireland, Denmark and México.

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Amanda Fay is currently a Research Intern with the Department of Atmospheric and Oceanic Sciences at the University of Wisconsin-Madison (USA). Currently, she is focusing on utilising surface ocean carbon measurements to develop a holistic understanding of carbon cycling in the global oceans.

# Estimating global ocean carbon trends using in-situ pCO<sub>2</sub> observations

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Oceanic uptake of carbon dioxide plays a key role in controlling the rate at which anthropogenic carbon accumulates in the atmosphere, effectively slowing global climate change. Some studies have suggested that the rate at which the oceans take up carbon has significantly decreased in recent years while others suggest that decadal variability obscures the detection of long term-trends. Through an analysis of surface ocean pCO<sub>2</sub> observations spanning 30 years (1981-2010) we examine trends in pCO<sub>2</sub> over large biogeographic regions, or biomes, of the global ocean. Our biomes are created using three climatological criteria (SST, chlorophyll-a, and MLD) similar to the method used by Sarmiento et al. (2004). This biome-scale approach is motivated by an interest in global-scale carbon partitioning and allows application of limited ocean observations at this scale.

Data was regridded to 1°x1° spatial and monthly temporal resolution. After eliminating the possibility for spatial aliasing, a harmonic fit captured an annual cycle and linear trend (in µatm/yr) for each biome (McKinley et al., 2011). By comparing these observed trends to trends in atmospheric carbon dioxide we show the variability of pCO<sub>2</sub>socn on varying timescales, ranging from decadal to multidecadal. By considering trends over these varying timescales we can detect influences of 1) climactic oscillations on interannual to decadal timescales as driven by major climate indices, such as ENSO or NAO and 2) longterm trends which average over climate variability and reveal the state of ocean carbon uptake on a multi-decadal timescale. Such long timescales can reveal the required timeseries length required to smooth over the influence of climatic events and to distinguish the ocean's response to the atmospheric pCO<sub>2</sub> increase, as well as mechanisms of carbonclimate feedbacks.

Results from this analysis covering the North Atlantic biomes were recently published in Nature Geosciences (McKinley et al., 2011).

On decadal timescales, trends in surface ocean pCO<sub>2</sub> in the individual biomes can be significantly greater, consistent with, or less than the atmospheric trend (Fig. 1b;d); however, on the longest timescale considered, 1981-2009, surface ocean pCO<sub>2</sub> trends in all three of the biomes were indistinguishable from the atmospheric trends (Fig. 1a;c). As shown in detail in McKinley et al. (2011), for biomes north of around 45°, it takes roughly 25 years for the pCO<sub>2</sub>socn trend to track the atmosphere, but there is significant sensitivity to the precise selection of years for pCO<sub>2</sub> timeseries shorter than 25 years. In the subtropical biome (STPS), climatic fluctuations are averaged out after 20 years, however a strong warming trend detected in this region for timeseries extending into the late 2000's indicates a negative feedback on the carbon sink. This suggests a reduced capacity for carbon uptake due to warming (Le Quéré et al., 2010; Sarmiento and Le Quéré, 1996). This warming has previously been shown to be due partially to anthropogenic forcing and partially to multidecadal climate variability (Löptien and Eden, 2010; Ting et al. 2009). In an updated analysis extending to 2010, we find that this warming signal is extending into the gulf-stream transition zone of the North Atlantic Ocean and is also evident in the subtropical gyre of the North Pacific (Fay and McKinley, in prep.).

Another area of high interest in surface ocean carbon analysis is the equatorial Pacific biome, which generally acts as a source of carbon to the atmosphere due to its warm temperatures and circulation patterns (Feely et al., 2006). ENSO signals clearly emerge in our analysis of this region on decadal timescales, but on timescales longer than 25 years trends largely indicate equilibration with the atmosphere (Fay and McKinley, in prep.). In the Southern Ocean, we find both long- term cooling and a pCO<sub>2</sub> trend less than the atmospheric pCO<sub>2</sub> trend, both consistent with increased upwelling of waters with low anthropogenic carbon content.

The biome-based approach offers an assessment of change in the ocean carbon cycle from observations across regions that are both physically and biogeochemically coherent and relevant to the global carbon budget. However, given the limited data, it is critical that these trends be considered across a wide range of start and end points so that their robustness can be assessed.

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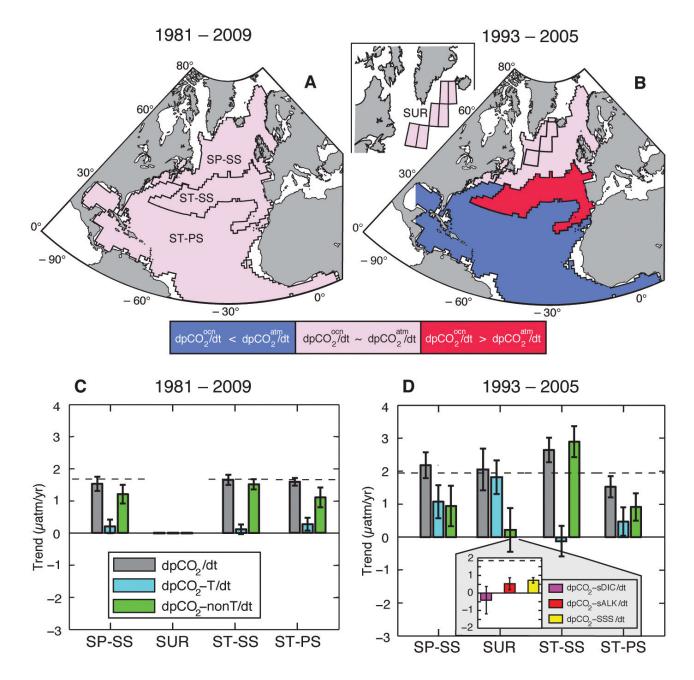
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### Acknowledgements

This work was funded by the NASA project 07-NIP07-0036, NNX11AF53G.



A Figure 1: Trends in oceanic pCO<sub>2</sub> for (a) 1981–2009 and (b) 1993–2005 compared to atmospheric pCO<sub>2</sub> trend. (a;b), Dark blue for oceanic pCO<sub>2</sub> trend less than atmospheric pCO<sub>2</sub> trend; pink for indistinguishable; red for larger oceanic trend. (c;d), Oceanic pCO<sub>2</sub> trends( grey), temperature (pCO<sub>2</sub>-T, light blue) and chemical (pCO<sub>2</sub>-nonT, green) components, with 1σ uncertainty, and atmospheric pCO<sub>2</sub> trend (dash). Refer to McKinley et al., 2011 for further details.



Matthieu Bressac is a PhD student at the Laboratoire d'Océanographie de Villefranche, University Paris VI (France). His main scientific interests include the impact of dust deposition on the particulate export to the deep ocean and the fate of atmospheric nutrients in surface waters with a focus on iron.

# Dust deposition: the fate of atmospheric new nutrients, interactions with organic matter and the impact on carbon export

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It has recently been postulated that atmospheric particles can act as ballast material and are, therefore, likely to act as a transport mechanism for fixed carbon to the deep ocean (Hamm, 2002). The increase in the carbon export efficiency following a dust event has recently been demonstrated through *in situ* observations (Ternon et al., 2010). Thereby, the overall role of a dust event is considered as a major control over the particulate organic carbon (POC) flux (Boyd and Trull, 2007). However, progress in establishing the respective proportion of POC export through 'fertilisation' is still needed.

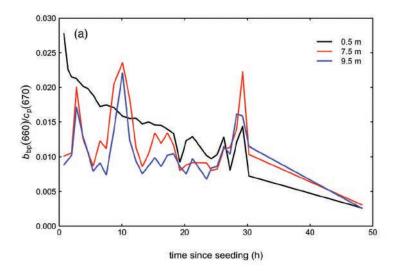
In the frame of the DUNE project, an artificial seeding experiment in large mesocosms (52 m³) was conducted in the natural assemblage typical of oligotrophic conditions. Through optical measurements, it has been demonstrated that (1) part of the dust pool had a rapid settling velocity (~24–86 m day¹) and (2) the particulate export following the seeding was a non-linear, multi-step process (Fig.1a), partly controlled by the formation of organic-mineral aggregates (Fig.1b) (Bressac et al., 2012); thus, confirming the lithogenic ballast hypothesis (Armstrong et al., 2002).

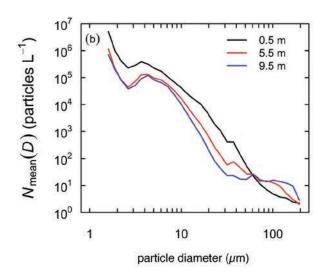
Nevertheless, the input of new atmospheric nutrients to the system (Pulido-Villena et al., 2010) induced a significant and rapid increase of total chlorophyll a which was concomitant with the increase of POC export. In consequence, this experimental approach conducted in biotic condition enabled us to highlight the overall effect of dust deposition in oligotrophic waters without strictly quantifying abiotic and biological contributions to the particulate export.

In this perspective, a second type of seeding experiment ('minicosm' of 0.3 m<sup>3</sup>) was conducted in abiotic conditions (seawater filtered 0.2 µm) within a clean room. This original experimental approach allowed the study of particles settling on a 1-m depth layer over a one week period; a realistic contact time between particles and seawater. Atmospheric iron dissolution is ultimately controlled by the continuum of organic ligands which composed the dissolved organic matter (DOM) pool and thus followed the seasonal trend of DOM (Wagener et al. 2008). These three abiotic experiments were conducted during contrasting biogeochemical situations in order to investigate the impact of

atmospheric particles – DOM interactions on (i) atmospheric new nutrients concentrations (focusing on iron and phosphorus); (ii) the particle transformations; and, (iii) the resulting POC export. Results suggested that the interactions between atmospheric particles and DOM present in the sampled seawater partly controlled the fate of new atmospheric nutrients. Indeed, high DOM content promoted the rapid formation of aggregates which, in turn, induced a negative feedback on dissolved nutrient concentrations through scavenging on the particulate phase while a fraction of these new nutrients were maintained in the dissolved phase through organic complexation. On the contrary, low DOM content suppressed aggregation allowing high dissolution to occur.

Thereafter, new atmospheric nutrients were rapidly removed from the dissolved phase by adsorption onto settling atmospheric particles. This experiment illustrates the role of the DOM and associated abiotic processes for the fate of new atmospheric nutrients in seawater and highlights the abiotic formation of mineral-organic aggregates in high DOM content condition.





A Figure 1: Results from the mesocosm experiment (natural assemblage) (adapted from Bressac et al., 2012). (a) Plot of the backscattering ratio (b<sub>bp</sub>(660)/c<sub>p</sub>(670)) at 0.5, 7.5 and 9.5m depths as a function of time after seeding. This ratio is commonly used as a proxy of the particle assemblage. Ratios of 0.03 and 0.005 are typical of mineral and organic particles respectively. The particulate export was dominated by mineral particles (~5, 10 and 30h after seeding) and organic-mineral aggregates (~15–30h after seeding). (b) Mean particles number concentrations measured along the experiment at 0.5, 5.5 and 9.5m depths. This graph supports the interpretations of a long residence time of smaller particles in subsurface layers and a formation of aggregates (>60μm) from these small particles during the transfer to deeper layers.

The next step of this study is to measure the particulate organic matter which is abiotically formed and exported toward the bottom of the 'minicosm'. Results from both the mesocosm (biotic conditions) and the minicosm (abiotic conditions) will help to estimate the biological contribution to the particulate export after a dust deposition event.

These studies taken together demonstrate that (1) dust deposition can be seen as a fertilizing event; (2) the fate of new atmospheric nutrients and, therefore, the intensity of the biological response depend on seawater biogeochemical conditions; (3) atmospheric particles act as ballast material; and, (4) these processes contribute to the increase of the carbon flux to the deep ocean.

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Luisa Galgani studied Environmental Sciences and Environmental Chemistry in Siena (Italy) and Granada (Spain). She is currently a PhD student of SOPRAN II project at Geomar (Kiel, Germany) investigating how climate change affects the interactions between ocean and atmosphere, with focus on surface films and organic marine aerosol export.

### The ocean has a gel-like skin made of proteins

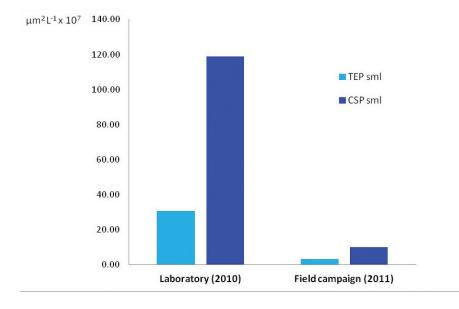
L. Galgani<sup>1,2</sup> and A. Engel<sup>2</sup>

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The very surface of the ocean is a peculiar environment responsible of mediating gas fluxes and organic matter transport between ocean and atmosphere. It is called the sea-surface microlayer (SML) and derives from the accumulation of organic material at the surface: These compounds produced by marine organisms form visible slicks that lower seawater surface tension thus influencing air-sea gas and energy exchange. The SML is susceptible to being altered by water movements, wind-driven atmospheric deposition, solar radiation and biological activity.

The SML has been hypothesised as being a hydrated gelatinous matrix of varying thickness entrapping several compounds like lipids, carbohydrates, proteins and specific bacterial communities known as bacterioneuston. Polysaccharides are the major constituent of phytoplankton exudates and comprise a considerable fraction of high molecular-weight dissolved organic matter (HMW>1kDa) in the surface ocean.

In the SML carbohydrates are also present as Transparent Exopolymer Particles (TEP), marine gels that concur to the gelatinous nature of the boundary layer, as recent studies have evidenced. Thanks to their sticky properties,



 $\Lambda$  Figure 1: TEP and CSP total area ( $\mu$ m<sup>2</sup> L<sup>-1</sup> x 10<sup>7</sup>) from the laboratory experiment at Alfred Wegener Institute (2010) and the fjord sampling in Bergen, Norway (2011).

TEPs play an important role in the formation of aggregates colonised by bacteria. Simultaneously, marine gels promote biofilm formation; act as a food source for microorganisms; and, mediate vertical carbon transport, either to the sea surface or to the deep ocean. While the SML enrichment in TEP has been recorded in previous studies, a

recently submitted paper (Galgani and Engel, 2012) demonstrated that the SML was not unambiguously dominated by polysaccharidic gel particles, but that proteinaceous compounds in the form of Coomassie Stainable Particles (CSP) were also present in the SML and even outnumbered TEP.

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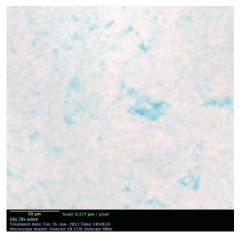
TEP and CSP are transparent, unless differentiated with an amino acid specific dye (Coomassie Brilliant Blue G, for CSP) or with a dye that complexes the carboxyl and halfester sulfate reactive groups of acidic polysaccharides (Alcian Blue for TEP). Whether these two kinds of gels represent subunits of the same gel particle or individual gels is currently not known. To address our research objectives, we investigated the gelatinous nature of the SML during two studies in the framework of the German BMBF-funded SOPRAN II project. We conducted indoor experiments with the diatom Thalassiosira weissflogii grown under different pCO2 and incubated in tanks (Galgani and Engel, 2012), and a field campaign in the Raune Fjord, Norway (unpublished data). Our sampling approach with the glass plate referred to the uppermost 100-200 µm of the sea surface. The water below the surface was sampled at a depth of approximately 20cm in both experiments, and enrichment factors (EF) to determine enrichment or depletion of a component in the SML were calculated as follows:

 $EF = [x]_{SML} / [x]_{BW}$ 

Where [x] is the concentration of a given parameter in the SML or in the bulk water (BW) (Liss and Duce, 1997).

Results from the indoor experiments evidenced predominantly proteinaceous composition of the surface film as CSP enrichment. These first observations were later confirmed by the field sampling in Norway, where CSP were more abundant in total area in SML with respect to TEP (Fig. 1). Moreover, in the fjord CSP were also characterized by bigger particles (Fig.2;3).

Our studies suggest that the microlayer has a proteinaceous gel-like composition with CSP



↑ Figure 2: TEP particles from SML of the fjord

derive from bacterial exudates and the cell's protein content that can be released through cell disruption and lysis. An enhanced concentration of CSP points out to the importance of bacterial metabolism in the SML. Activities of microbes inhabiting the SML continuously alter its composition and render the very surface of the sea into a unique and mutable environment (Fig.4). Heterotrophic bacteria have been shown to respond to rising CO<sub>2</sub> and sea-surface temperatures: They may mediate air-sea gas exchange processes at the interface between ocean and atmosphere, crucial to understand future feedbacks of climate change.

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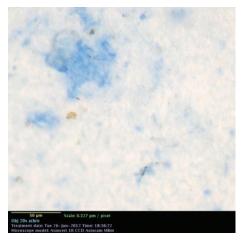
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↑ Figure 4: Sampling the SML in the Fjord



↑ Figure 3: CSP particles from SML of the fjord

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### Acknowledgments

This work is supported by German Federal Ministry of Education and Research (BMBF) and SOPRAN II project.



Helmke Hepach has been a PhD student at GEOMAR, Kiel (Germany), since 2009. Her research focuses on characterizing halogenated VSLS in and above the tropical ocean, as well as their emissions and further determining their drivers and sources.

### Halogenated very short lived substances in the tropical western Pacific region

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Halogenated very short-lived substances (VSLS) are produced naturally in the oceans and can be released to the atmosphere. The mainly iodine- and bromine-containing organic compounds take part in ozone destroying catalytic cycles in both the troposphere and stratosphere (Montzka et al., 2002). There is still great uncertainty with regard to production of these compounds. Bromoform (CHBr<sub>3</sub>) is the major carrier of organic bromine from the ocean to the stratosphere. Emissions from both macroalgae and phytoplankton have often been suggested as major release mechanism for CHBr<sub>3</sub> (Quack and Wallace 2003). Once these compounds are produced in the ocean, they are released to the lower atmosphere by air-sea gas exchange. In the tropics, they can be transported rapidly into the tropical tropopause layer by tropical deep convection from where they can reach the stratosphere.

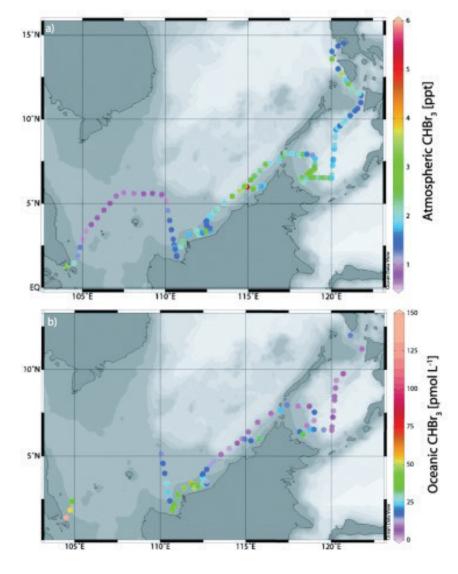
The western tropical Pacific region is, up to now, very uncharacterized with respect to halogenated VSLS and their degradation products. The SHIVA-Sonne campaign consisted of ship-, aircraft- and land-based measurements. It aimed at reducing the uncertainties in the emission strength and the vertical and horizontal transport of halogenated VSLS and other ozone depleting substances in the atmosphere.

In November 2011, the R/V Sonne followed a cruise track from Singapore to Manila, Philippines along the coast of Borneo and through the Sulu Sea. During the campaign VSLS concentrations where determined in water and air, including their sea-to-air fluxes and their sources. Furthermore, other atmospheric trace gases, transport processes and oceanic chemical, physical and biological parameters were determined. At the same time, the German aircraft Falcon, based at Miri, Borneo, measured related parameters in different altitudes in the atmosphere in consultation with the Sonne. The results of the campaign will increase the understanding of the origin and fate of halogenated VSLS in the tropical Pacific region. They will also help validating and improving models focusing on ozone depletion and involved reaction mechanisms. During the cruise, sea water concentrations of VSLS were measured in situ for both sea surface water and oceanic vertical profiles. Air for atmospheric samples was sucked into stainless steel canisters and then analyzed in Miami. First results for the CHBr<sub>3</sub> distribution in surface water and air are shown in Figure 1a and 1b.

Atmospheric CHBr<sub>3</sub> of up to 5ppt was measured at the northern coast of Borneo. It generally ranged between 2-3ppt in coastal regions and decreased above the

more open ocean waters. Oceanic CHBr<sub>3</sub> was elevated in coastal waters as well, but was more pronounced at the southern coast. Concentrations there ranged between 12 and 57pmol.L<sup>-1</sup>. Possible reasons for elevated CHBr<sub>3</sub> close to Singapore and Borneo include river runoff as well as biological production: CHBr<sub>3</sub> maxima in deeper waters often coincided with chlorophyll a maxima suggesting a biological source.

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↑ Figure 1: Atmospheric (a) and oceanic (b) CHBr₃ in and above the tropical Western Pacific during the SHIVA campaign in November 2011.

Compared to other tropical regions such as the Atlantic and the open tropical Pacific (Quack and Krüger 2010; Hepach et al., 2012), coastal oceanic concentrations were slightly higher here. Close to the Mauritanian coast, between 8 and 42pmol.L<sup>-1</sup> CHBr<sub>3</sub> was measured. In contrast to this, atmospheric CHBr₃ above the Mauritanian upwelling was generally higher with 4-9ppt. Tropical convection above the western Pacific is more pronounced and intensive than above the tropical Atlantic upwelling systems which leads to enhanced vertical transport of halogenated VSLS projected by our FLEXPART model calculations (Tegtmeier et al., 2012). This in combination with elevated water concentrations and oceanic emissions underlines the importance of this region.

Future work will include comparison to oceanic parameters, as well as to atmospheric features in combination with the aircraft measurements. These data will reduce the present-day uncertainties in the transport and fate of halogenated VSLS from the oceanic source to the stratosphere.

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### Acknowledgements

This work is part of the EU funded FP7 project SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere, SHIVA-226224-FP7-ENV-2008-1).



Emilie Journet obtained her PhD in Atmospheric Sciences in 2008 from University Paris Diderot (France) before joining the University of Bristol (UK) for a post-doc position. Since 2010, she is a research associate at the LISA (France). She has been working a lot on iron solubility and on dust mineralogy in North Africa and start to work on Patagonian Dust.

### Iron solubility and dust mineralogy

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Dust aerosols are emitted in large quantities in the atmosphere by wind erosion on arid and semi-arid soils and can be transported over long distances. As they deposit to the ocean surface, they contribute to supply important nutrients, such as iron, to marine biota (Duce and Tindale, 1991). In some oceanic regions, characterized by low biological activity, dust deposition is assumed to enhance phytoplankton activities and thus can promote the biological pump of CO<sub>2</sub> (Moore et al., 2006).

As only dissolved nutrients can be assimilated by phytoplankton, we need to understand the dust dissolution process and to quantify the soluble fraction of the aerosol. We now know that iron solubility is highly variable in space and time, between 0.01% and 80% according to Mahowald et al. (2005). Among the various parameters which explain this variability, the mineralogy of iron in the aerosol was identified as a key parameter that can help to quantify iron solubility (Journet et al., 2008). Mineral dust typically contain a mixture of several Fe-bearing minerals including crystalline hematite (Fe<sub>2</sub>O<sub>3</sub>), goethite (FeOOH) and Fe-bearing clay minerals, such as illite, mixedlayer illite/smectite, and smectite (Shi et al., 2012).

Dissolution experiments that we have conducted on "pure" minerals show that iron solubility at pH 4.7 (rainwater pH) varies considerably depending on mineral types, from 0.001% for hematite and goethite to 0.5% and 1% respectively for illite and smectite. These results have been faced with the behavior of iron in the real desert dust collected in source area during the AMMA campaign (http://www.ammainternational.org). The dissolution experiments conducted on dust collected in the area of West African revealed a low and homogeneous solubility of iron (<1%), regardless of location or time of collection, and is in very good agreement with those calculated from the solubility of illite and smectite. These new results confirms that the mineralogical composition of desert dust thus appears today as a key factor for understanding the role of aerosols on climate, whatsoever in terms of impact on carbon cycle (Journet et al., 2008; Schroth et al., 2009) or in terms of radiative impact (Sokolik and Toon, 1999).

Reflecting variability in terrestrial soils, the mineralogical composition and so the properties of desert dust vary according to their emission region (e.g. Formenti et al.,

2011). As the mineralogy of dust is directly related to the erodible fraction of soil source, it appears that detailed knowledge of the mineralogical composition of source soils at the global level would significantly improve our knowledge about environmental and climate impact of desert dust particles.

Thus, we have created a new database describing the mineralogical composition of soils that can be used to describe the mineralogical composition of dust emitted from these soils. My job was to update and improve the database on the mineralogical nature of arid and semi-arid provided by Claquin et al. (1999). To build this new database, I began by collecting information on eleven major minerals (quartz, feldspar, calcite, gypsum, illite, kaolinite, montmorillonite, chlorite, vermiculite hematite and goethite).

Then an average size-resolved mineralogical composition was imputed to each soil unit described by the FAO HWSD (Harmonized World Soil Database). This new mineralogical database is digitized under the form of mineralogical maps (an example of the illite content in soils is shown in Fig. 1), then it will be easy to incorporate information on the mineralogical composition of soils in global

climate models that include the cycle of mineral dust. This will make it possible to determine whether information on the mineralogical composition of mineral dust can reduce the uncertainty associated with their climate impact.

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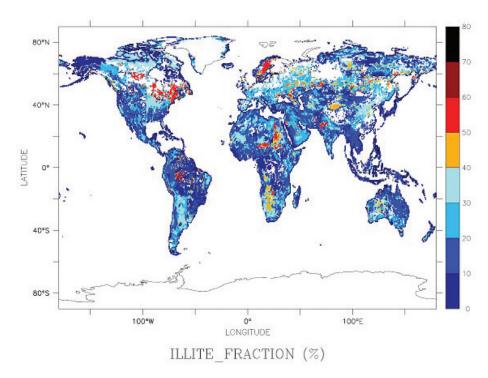
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 $\Lambda$  Figure 1: Amount (in % by weight) of Illite in the clay fraction (<2 $\mu$ m) at the surface of soils.

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Aurélien Paulmier is Researcher currently working in cooperation in Peru, co-initiator of the Oxygen Minimum Zones and Eastern boundary upwelling systems (OMZ-EBUS) SOLAS Mid-Term Strategy. Since 1999-2000, he has studied the impact and feedback effects of climate change on marine biogeochemistry, focussing on the OMZs using complementary approaches (*in situ* observations; experiments; data analysis; modelling).

# AMOP: Activity of research dedicated to the Minimum of Oxygen in the Eastern Pacific

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Oxygen Minimum Zones (OMZs) as suboxic layers are known to play a key-role on the evolution of climate (greenhouse gases production) and living resources from ecosystems to fisheries (nitrogen loss, respiratory barrier for zooplankton and fishes). In response to climate and environmental changes, OMZs would contract during cold periods and extend during warm periods. Despite their importance and the worrying problem of the ocean deoxygenation due to global warming and human activities, most of the OMZs have not been extensively studied. State-of-the-art numerical models exhibit

severe biases in simulating the vertical and horizontal  $O_2$  distribution in OMZs, although oxygen is one of the first measured parameters in oceanography. In particular, the origin of the OMZs existence, as well as their variability associated with a very large spatiotemporal scales range, remains unresolved.

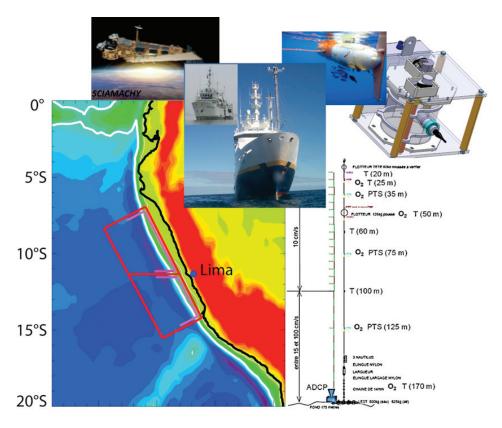
The central hypothesis of this project is that the physical and biogeochemical  $O_2$  contribution to the OMZ, its maintenance and variability, depends on the different OMZ layers; in particular, the oxycline which would be the engine of an intense but intermittent biogeochemical and ecosystem

activity (e.g.  $O_2$  consumption). AMOP aims at testing this hypothesis in the largest OMZ and the most productive upwelling systems: The Peru system in the Eastern Pacific Ocean. Conversely to other projects dedicated to different OMZ impacts study, AMOP is specifically oriented on the oxygen parameter, with the objective to carry out the most complete  $O_2$  budget; taking into account physical (advection/diffusion) and biological (e.g.  $O_2$  consumption/production through bacteria, phytoplankton and zooplankton) contributions.

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The project implies a transdisciplinary approach: biogeochemistry, microbiology and physics coupled with the atmosphere, acoustics, ecology, benthic studies, palaeoceanography; disciplines all aiming towards the understanding of the O<sub>2</sub> fluxes. The approach is based on i) a 30-day cruise with two ships working simultaneously (R/V L'Atalante from IFREMER and the R/V Jose Olaya Balandra from IMARPE) and associated gliders and Argo floats experiments (Fig. 1); ii) a fixed mooring (> 3yr) coupling water column and sediments located on one of the historical stations sampled by IMARPE; iii) a modeling component in order to a) bridge the gap between sampled and non-sampled spatio-temporal scales; and b) to assist the interpretation of our full data set (from in vitro to satellite observations). The cruise will include on-board experimentations and the use of innovative technologies (e.g. Pump-CTD, HPBs-O<sub>2</sub>, IODAs/sediment traps/ANESIS) and is focused on nine fixed stations (3-day) and on three transects in the North (7°S), Centre (12°S) and South (14°S), covering three distinct topographic conditions of the OMZ system: the continental shelf, the slope and the open deep ocean.

To fulfill the objectives of this ambitious program, AMOP will involve 13 research units in France, seven research units from two Institutes in Peru and ten Institutions in six other countries (China, Denmark, Germany, Ireland, Mexico, Spain) acting as an international consortium on the deoxygenation topic (~100 participants). It benefits from the dynamics of national and international programs (RTRA/MAISOE, LMI-DISCOH, SENSEnet, HYPOX, EURO-ARGO, EUR-OCEANS Oceanflux, SOLAS, IMBER, GEOTRACES). AMOP is viewed as one of the



↑ Figure 1: General schematic AMOP strategy (below on the left) including in situ observations: French (red track) and Peruvian (pink track) Research Vessels, a subsurface mooring, gliders, innovative systems (e.g. *In situ* Oxygen Dynamics Autoanalyzer: IODA) as well as satellite and modeling approaches.

main pilot projects of an initiative to coordinate, on the OMZ and in partnership with Peruvian Institutions, international actions (e.g. German SFB754 and US Torero initiatives) from 2012-2013: cruises, scientific flights, experiments, long-term monitoring, and modelling. Presently, the AMOP project is approved and labeled by LEFE-CYBER and LEFE-GMMC from the National Institute of Universe Sciences. The modelling activity has already begun at a regional scale (dynamics and biogeochemistry coupling) and microbial scales (e.g.  $O_2$  consumption). The AMOP-mooring, including one Acoustic Doppler Current Profiler (ADCP) and a suite of biogeochemical sensors will be implemented in January 2013. The planning for cruise, including the glider and ARGO-floats activities in 2013-2014, still needs to be confirmed. More details will soon be available on a dedicated AMOP website.



Susana Flecha Saura is a PhD student at the Instituto de Ciencias Marinas de Andalucía, CSIC (Spain). Her research is focused on the carbon cycle processes in aquatic ecosystems including open ocean, coastal areas, estuaries and wetlands. At present, she is a visiting student at the Chemical Oceanography group of the University of Washington, USA.

# The characterisation and quantification of carbon cycle processes in the Gulf of Cádiz and the Strait of Gibraltar

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Since the last century  $CO_2$  emissions from human activity, deforestation and fuel burning are gradually increasing. Nevertheless atmospheric concentrations of these greenhouse gas do not present the high values expected due to these anthropogenic emissions. The remaining carbon dioxide is

being removed by natural sinks, the land and ocean; both with approximately the same percentage of  $CO_2$  capture (Le Quere et al. 2009) . In the global ocean, several studies have confirmed that the North Atlantic is the most important sink for atmospheric  $CO_2$  (Sabine et al., 2004; Takahashi, 2009),

although there still remain uncertainties about the total amount stored by this oceanic region. In the past, the contribution of areas such as marginal seas, semi-enclosed seas and continental shelves (including estuaries and wetlands) to the global carbon inventories was understudied. Nevertheless,

recent studies have demonstrated that these areas play an important role in CO<sub>2</sub> exchange due to the magnitude of the biochemical processes in them. At the Ecology and Coastal Department in the Instituto de Ciencias de Andalucia (CSIC) in Spain, Flecha's research focuses on the characterisation and quantification of the main processes involved in the carbon cycle in the Gulf of Cádiz and the Strait of Gibraltar. This area, located in the southwest of the Iberian Peninsula (Fig. 1) notably participates in the general circulation of the North Atlantic owing to the channelisation of the water exchange that takes place between the Atlantic and the Mediterranean Sea through the Strait (Criado-Aldeanueva et al., 2009; Péliz et al., 2009). Thus, the entrainment of North Atlantic Central Water (NACW) by the Mediterranean Outflow Water (MOW) as it descends the northern slope of the Gulf of Cádiz markedly contributes to the generation of the Azores current and also drives upper slope currents in the basin (Péliz et al., 2009). The concentrations of anthropogenic carbon C<sub>ANT</sub> have been estimated using several methods for each water mass (Fig. 1f;g). This study has shown that, in spite of the high inorganic carbon content of the MOW (Fig. 1e), the flux of anthropogenic carbon goes from the Atlantic Ocean towards the Mediterranean Sea and through the Alborán Sea, since the NACW contains higher C<sub>ANT</sub> concentrations than the MOW (Flecha et al., 2012; Huertas et al., 2009).

Her research also covers the carbon exchange mechanisms between the Guadalquivir River estuary and the continental shelf of the Gulf of Cádiz. The supply of high nutrients loads from the river and the export of inorganic carbon regulate the biological productivity of the basin. Previous studies have emphasised that Guadalquivir estuarine waters are oversaturated with respect to the atmosphere, with pCO<sub>2</sub> levels decreasing from the inner estuary to the river mouth (de la Paz et al., 2007; Flecha et al., in prep.) (Fig.1b). In the coastal area, these inputs along with changes in the incident irradiance modulate the development of phytoplankton blooms that occur in spring and autumn (Fig. 1a). Consequently, changes in the biological activity and local meteorological conditions (including events of strong winds) have a marked influence on the air-sea CO<sub>2</sub> fluxes and, on annual basis, the coastal area of the Gulf of Cádiz acts as a net sink for atmospheric CO2 (Huertas et al., 2006) (Fig.1c).

Finally, the contribution of the Doñana wetlands to the regional air-sea CO<sub>2</sub> fluxes is also being examined. The Doñana National Park, located on the western margin of the Guadalquivir estuary, is one of the largest heronries in the Mediterranean region and the wintering site for more than 500,000 water fowl each year. Its aquatic compartment is composed by water bodies of different nature and origin, including salt marshes, permanent freshwater lagoons and river streams. Despite its relevance in the biodiversity conservation, seldom studies have analyzed in details the biogeochemistry of the aquatic systems of Doñana and their influence on biological productivity and carbon fluxes. Therefore, a monitoring program aimed at analyzing the temporal carbon dynamics in the most representative aquatic systems of the Doñana wetlands has been implemented.

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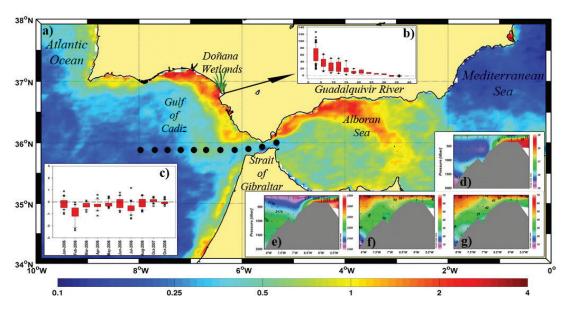
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A Figure 1: Map of the south of the Iberian Peninsula area. (a) March, 2008, monthly averaged Chlorophyll-a from satellite (mg m-3) from Globcolour products, ESA; (b) Air-Water CO2 fluxes (mmol m2 d-1) plotted against salinity in the Guadalquivir estuary; (c) Air-Sea CO2 fluxes (mmol m2 d-1) plotted against time in the continental shelf of the Gulf of Cádiz; (d-g)Salinity, Dissolved Inorganic Carbon (μmol kg-1), CANT (φCT° method) and CANT (ΔC\*method) in μmol kg-1 in a transect throughout the Strait of Gibraltar (black dots).



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### Interfacial gas exchange in the sea-ice zone

3. Loose

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The Arctic and Southern Oceans are recognised as important regions in the global carbon cycle. For example, the Southern Ocean (SO) is thought to be the most important surface ocean region for regulation of atmospheric CO<sub>2</sub> because of (1) restriction of the ventilation of the deep ocean carbon and (2) biological export production. Within these oceans, seasonal sea ice zones (SSIZ) play a critical role by producing intense springtime primary production, by mitigating the escape of deep ocean CO<sub>2</sub>, and by the formation of deep water. These processes have implications for our understanding of how the climate transitions from glacial to interglacial states, and for the proper estimation of the uptake of anthropogenic carbon by the deep ocean. Moreover, the net impact of human-induced climate change on the polar ocean is not fully understood, but early results suggest that Arctic Ocean biogeochemistry has already been substantially modified. In the Arctic, sea ice has undergone a dramatic decline in recent years. Melt is starting earlier and freezing onset is later, causing more solar radiation absorption in the surface ocean . Such changes will have consequences for biogeochemical processes and gas exchange that are necessary to measure and forecast.

One of the principal deficiencies inhibiting our forecast of sea-ice effects on the carbon cycle is a constraint on the rates and pathways that govern gas transport in the SSIZ, and the process is significantly complicated by the presence of sea ice. Sea ice has traditionally been treated as an impermeable lid, but it is actuality a porous medium that functions as a reservoir and a transport pathway for biogenic gases such as (O<sub>2</sub>, CO<sub>2</sub> and DMS). From this perspective, ocean-ice-atmosphere transport can proceed along two pathways: (1) diffusive flux through the sea ice microstructure; and, (2) interfacial flux across the water surface within leads and other openings in the ice (Fig. 1).

The first of these two pathways was the subject of laboratory experiments by Loose et al., whose results indicate that diffusion through columnar sea ice in winter is within a factor of 10 of molecular diffusion in water (e.g. ~10-4cm².s-¹), and represents a very restricted pathway for exchange when ice is cold, and is therefore not a significant factor in ventilation of the ocean mixed layer. Gas exchange between the air and ice is an active area of research and field studies measuring significant quantities of authigenic gases in the ice, however the net seasonal magnitude and direction of these fluxes has not yet been established.

Likewise, interfacial (air-sea) exchange through openings in the ice pack is not well constrained, and we have observed that wind speed derived parameterizations of gas exchange may be inadequate given the importance of shear and buoyant convection in the ice-ocean boundary layer; as well as the interaction between short period waves and ice floes. The few data-based estimates of air-sea gas exchange in the sea ice zone may in fact enhance the rate of gas transfer that occurs in leads and polynyas.

These additional turbulence production mechanisms are particularly important in the marginal ice zone (MIZ) where the floe sizes are small and air-sea momentum transfer is enhanced. Consequently the MIZ may be responsible for more than 50% of

the net annual sea-air CO<sub>2</sub> exchange despite high rates of primary production (Loose and Schlosser, 2011; Fig.2). To parameterise the biogenic gas fluxes in the sea ice zone, it will be necessary to establish and prioritize the turbulent forcing mechanisms as well as the strength and timing of the phytoplankton bloom, in relation to the retreat of the ice edge in spring. We are currently conducting experiments at the USACE Cold Regions Research and Engineering Laboratory to measure gas exchange under a spectrum of IOBL forcing mechanisms.

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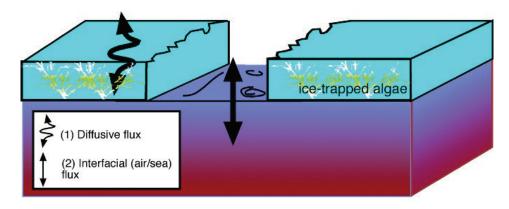
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↑ Figure 1: Diagram of gas transport pathways in the sea-ice zone.

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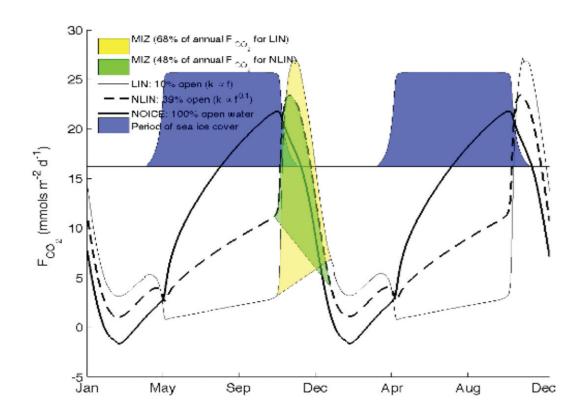
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A Figure 2: The seasonal cycle in the instantaneous CO₂ flux, FCO₂, over a 2 year period, depicting the timing of the maxima and minima in FCO₂ in relationship to the sea ice cycle in a 1D transport model. The shaded areas underneath the LIN and NLIN parameterizations of gas exchange indicate the area under these curves for the first 90 d immediately following ice cover retreat. For LIN this area represents 68% of the net annual sum of FCO₂ (see: Loose, B. and Schlosser, P. (2011). Sea ice and its effect on CO₂ flux between the atmosphere and the Southern Ocean interior. J. Geophys. Res. 116:C11019.)



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# Field measured atmospheric deposition fluxes over the Southern Ocean

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Atmospheric deposition is one of the major sources of nutrients bringing trace metals to the remote marine biota. Soil-derived atmospheric particles, which are our interest here, are produced by aeolian erosion in arid and semi-arid areas, transported over long distances and deposited onto remote oceanic areas. They are necessary for phytoplankton growth at extremely low concentrations.

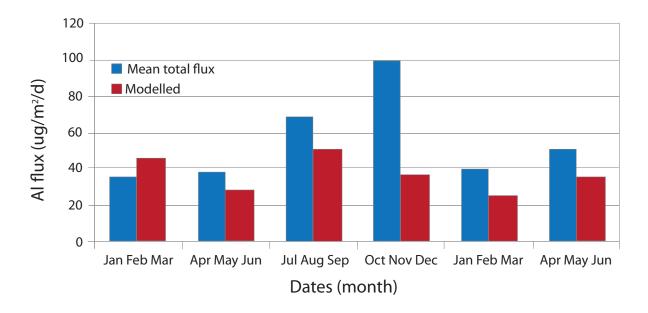
The High-Nutrient-Low-Chlorophyll (HNLC) Southern Ocean (between 40° and 65°S) is characterized by a lack of micronutrients, especially iron: Available trace metals depending on dust deposition could be a severe limiting factor for phytoplankton growth in this ocean. The Southern Ocean is one of the major sinks of CO<sub>2</sub> on Earth, and so its primary production can play a critical role in controlling climate. The recent inventory of iron deposition measurements to the world ocean in Mahowald et al. (2009) reveals the scarcity of deposition

measurements between 30°S and 60°S. In the Kerguelen oceanic area (49°S; 70°E), Wagener et al. (2008) used unique observation-derived data on dust deposition deduced from aerosol sampling at sea level and hypothetical modelled scavenging ratios available from the literature. He estimated a dust flux of 38±14µg.m-2.d-1 up to one order of magnitude lower than former prediction (Jickells et al., 2005; Mahowald et al., 2007).

In 2007-2011, we carried out the program FLATOCOA ("Flux Atmosphérique d'Origine Continentale sur l'Ocean Austral") supported by "Institut polaire français Paul Emile Victor", whose aim is to estimate the amount of atmospheric dust that reach the Southern Ocean from continental sources. Direct total atmospheric deposition and crustal aerosols sampling were continuously monitored over 18 months (2009-2010) at Kerguelen archipelago (49°18'S; 70°07'E) and one year (2010) at Crozet islands

(46°20'S; 51°40'E). Total deposition was sampled by duplicate devices erected on a 2m high PVC pipe. Each sampler was a 120 mm diameter PTFE Teflon® funnel screwed onto a 1L polypropylene bottle loaded with 50mL of 10% v/v Romil-UpA™ ultra pure nitric acid in ultra pure water. Aerosol samples were performed on Zefluor® filters using an open-face filter holder system with a 1m<sup>3</sup>.h<sup>-1</sup> pumping rate and protected into a bend pipe erected at 2m high. Since the air quality of the studied area is similar to ISO 4 clean conditions, all the sampling materials were carefully washed into different acid baths and then prepared in a clean room under ISO 1 laminar flow bench before being used.

Back in the laboratory, deposition samples were analysed by ICP-AES and HR-ICP-MS for several elements, mainly metals; aerosol filters by X-ray fluorescence. Results from our continuous time series show very low levels of dust and trace metal concentrations



↑ Figure 1: Three-month averaged total deposition fluxes of Al over the entire sampling period (from January 2009 to June 2010). Field measurements are in blue (left bar) and corresponding modelled outputs in red (right bar).

in the atmosphere comparable with those previously measured during oceanic cruises (Wagener et al., 2008).

Total dust deposition flux as derived from Al deposition measurements is 650µg.m<sup>-2</sup>.d<sup>-1</sup> on average over the entire sampling period and for the both locations. It is in relatively good agreement with current atmospheric models (Jickells et al., 2005; Mahowald et al., 2007). Over the studied area, we ran a chemical transport model based on reanalysis winds (Mahowald et al., 1997) using an emission and deposition module (Zender et al., 2003): Modelled results fit with observations pretty well during the entire sampling period expect from October to December 2009 (corresponding to spring in the Southern Hemisphere) where the model underestimates measured fluxes (Fig.1;2).

Measured dust deposition flux is one order of magnitude higher than the one proposed by Wagener et al. (2008), suggesting that surface concentrations are not representative of the concentration where dust is scavenged

by rain. This leads to very large computed scavenging ratio much larger than possible; and to the conclusion that deposition flux is difficult to derive from atmospheric concentrations at remote ocean sites (Heimburger et al., in review).

Our next step is to determine i) sources of the deposited dust using elemental composition signatures and ii) bioavailability for phytoplankton of deposited trace metals.

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### Nitrous oxide in the tropical Atlantic Ocean

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Although it is well known that the coastal and equatorial upwelling regions of the oceans are hot-spots for emissions of nitrous oxide ( $N_2O$ ) (Nevison et al., 1995), the  $N_2O$  emissions from upwelling regions are still associated with large uncertainties, as these regions display a large spatiotemporal variability in strength and extend of the upwelling. Therefore, a thorough investigation of the  $N_2O$  distribution and their transport processes in different upwelling areas will improve emission estimates from these regions.

Having conducted an extended measurement campaign in the upwelling region off Mauritania (Kock et al., 2012; Wittke et al., 2010), we took part in two cruises (Maria S. Merian Cruise MSM 18-2 and 18-3) to the equatorial Atlantic as part of the German SOPRAN project to collect data on N<sub>2</sub>O surface and water column distribution along with hydrographic, nutrient and oxygen data and microstructure profiles, allowing for the quantification of an N<sub>2</sub>O mixed layer budget in this area. The cruises took place in the equatorial Atlantic between 23°W and 0°W from May to July 2011. They covered the area of the Atlantic cold tongue where intense upwelling evolves in between May and October (Weingartner and Weisberg, 1991).

During MSM18-2 (*R/V Maria S. Merian*), we were able to observe the onset of the equatorial upwelling: two sections along the

equator with very similar cruise tracks between 23°W and 10°W were sampled with a time lag of three weeks, thereby covering the development of the cold tongue which was characterized by a significant drop in SST especially in the eastern part of the transect. Accordingly, the vertical N<sub>2</sub>O distribution in the upper 120 m changed significantly between the two transects, showing elevated surface N2O concentrations in the second transect. Both transects showed higher surface N2O concentrations towards the east of the sections (Fig. 1), which corresponds well to the location of the cold tongue which centres around 10°W. Surface waters showed supersaturations between 100 and 112% during the first transect, while N2O saturations rose from 110% at 23°W to 150% at 10°W during the second transect.

Highest supersaturations of about 200% were measured during the following cruise MSM 18-3 at 10°W, associated with the most intense upwelling encountered during both cruises. These saturations are relatively low compared to measurements from other upwelling areas (e.g. Bange et al., 2001; Charpentier et al., 2010) due to relatively low N<sub>2</sub>O concentrations in subsurface waters at the equator. Given the large area of the Atlantic cold tongue (Helber et al., 2007), this region could nevertheless make a significant contribution to the global oceanic emissions.

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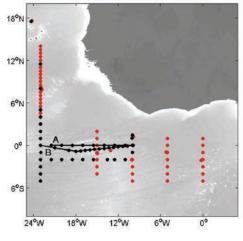
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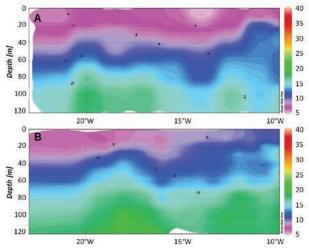
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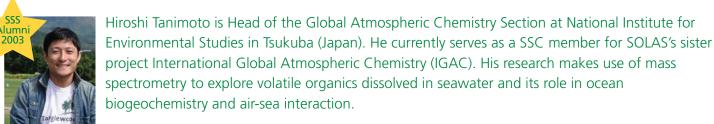
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↑ Figure 1: Station map of the MSM18-2 (black) and MSM18-3 (red) cruises to the equatorial Atlantic (left). The N₂O distribution in the upper 120 m along section A and B is shown on the right. Section A was sampled 17-23 May 2011, while section B was sampled 08-12 June 2011.







# High-resolution measurement of volatile organic compounds dissolved in seawater using proton transfer reaction-mass spectrometry (PTR-MS)

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Air-sea exchange of volatile organic compounds (VOCs) plays an important role in the Earth's biogeochemical cycles and the chemistry of the atmosphere. Dimethylsulphide (DMS) is photo-oxidized to form sulphate aerosols, which may affect the radiative budget of the atmosphere. Non-methane hydrocarbons (NMHCs) including alkanes, alkenes, aromatics and oxygenated VOCs, including aldehydes, ketones, and alcohols, contribute to the formation of photochemical oxidants and secondary organic aerosols. The ocean surface is a substantial natural source of atmospheric VOCs through a variety of biogeochemical and photo-induced processes. However, information on the distribution of VOCs in seawater, and the formation and destruction processes of VOCs in seawater are still largely unknown. Some of the uncertainty results from the

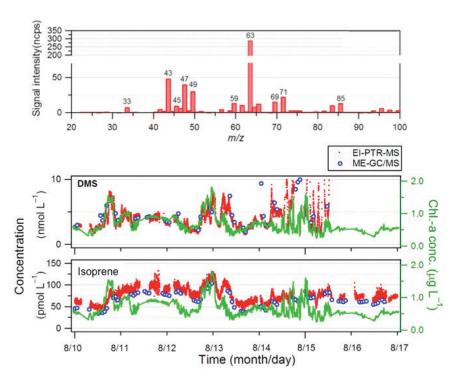
limited number of measurements of dissolved VOC concentrations in seawater. For example, although much attention has focused on describing DMS concentrations in the sea surface layer, previous studies showed large uncertainties and spatial differences of sea surface DMS concentrations (Kettle et al., 1999; Lana et al., 2011). Thus, our current understanding of ocean VOCs is greatly data-limited.

We have recently developed an equilibrator inlet–proton transfer reaction–mass spectrometry (EI-PTR-MS) system for high-resolution measurement of the concentrations of multiple VOCs dissolved in seawater. The equilibration of six VOCs (DMS, isoprene, propene, acetone, acetaldehyde, and methanol) between seawater samples and the carrier gas, and the response time of the system, were evaluated by means of a series of laboratory

experiments. Equilibrium between the seawater sample and the carrier gas in the equilibrator was not achieved for isoprene and propene (because of their low water solubility), but the other species did reach equilibrium. The detection limits are subnmol L-1 level at a 1-min time resolution (Kameyama et al., 2009; 2010).

In the past four years, we deployed the EI-PTR-MS instrument on R/V Hakuho-Maru during the Japanese SOLAS cruises conducted in the North Pacific Ocean. Rigorous intercomparison of PTR-MS to gas chromatography (GC) was made for measurements of DMS and isoprene, showing good agreement in general. Figure 1 shows an example of PTR mass spectrum of VOCs in surface seawater samples obtained in the North Pacific Ocean. The mass spectrum exhibited significant PTR signals from VOCs at m/z 33, 43, 45, 47, 49, 59, 63, 69, 71, and 85, which were assigned to methanol, propene, acetaldehyde, ethanol, methanethiol, acetone, DMS, isoprene, total C<sub>5</sub> alkenes  $(C_5H_{10}\bullet H^+)$ , and total  $C_6$  alkenes  $(C_6H_{12}\bullet H^+)$ , respectively. Also shown is the time-series of DMS and isoprene dissolved in surface seawater, together with chlorophyll-a concentrations observed in the North Pacific Ocean in summer 2008. EI-PTR-MS captured small-scale variability of DMS and isoprene dissolved in surface seawater, including elevated peaks associated with patches of high biogenic activity. This suggests that there are "hot spots" in the western North Pacific Ocean, and previous shipboard GC surveys may often have underestimated the variability in surface water concentrations. These field results demonstrate that the performance of the EI-PTR-MS system was sufficient for simultaneous and continuous measurements of multiple VOCs of environmental importance in seawater.





↑ Figure 1: (top) PTR mass spectra of VOCs dissolved in surface seawater in the North Pacific Ocean. (bottom) Temporal variations of DMS and isoprene dissolved in surface seawater during the 2008 cruise. Data collected at 5-s integration are plotted at 1-min intervals for EI-PTR-MS (red dots), overlaid with ME-GC/MS data (open blue circles) and chlorophyll-a concentrations (green line).

The EI-PTR-MS will be a powerful tool for hot-spot identification in the cruises; longterm baseline monitoring; and, incubation experiments, etc. (Kameyama et al., 2010). Together with other groups' mass spectrometric techniques (e.g., Saltzman et al., 2009; Tortell, 2005), our EI-PTR-MS would greatly contribute to increase the amount of data for dissolved VOCs; and, thereby enhance the spatial and temporal coverage of dissolved VOCs over wide regions of the ocean. Further measurements will improve our understanding of the biogeochemical mechanisms of the production, consumption and distribution of VOCs on the ocean surface and, hence, the air-sea flux of VOCs. Intercomparison exercises of conventional GC versus novel MS techniques and amongst different MS instruments should be made as a part of community effort.

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### Acknowledgments

This work is based on great contribution from postdoctoral scientists in our group at NIES, Sohiko Kamayema (now Assistant Professor at Hokkaido University) and Yuko Omori. Funding support is provided by the Ministry of the Environment, Japan, and the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.



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# Ocean Deoxygenation: Insights from Apparent Oxygen Utilization Rates in the Sargasso Sea

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Recent reports in the literature suggest that the oxygen content in the ocean is declining over time. This so-called " ocean deoxygenation" is important because low oxygen concentrations can have profound effects on ocean biota. Furthermore, changing oxygen concentrations can affect the biogeochemical cycles of many elements. Ocean deoxygenation is an expected effect of climate change due to the ocean becoming warmer and more stratified. Long time-series records of oxygen concentrations are crucial for investigating ocean deoxygenation. Additionally, in order to better understand the causes for deoxygenation, it is necessary to quantify oxygen sinks within the water column.

A major sink of oxygen in the interior of the ocean is the oxidation of organic matter that has been exported from the surface. This sink can be quantified by measuring Apparent Oxygen Utilization Rates (AOUR), a metric of export production that integrates over a large geographic area. AOUR estimates are particularly useful for studies of ocean deoxygenation because they allow separation of oxygen change into two components: a change in ventilation and a change in oxygen consumption rates. Thus AOUR allow scientists to answer the important question of whether oxygen is changing in a given location due to physical reasons or biological ones.

In a recently published paper, we determined AOUR at the Bermuda Atlantic Time-series Site (BATS) between 2003 and 2006 by combining records of oxygen concentration with water ages calculated from tritium/helium data using a transit time distribution (TTD) approach. The AOUR at a given depth and location is the cumulative sum of oxygen consumption over the entire trajectory of that water parcel since it left the ocean surface. Thus the depth-integrated AOUR is a projection of geographic and horizontally distributed processes and consequently

represents a regional view of export flux. We found that depth-integrated AOUR at BATS, which roughly represents export from the Eastern Subtropical North Atlantic, was equal to  $3.1 \pm 0.5$  mol  $O_2$  m<sup>-2</sup> y<sup>-1</sup>.

We then compared AOUR in 2003-2006 to AOUR calculated from data from the 1970s and 1980s (Fig.1). We found that AOUR in 2003 to 2006 was significantly greater than AOUR from 1977-1988. What is the reason for this apparent increase in AOUR with time? Is it a sign of ocean deoxygenation? When we separated AOUR into its two components – the apparent oxygen utilization (AOU) and the mean age of the water, we found that the ventilation age of the water did not change but that AOU was significantly greater in 2003-2006 than in 1977-1988. Thus the observed change in AOUR is not due to physical changes in ventilation but rather due to a changing AOU.

The change in AOU could be due to changes in export production associated with climate change or climate variability; or the AOU change could be due to methodological artifacts – oxygen is not easy to measure and older oxygen data is often flawed due to leaky collection bottles (often Nansen bottles rather than Niskin bottles) or due to bubble entrainment occurring during sample collection or titration. By examining the deep (>2000m) oxygen record at BATS and nearby Station S, we concluded that the change in AOUR in this case is most likely due to methodological artifacts. Although oxygen in such deep water is not expected to change much, the deep O<sub>2</sub> concentrations were much more scattered and significantly greater in the 1970s and 1980s than from 1992 onwards. Additionally, these deep O<sub>2</sub> variations were not correlated with changes in temperature or salinity, as would be likely if they reflected real

oceanographic changing conditions. Furthermore, for one time and location at which we also have oxygen data determined by a different program, the deep O<sub>2</sub> concentration recorded in the BATS/Station S record was significantly larger than the other program's. The conclusion that the differences in AOUR observed in this study are likely due to methodological artifacts suggests that caution should be applied when O<sub>2</sub> inventories are compared at other locations; scientists should not simply use historical oxygen data without carefully analyzing them for potential methodological issues.

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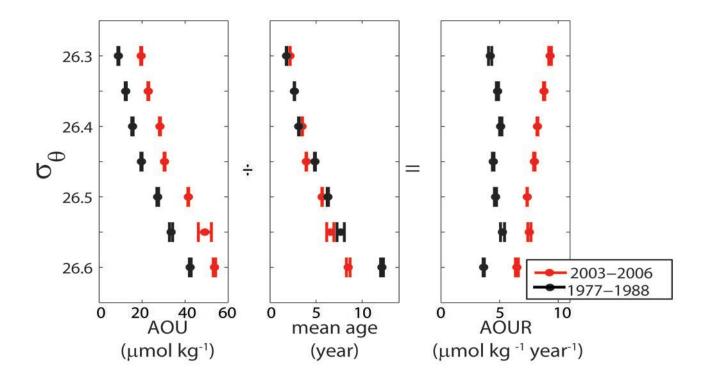
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↑ Figure 1: Verticle profiles of the Apparent Oxygen Utilization (AOU), mean age of water, and Apparent Oxygen Utilization Rates (AOUR) at the BATS site from 2003-2006 (red) and from 1977-1988 (black), averaged over isopyncal surfaces, in the upper 500 m of the water column. The AOUR is significantly greater in 2003-2006 than in 1977-1988 due to changes in AOU, rather than to changes in mean age. This suggests that changing oceanic ventilation is not responsible for the change in AOUR at this location. Figure modified from Stanley et al., 2012.



Tom Bell began his scientific career at the University of East Anglia (UK) focusing on marine dimethylsulphide (DMS) and ammonia cycling. He then worked with the international SOLAS community to improve estimates of global air-sea fluxes. Tom is currently at the University of California, Irvine (USA) making measurements of DMS flux by eddy covariance.

### Dimethylsulphide (DMS) air-sea gas exchange in the North Atlantic

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Gas exchange between the ocean and atmosphere (or air-sea flux) is a major term in the global budgets of many compounds of biogeochemical and climatic importance (e.g. CO<sub>2</sub>, DMS, O<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, halocarbons, and NH<sub>3</sub>). The primary physical forcing for air-sea gas transfer is horizontal wind speed (stress) at the ocean surface.

Parameterisation of air-sea gas transfer is a major uncertainty in global biogeochemical models. Improvements are necessary in order to predict how air-sea fluxes will vary in the future in response to changing climate.

Eddy covariance involves the direct determination of air-sea gas fluxes on the atmospheric side of the interface. This technique has been applied at sea to CO<sub>2</sub> and DMS (e.g. Marandino et al., 2007; McGillis et al., 2001; Yang et al., 2011). The flux of DMS is determined using the covariance between fluctuations in the vertical winds and atmospheric DMS concentrations. In contrast to integrated geochemical or surface ocean budget techniques, eddy covariance measures air-sea fluxes on a timescale of minutes. This enables the study of gas exchange in response to more rapid variations in the dynamics of the air-sea interface.

Eddy covariance DMS flux measurements were made aboard the RV Knorr during a 2011 cruise to the summertime, high-latitude North Atlantic. DMS was measured continuously in seawater and air using atmospheric pressure chemical ionization mass spectrometry (Marandino et al., 2007; Saltzman et al., 2009). Gas transfer coefficients were calculated from:

$$K_{DMS} = F_{DMS} = F_{DMS}$$

$$\Delta C DMS_{sw} - DMS_{air} .H_{DMS}$$

Where the gas transfer coefficient is in water side units ( $K_{DMS}$  in ms<sup>-1</sup>; Liss and Slater, 1974) and  $F_{DMS}$  is the DMS air-sea flux (mol.m-<sup>2</sup>.s-<sup>1</sup>). The concentration difference across the interface,  $\Delta C$ , is calculated from seawater DMS (DMS<sub>sw</sub> in mol.m-<sup>3</sup>), atmospheric DMS (DMS<sub>a</sub> partial pressure, in atm) and the temperature-dependent DMS solubility in seawater ( $H_{DMS}$  in mol.atm-<sup>1</sup>.m-<sup>3</sup>; Dacey et al., 1984).

Figure 1 shows the relationship between gas transfer coefficient and horizontal wind speed for four stations occupied for 24-36 hours during the cruise. Model estimates of gas transfer coefficients for CO<sub>2</sub> and DMS are also shown (COARE v3.1; Fairall et al., 2011). Observed DMS gas transfer coefficients are lower than those predicted for CO<sub>2</sub>. This agrees with previous results (Huebert et al., 2004; Huebert et al., 2010; Marandino et al., 2009) and is expected: DMS is a more soluble gas than CO<sub>2</sub> and bubble-mediated transfer is less effective at intermediate/high wind speeds (Blomguist et al., 2006). The current version of the COARE model includes the bubble effect and the modeled CO<sub>2</sub> and DMS curves are the result of the solubility difference between the two gases (Fig. 1).

The four stations of data in Figure 1 exhibit different functional relationships in gas transfer coefficient versus wind speed. For example, Station 187 (ST187) has a much steeper slope than ST191. The data suggest that the process of gas transfer responds to in situ conditions that are not directly related to wind speed. Variations in wave age, wind/wave direction, surfactant coverage, microlayer processes, whitecap coverage and/or bubble spectra could all play a role in determining the relationship between the gas transfer coefficient and wind speed.

The cruise data exhibit a surprising lack of wind speed-dependence above 10ms-1. The high wind speed data is dominated by measurements made during ST191. This behaviour is not predicted by the COARE DMS model, which assumes that interfacial gas transfer is nearly linear with wind speed based on the work of Mueller and Veron (2009). The relatively invariant observed gas transfer coefficients when wind speeds are greater than 10ms-1suggest more complex behaviour (e.g. Soloviev, 2007). Flow separation at the air-sea interface (wave shielding) has been observed in a windwave tank (Reul et al., 1999; Reul et al., 2008). Surfactants suppress the fluxcarrying capillary waves on the sea surface (Salter et al., 2011). Increased whitecap coverage at intermediate/high wind speeds

may result in bubbles bringing more surfactants to the sea surface.

Eddy covariance data are beginning to shed light on the variability in gas transfer coefficients and the processes that help to determine air-sea fluxes. The next step is to make more of such measurements coupled with observations that describe the air-sea interface, particularly at intermediate/high wind speeds.

http://www.mendeley.com/profiles/tom-bell/

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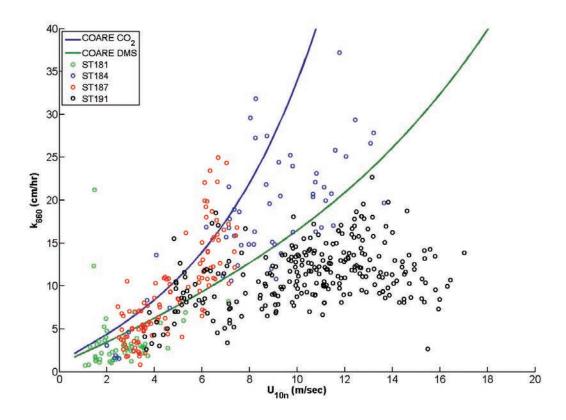
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 $\Lambda$  Figure 1: Scatterplot of  $k_{660}$  (water side-only gas transfer coefficient, normalised to a single diffusivity (Schmidt number=660) versus  $U_{10}$  (horizontal wind speed adjusted to 10m above the sea surface and to neutral buoyancy conditions). Individual data points represent 10 minute averages from four stations in the North Atlantic. The NOAA COARE model v3.1 (A=1.6, B=1.8) was run using mean Knorr\_11 input values and the output for DMS and CO<sub>2</sub> are plotted for reference.



Matt Woodhouse was a SOLAS-funded PhD student at the University of Leeds (UK), finishing in 2010. During his PhD, he used a global model of aerosol processes (GLOMAP) to investigate the role of DMS in atmospheric aerosol, in order to evaluate the strength of the CLAW feedback. Matt currently works on the EU Monitoring Atmospheric Composition and Climate (MACC) project at Leeds.

### Clouds limit CLAW feedback

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In 1987, Charlson et al. proposed a link between climate, phytoplankton and clouds, an idea which became a fundamental driver of SOLAS science. The idea, known since as the CLAW hypothesis, suggested that a warming ocean might promote more phytoplankton activity, in turn leading to increased sea-air fluxes of the gas dimethylsulphide (DMS). The flux of DMS to the atmosphere is important as DMS oxidation products contribute significantly to marine aerosol. The atmospheric sulphur cycle is shown in Figure 1. An increased flux of DMS was suggested to increase the abundance of cloud condensation nuclei (CCN), making clouds more reflective (the first aerosol

indirect effect). Charlson et al. (1987) therefore outlined a climate feedback that could potentially offset some of the warming from anthropogenic greenhouse gas emissions.

Article continues on next page

However, CLAW has proven difficult to pin down. Studying CLAW means spanning scales from nanometre-sized aerosol, through micron-sized phytoplankton, and all the way up to large marine stratocumulus cloud decks. Due to the time taken to convert DMS to cloud-relevant aerosol - perhaps up to a few days - any signal of altered aerosol or cloud optical properties resulting from a sudden influx of DMS (from a phytoplankton bloom for example) is very difficult to detect. Satellite observations and in situ studies therefore struggle to detect a CLAW signal.

From the aerosol perspective, to demonstrate the feasibility of the CLAW feedback, it is necessary to show a strong link between emission of DMS and formation of new CCN. Without this link, the CLAW feedback cannot operate (any chain is only as strong as its weakest link).

Detailed enough representations of aerosol microphysics to probe CLAW have only recently become available. The previous generation of aerosol models typically relied on a fixed (empirical) relationship between sulphate mass and aerosol number.

In reality, aerosol microphysics mean a complex fate for DMS-derived sulphur (Fig. 1). We highlighted this complexity in Woodhouse et al. (2008). More sophisticated aerosol models (like GLOMAP, Mann et al., 2010) can track the mass, size and number of aerosol particles necessary to represent the conversion of DMS to aerosol.

Using an array of model-derived sea-surface DMS climatologies and the GLOMAP model, we also quantified the response of CCN to changes in the flux of DMS, terming it CCN sensitivity: dCCN/dFlux (DMS) (Woodhouse et al., 2010). In relative terms, the global mean CCN sensitivity was found to be approximately 0.05. To state that in a different way, to yield an increase of CCN of 5%, DMS flux would have to have to increase by 100%. The conversion of DMS to CCN is therefore a weak link in the CLAW chain.

These modelling results, and the recent review of Quinn and Bates (2011), lead to the conclusion that after two decades of research, the weight of evidence suggests a negligible role for DMS in present-day

climate regulation. Despite this negative result, marine science has progressed enormously as a result of interest in the CLAW feedback.

So we are now left with the question "why is the CLAW feedback so weak?". The answer lies in the fate of DMS-derived sulphur in the atmosphere. Observations (Andreae et al., 1999; O'Dowd et al., 1999) have shown that most sulphate production occurs in cloud in regions of extensive stratocumulus. This aqueous-phase oxidation process converts SO<sub>2</sub> into sulphate in cloud droplets, effectively increasing the size of existing CCN. Crucially, this process does not create new CCN (Fig. 1), a necessary step to alter the optical properties of clouds via the aerosol indirect effect. From the atmospheric side of things, the oxidation of SO<sub>2</sub> in the aqueous-phase can be considered the limiting step - most of the SO<sub>2</sub> derived from DMS is hoovered up by clouds in such a way that no new CCN can be formed, hence the weak CLAW feedback.

Perhaps the door is still open for CLAW in other periods in Earth history, including in the much cleaner pre-industrial period. Our observations are of course limited to the present-day, and my modelling work has focused only on the present-day, so maybe there was a role for CLAW sometime in the past.

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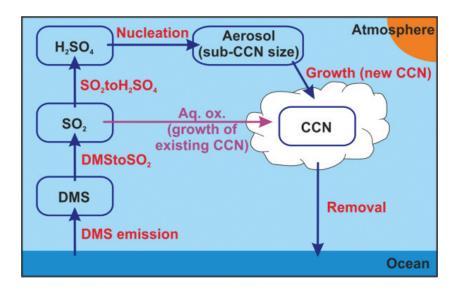
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↑ Figure 1:The marine atmospheric sulphur cycle. Aqueous-phase oxidation does not lead to the formation of new CCN, but only grows existing CCN in cloud droplets.



Mingxi Yang was raised in China, schooled in America and currently performing research in the UK. Having spent time on both research ships and aircraft, he straddles the boundary between chemical oceanography and atmospheric chemistry. Outside of work, he has extended his experience in air-sea gas exchange to beer brewing.

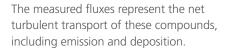
### Air-Surface Fluxes of Oxygenated Volatile Organic Compounds

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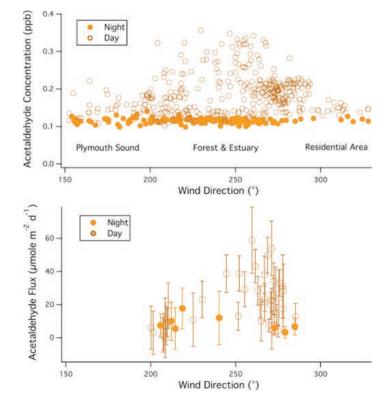
Oxygenated Volatile Organic Compounds (OVOCs), such as alcohols, ketones, and aldehydes, are low molecular weight carbon-containing compounds found ubiquitously in the lower atmosphere. They can be emitted from natural or anthropogenic sources, (photo)chemically produced or destroyed in air, and lost to the surface via deposition. OVOCS are important in atmospheric chemistry and climate because they alter the tropospheric oxidative capacity by influencing the cycling of ozone and the hydroxyl radical (OH). Terrestrial plants are found to be the predominant source of OVOCs thus far. The role of the ocean to these compounds, however, remains poorly quantified. Some OVOCs may be produced in the ocean and emitted to the atmosphere, while others are released to the air from other sources and dissolve into the ocean. The major uncertainty stems from the scarcity of air-sea flux and concentration measurements.

As part of his current research, Mingxi directly measure the vertical turbulent fluxes of methanol, acetone, and acetaldehyde concurrently using the eddy covariance method. For proof of concept and characterization of the instrument, measurements have been made from the rooftop of the Plymouth Marine Laboratory (~40m above sea level), which faces the Plymouth Sound (sea) to the S (~200m from shoreline); the Tamar Estuary to the SW/W; and, residential areas in the other wind sectors. A large, forested park of mostly broad-leaf trees stands across the estuary in the WSW. The concentrations of OVOCs are quantified by a proton-transfer-reaction mass spectrometer (PTR-MS) at a high frequency and further calibrated by a continuous isotopic standard. The eddy turbulent fluxes are calculated as the hourly means of the products between concentrations and vertical wind velocity, the latter measured by a sonic anemometer.



Because of their varying chemical lifetimes in the atmosphere, distributions of methanol, acetone, and acetaldehyde show different patterns from their sources. With a short lifetime of only several hours in the troposphere due to reaction with OH and photolysis, acetaldehyde concentration responds the mostly directly to local emissions, and is less influenced by long distance transport. Figure 1 plots the atmospheric acetaldehyde concentration vs. wind direction on top, and its vertical flux vs. wind direction on the bottom for selected periods in May and June. Higher acetaldehyde concentrations are observed during the day, peaking in the direction of WSW (forest and estuary), while nighttime concentrations are low and relatively independent of wind direction. The directionality in the concentrations suggests a greater daytime emission of acetaldehyde from the forest, which is confirmed by the clear day/night difference in the turbulent fluxes from WSW. In contrast, acetaldehyde fluxes from the direction of Plymouth Sound are fairly constant and low, with an average of ~7 µmoles.m-2.day-1, implying a small seato-air emission. This measured flux is in broad agreement with predictions using gas exchange formulation, atmospheric, and seawater concentrations of acetaldehyde in the Plymouth Sound. Details of these flux measurements and analysis will be presented in a manuscript currently in preparation.

Mingxi's next goal is to measure the air-sea fluxes of methanol, acetone, and acetaldehyde over the open ocean, which, if successful, would represent a significant step forward in the study of global cycling of OVOCs. In addition, combining with concurrent seawater concentrations of these compounds should allow for verifications of their air-sea transfer velocities, which hopefully will further our understanding in the physics involved in gas exchange. He will attempt these measurements on the Atlantic Meridional Transect cruise from the U.K. to Chile this autumn, going through several distinct oceanic provinces.



↑ Figure 1:Atmospheric acetaldehyde concentration (5 minute averages) vs. wind direction (top); acetaldehyde flux (hourly averages) vs. wind direction (bottom) for selected periods in May and June 2012. The 'day' and 'night' filters approximately correspond to one hour after sunrise to one hour before sunset, and one hour after sunset to one hour before sunrise, respectively.



Cathleen Zindler obtained her BSc in biological sciences from Muenster University (Germany) and her MSc in biological oceanography from University of Southern Denmark, Odense. Since 2008, she has been a PhD student at the Helmholtz Centre for Ocean Research Kiel, GEOMAR (Germany) investigating the surface seawater cycling of trace gases such as OVOCs and DMS.

# Marine Sources and Sinks of Oxygenated Volatile Organic Compounds (OVOC)

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Ketones, aldehydes, alcohols and carboxylic acids (e. g. acetone, acetaldehyde, ethanol, and formic acids) are known as oxygenated volatile organic compounds (OVOC). Most of them are ubiquitous in the atmosphere (Singh et al., 1995) and play an important role in atmospheric HOx, O3, PAN, and secondary organic aerosol formation (Blando and Turpin, 2000; Singh et al., 1994; 1995; Lary and Shallcross, 2000; Monks 2005; Mueller and Brasseur, 1999; Wennberg et al., 1998;). Although different atmospheric sources (anthropogenic and biogenic emissions, biomass burning, atmospheric oxidation of precursors, and plant decay) and sinks (wet and dry deposition, reaction with OH, and photochemical oxidation) for OVOCs are known; the budget is not balanced. One of the largest uncertainties lies in the role of the ocean. There are limited data which identified possible sources in the surface ocean, such as photochemical and photosensitized oxidation of colored dissolved organic matter (CDOM) (de Bruyn et al., 2011; Ehrhardt and Weber, 1991; Kieber et al., 1990). Additional sources might be biological production, air/sea gas exchange and CDOM oxidation due to radicals (Dixon et al., 2011a; b; Nemecek-Marshall et al., 1995; Mopper and Stahovec, 1986; Singh et al. 2003; 2004). Possible oceanic sinks for OVOCs might be biological consumption, air/sea gas exchange, and photochemical and radical oxidation of OVOCs (Obernosterer et al., 1999; Singh et al., 2003; 2004; Sinha et al., 2007; Sluis and Ensign, 1997). Whether the ocean is a source or a sink of these compounds to the atmosphere is still debated. For example, Jacob et al. (2002) modeled the ocean to be a source for acetone, while Marandino et al. (2005) measured direct flux of acetone in the Pacific Ocean and identified the ocean as a sink.

Due measurement difficulties, complete understanding of marine sources and sinks of OVOCs, as well as the magnitude and direction of their air-sea exchange, has not been obtained. In order to gain further understanding of surface-ocean OVOC cycling, we conducted incubation

experiments in the Baltic Sea and in the equatorial Atlantic Ocean in March/April and July 2011, respectively, to identify possible biological and chemical sources and sinks for acetone and acetaldehyde. We measured water samples using a purge and trap system coupled to a gas chromatograph and a mass-spectrometer. Surface seawater was sampled and split into four treatments: filtered in light (FL), filtered without light (FD), unfiltered with light (UL), and unfiltered without light (UD). The treatments were spiked with  $C^{13}$ labeled OVOCs and and both C13 and natural C<sup>12</sup> OVOCs were measured over 12 to 24 hours in order to determine the consumption and production rates. Other parameters were measured simultaneously, such as pigments, bacterial cell numbers, light, nutrients, temperature, and CDOM, in order to understand what variables control the production and consumption rates. Preliminary results showed two orders of magnitude higher consumption and production rates in the coastal Baltic Sea compare to the upwelling in the Atlantic Ocean for both acetone and acetaldehyde. We speculate that this is due to higher concentrations of CDOM and higher productivity in the Baltic waters. The UL (full biological community preserved) samples showed higher production rates than the FL and FD samples (either no phytoplankton or autoclaved to also contain less bacteria). However, the final workup of the ancillary data has not yet been performed and is needed to determine the difference in the rates. We could also detect differences between acetone and acetaldehyde rates. The UL treatment indicated the highest consumption and production rates for acetone, which was not the case for acetaldehyde.

Possibly, photosensitive organisms are responsible for the acetone production in surface seawaters. Lower production rates in general were found for acetaldehyde compared to acetone in both regions. It is possible that the ocean is a stronger source

for acetone than for acethaldehyde. We see that the ocean can be both a source and sink for OVOCs depending on the region, biological activities, and light conditions, which is in agreement with Sinha et al. (2007). In the future, we hope to perform these incubation experiments for a broader range of oxygenated compounds.

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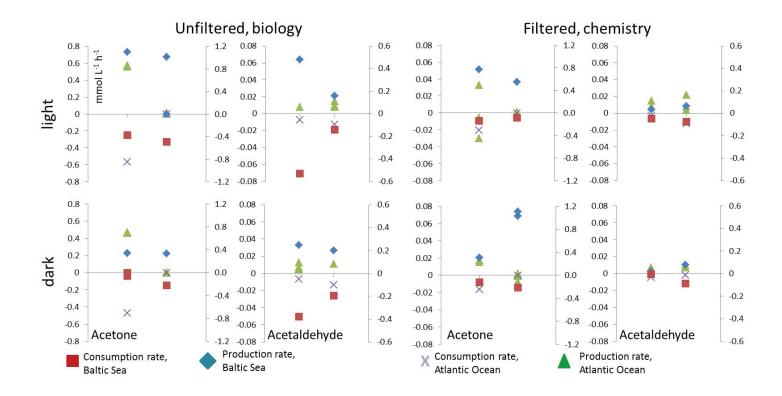
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↑ Figure 1: Acetone and acetaldehyde production and consumption rates measured during two incubation experiments conducted in the Baltic Sea and equatorial Atlantic Ocean in March/April and July 2011, respectively. The upper panels show samples which were exposed to natural light and the lower panels show samples incubated in the dark. The four panels on the left hand side are unfiltered samples (biologically active) and the four panels on right hand side are filtered and autoclaved (only for the Atlantic samples) to investigate chemical processes. Sometimes more than one production rate per experiment is shown because the intensity of the production rates changed over time within the incubation experiments.



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Mesoscale cyclonic eddies influence the carbonate chemistry and stimulate productivity in coastal ocean: A case study in the western

### South China Sea

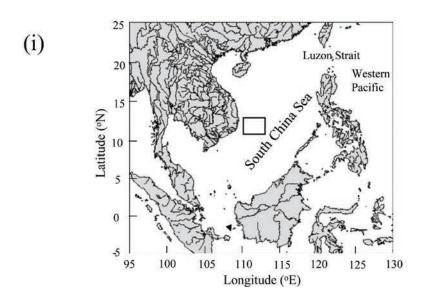
X. Guo

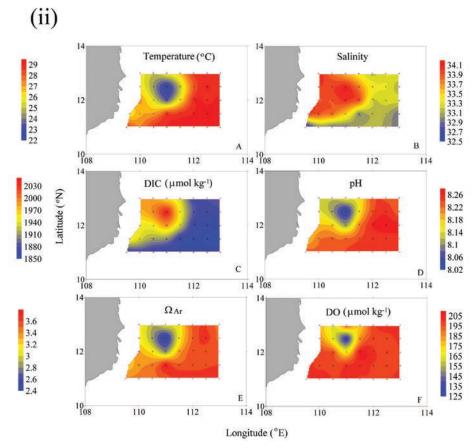
Xianghui Guo, State Key Laboratory of Marine Environmental Science, Xiamen University, Xiamen, China. Contact: xhguo@xmu.edu.cn

The western South China Sea (WSCS) is located in a tropical zone. The continental shelf of the WSCS off central Vietnam is very narrow. There form a northerly coastal jet off the coast of Vietnam, which turns eastward into the interior of the WSCS. The strong eastward baroclinic jet is likely to generate eddies (Gan and Qu, 2008). The Mekong River is the largest river emptying into the WSCS with an annual freshwater discharge of 4.7x10<sup>11</sup>m<sup>3</sup> (MRC, 2008). To study the kinetics and biogeochemical influences of the eddies on the WSCS, a cruise that conducted interdisciplinary study of physical, chemical, biological and geological oceanography was organized in September of 2007.

The eddy was centered at 111 °E, 12.5 °N with a diameter >160 km (Fig.1). The Mekong River plume water covered most of the study area beyond the eddy. Temperature, pH and dissolved oxygen (DO) in the eddy core were ~ 6°C, 0.1-0.2 and ~50 µmol.kg-1 lower, while salinity and dissolved inorganic carbon (DIC) were 0.5-1.0 and 100-150µµmol.kg-1 higher than in the ambient waters. Saturation state of aragonite ( $\Omega_{Ar}$ ) in the eddy core was 2.4, which was 1.0-1.2 lower than in the ambient water. The eddy intensity was substantially weakened below the pycnocline at ~100 m.

The water mass mixing ratios were calculated using a three end-member mixing model; and the DIC removal was estimated thereby. The difference between the observed DIC and the expected conservatively mixed DIC was defined as DDIC. In the study area beyond the eddy, ΔDIC was -7.7(±23.1) μμmol.kg<sup>-1</sup> in the water column of the upper 25 m, which means removal. Using a water residence time of 14 days (Chen et al., 2010), the DIC removal rate was 0.17(±0.51) g.C.m<sup>-2</sup>.d<sup>-1</sup>.





 $\Lambda$  Figure 1: (i) Map of the South China Sea and (ii) Horizontal distribution of temperature, salinity, dissolved inorganic carbon (DIC), pH, saturation state of aragonite ( $\Omega_{Ar}$ ) and dissolved oxygen (DO) at 25 m in the western South China Sea during the survey. The rectangle in panel (i) is the study area.

### national report

As both biological uptake and  $CO_2$  exchange between the water and the atmosphere influence DIC, subtracting the  $CO_2$  evasion rate (0.02±0.01 g.C.m<sup>-2</sup>.d<sup>-1</sup>, Dai et al., unpublished), the net community production (NCP) rate of 0.15(±0.51) µmol.kg<sup>-1</sup> was estimated. It agreed with the estimated new production in the WSCS (0.09-0.18 g.C.m<sup>-2</sup>.d<sup>-1</sup> based on primary production and the ratio of new production to primary production).

In contrast,  $\Delta$ DIC in the eddy was -19.1 (±6.9) μmol.kg<sup>-1</sup> in the water column of the upper 25 m and -10.4(±5.8) µmol.kg-1 in the upper 50. Using a period of 12 days between the formation of the eddy and the sampling time (http://argo.colorado.edu/ ~realtime/gsfc\_global-real-time\_ssh/), the DIC removal rate was 0.49(±0.18) g.C.m<sup>-2</sup>.d<sup>-1</sup> in the water column of the upper 25m and 0.53(±0.30) g.C.m<sup>-2</sup>.d<sup>-1</sup> in the upper 50m. Subtracting the CO<sub>2</sub> evasion rate (0.08±0.02 g.C.m<sup>-2</sup>.d<sup>-1</sup>, Dai et al., unpublished), NCP rates of 0.41(±0.18) and  $0.45(\pm 0.30)$  g.C.m<sup>-2</sup>.d<sup>-1</sup> were estimated in the water columns of the upper 25m and 50m. Compared with the area beyond the eddy, NCP rate in the eddy was improved by ~two times.

The enhanced productivity in the cyclonic eddy increased pH and saturation state of calcium carbonate. It relieved the acidification effect induced by the cyclonic eddy and added complexity in the carbon biogeochemistry in the upper WSCS.

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#### **SOLAS** Australia

The Antarctic Climate and Ecosystems, CRC, has investigated the distribution of a variety of micronutrient trace metals in sea ice, to determine a possible co-limiting affect of these metals on primary production in the Southern Ocean. The first detailed study of Antarctic pack ice (SIPEX voyage, September/October 2007) found trace metals were concentrated in sea ice but at levels not toxic or limiting for algal growth (Lannuzel et al., 2011, van der Merwe et al., 2011a). A second study of land-fast ice off the coast of Antarctica's Casey station during austral spring/summer 2009 (van der Merwe et al., 2011b), assessed, for the first time, detailed particulate size fractionation of metals during melting of sea-ice (Lannuzel et al., in prep).

Scientists at the Centre for Australian Weather and Climate Research (CAWCR) at CSIRO are developing a scientific observation framework and research tool to more accurately determine the efficiency and temporal behaviour of the Southern Ocean CO<sub>2</sub> sink. This involves atmospheric inversion modelling utilising a high precision Southern Ocean atmospheric observation network and state of the art oceanic modelling. Instrumental and site biases are being addressed, as well as linking datasets collected at Baring Head, Macquarie Island, Cape Grim, and Amsterdam Island, to a common derived calibration scale.

Australia's new Ocean-going future research vessel, the RV Investigator, is due for completion in June 2013. The RV Investigator will have dedicated atmospheric composition laboratories, can accommodate 40 scientists and will be used by Australian universities, research organisations and international collaborators. For more information, please visit: http://www.marine.csiro.au/nationalfacility/Investigator/index.htm

Two Special Editions of Deep Sea Research Part II were published in 2011 containing publications from Australian authors: The SOLAS Air-Gas Exchange (SAGE) Experiment 2004 and Biogeochemistry of the Australian Sector of the Southern Ocean.

The GEOTRACES section GP13 leg in Southwest Pacific Ocean was completed by Australian scientists, May –June 2011, along approximately 30°S. For science highlights, please visit: http://www.marine.csiro.au/nationalfacility/sciencehighlights/2011/MNF-SH\_ss2011\_v02.pdf and view the report at: http://www.marine.csiro.au/nationalfacility/voyagedocs/2011/MNF-SS2011\_v02\_summary.pdf

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# IMPORTANT NEWS - New SOLAS website coming soon!

The SOLAS website is currently receiving a facelift where, we endeavour, it will become brighter, easy-to-search and updated with news as soon as it comes in. The new website will become active very shortly so if you notice that the SOLAS website is down, this is simply due to the transfer between servers.

This will be a short process so please keep checking. The web address will remain the same and we really hope you like it.

http://www.solas-int.org/

# SOLAS Open Science Conference 2012



The SOLAS Open Science Conference was held against the striking background of Suncadia Resort in Cle Elum, Washington State (USA). Organised and run by a committee of 16 nationalities, the conference welcomed 190 attendees from over 25 countries to share their research and knowledge of SOLAS science.

The four-day conference encompassed a spectrum of modes of communication, including plenary talks from experts, planning and synthesis sessions, and poster sessions from a large number of scientists, all wanting to share and explore the work of the SOLAS research community.

The lectures ranged over the whole spectrum of SOLAS science covering the following themes:

- Sea-ice biogeochemistry and interactions with the atmosphere
- Long-lived greenhouse gases: sea-air exchange and impact
- Ocean-derived aerosols: production, evolution and impacts
- Physics or air-sea exchange
- Atmospheric control of nutrient cycling and production in the surface ocean
- SOLAS and the future ocean
- Air-sea gas fluxes at Eastern boundary upwelling and oxygen minimum zone (OMZ) systems
- Emerging issues.

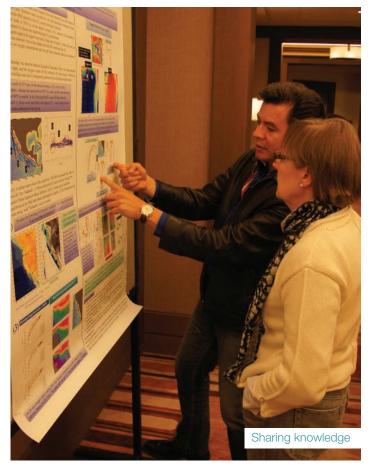
Not only did the conference allow subject specialists to give lectures to the attendees but it created a location for current projects and ideas to be put forward in the discussions sessions; the outcomes of some of these sessions are presented in this issue of SOLAS news.

The conference also offered these benefits to all who displayed their posters. These sessions were held over the first three days of the conference, permitting researchers to communicate their findings with others working over the whole spectrum of SOLAS science.











SOLAS would like to take this opportunity to thank all who contributed to making the SOLAS Open Science Conference 2012 a success: the Local Organising Committee; the Scientific Organising Committee; all plenary and discussion session chairs, speakers (Caroline Leck, Véronique Schoemann, Mónica Orellana, Anna Granfors, Yukihiro Nojiri, Dorothee Bakker, Annette Kock, Christoph Heinze, Cristina Facchini, Elizabeth Minor, Ilan Koren, Rainer Volkamer, Carol-Anne Clayson, Christoph Garbe, Mingzi Yang, Wade McGillis, Emilio Marañón, Huiwang Gao, Mark Moore, Tim Jickells, Scott Doney, Cliff Law, Andreas Oschlies, Sophie Bonnet, Damodar Shenoy, Martín Hérnández-Ayón, MIchio Aoyama, Xiaohong Yao, Roberta Hamma and Lihini Aluwihare); and, finally all who attended.

Georgia Bayliss-Brown SOLAS Project Officer

All photos: Stefan Kontradowitz





# SOLAS Open Science Conference 2012

# CMOS Student Poster Awards at the SOLAS Open Science Conference

In a new collaboration between two organizations with a natural affinity, the Canadian Meteorological and Oceanographic Society (CMOS) sponsored the student poster prizes at the Surface Ocean-Lower Atmosphere Study (SOLAS) Open Science Conference held in Washington State in early May.

Thanks to a donation from CMOS, Prof. Roberta Hamme (UVic) awarded prizes of US\$100 to each of five students whose poster presentations demonstrated outstanding originality, scientific quality and clarity. The SOLAS community thanks CMOS for their support, encouragement, and recognition of these exemplars of the best of future ocean-atmosphere scientists.



These posters can be viewed at http://www.solas-int.org/news/conferencemeetings/OSC2012/posters.html





### Winner Matthieu Bressac

## Impact of Saharan dust deposition on dissolved-colloidal-particulate nutrient distribution in seawater

<sup>1,2</sup>M. Bressac, <sup>2</sup>C. Guieu, <sup>2</sup>J. Louis and <sup>2</sup>M.-L. Pedrotti <sup>1</sup>ACRI-ST, Sophia Antipolis, France <sup>2</sup>Laboratoire d'Océanographie de Villefranche/Mer, CNRS-INSU-UPMC, Villefranche-sur-Mer, France. Contact: bressac@obs-vlfr.fr

In this study, we explored the role of dust deposition on the aggregation process in the surface ocean and its impact on the fate of new atmospheric nutrients. Three experiments were conducted in abiotic conditions at different seasons (bloom, stratified and mixing periods characterised by contrasting dissolved organic matter (DOM) content) by artificially seeding a 300-litre, 0.2µm-filtered seawater tank (clean sampled). Changes in Fe and P concentrations following the seeding were measured for six days.

Results suggest that interactions between lithogenic particles and DOM partially control the evolution of the physical speciation of nutrients. Indeed, the seeding led to a huge input of new dissolved Fe and P with very fast dissolution kinetics. Thereafter, high DOM content promoted the formation of mineral-organic aggregates which, in turn, induced a negative feedback on dissolved nutrient concentrations through scavenging on the particulate phase. This study illustrates the importance of the DOM and associated abiotic processes for the fate of new atmospheric nutrients in seawater.



### Winner Kristina Brown

Observations of air-ice-ocean-CO2 cycling during spring melt in Resolute Passage, Nunavut (Arctic-ICE 2010)

<sup>1</sup>K. Brown, <sup>2</sup>L. Miller, <sup>3</sup>C. Mundy, <sup>3</sup>T. Papakyriakou, <sup>4</sup>M. Gosselin, <sup>3</sup>K. Swystun, <sup>1</sup>P. Tortell and <sup>1</sup>R. François <sup>1</sup> University of British Columbia, Vancouver, Canada; <sup>2</sup> Fisheries and Oceans Canada, Institute of Ocean Sciences, Sidney, Canada; <sup>3</sup> University of Manitoba, Winnipeg, Canada; <sup>4</sup> University of Quebec at Rimouski, Rimouski, Canada. Contact: kbrown@eos.ubc.ca

Increasing porosity in spring sea-ice can result in the release of trapped brine and gases to underlying surface waters. This, in combination with ice-melt derived surface freshening, can influence  $CO_2$  transfer between the atmosphere and the ocean, potentially enhancing  $CO_2$  export below the mixed layer as seasonal sea ice recedes. Here we present a five-week time series of discrete carbonate system (DIC, Alk, pCO<sub>2</sub>) and isotopic tracer (del<sup>13</sup>C-DIC and del<sup>18</sup>O-H<sub>2</sub>O) measurements from sea ice, sack hole brine, and the underlying water column during the 2010 winter-spring transition in Resolute Passage, Nunavut. We observed significant changes in bulk sea-ice and sack-hole brine carbonate system parameters associated with increasing sea ice temperatures and high bottom ice chlorophyll a, despite little change in the water column over the same period. Stable isotope composition of sack hole brine samples illustrated carbon-13 enrichment as temperatures increased, possibly indicating the re-dissolution of CaCO<sub>3</sub> in the warming, freshening fast ice.



### Winner Joëlle Buxmann

### "Chlorine explosion" - an autocatalytic release from sea-salt aerosols

<sup>1</sup>J. Buxmann, <sup>2</sup>S. Bleicher, <sup>2</sup>, <sup>3</sup>C. Zetzsch and <sup>1</sup>U. Platt 1Institute of Environmental Physics, University of Heidelberg, Germany <sup>2</sup>Atmospheric Chemistry Research Laboratory, University of Bayreuth, Germany <sup>3</sup>Fraunhofer-Institute for Toxicology and Expeimental Medicine, Hannover, Germany. Contact: joelle.buxmann@uni-heidelberg.de

Sea salt aerosol is an important source for Reactive-Halogen-Species (RHS), which affect  $O_3$  and the chemical balance of  $NO_x$ (= $NO_2$  +NO); in particular, the abundance and role of chlorine in the marine boundary layer is still unclear.

We present the first direct and simultaneous detection of CIO and OCIO radicals from the "chlorine explosion" and BrO by Differential-Optical-Absorption-Spectroscopy in smog chamber experiments with sea salt aerosol (with and without  $NO_{x}$ ,600ppb  $CH_{d}$ ).

In the absence of  $NO_x$ , the BrO mixing ratio rises up to  $430\pm35$ ppt and OCIO is close to the detection limit of 100ppt. At high  $NO_x$  levels, formation of BrO is delayed, while >3ppb CIO and 7ppb OCIO are observed. Formation of OCIO, CINO<sub>2</sub>, and CIONO<sub>2</sub> and acidification of the aerosol by HNO<sub>3</sub> or HONO play key roles. The chlorine mechanism might become important in highly polluted marine areas, where high  $NO_2$  and  $O_3$  levels are present.









### Winner Marcela Ewert

Transport of marine microbes and polysaccharides from first-year sea ice into snow and implications for marine-atmospheric exchange

M. Ewert, S. Carpenter, J. Colangelo-Lillis and J. Deming School of Oceanography, University of Washington, Seattle, WA, USA. Contact: mewerts@uw.edu

In high latitude oceans, exchanges between the surface ocean and the lower atmosphere are mediated by sea ice. During freeze up and consolidation, sea ice rejects, to its surface, brines containing high concentrations of salts, bacteria and extracellular polysaccharide substances (EPS) which become available for incorporation in the snow. In this study, we present evidence of the incorporation of sea-ice bacteria and EPS in the snow, based on vertical profiles of temperature, salinity, bacterial abundance and EPS through Arctic snow and first-year sea ice. Samples, collected in two consecutive winters near Barrow, Alaska, indicate a strong influence of snow depth, wind and temperature regimes in bacterial transport and persistence in the snow.



### Winner Tianran Zhang

Impacts of Sources and Atmospheric Processing on Fe Solubility in Aerosols over the Yellow Sea, China

<sup>1</sup>T. Zhang, <sup>1</sup>J. Shi, <sup>1</sup>H. Gao, <sup>2</sup>J. Zhang and <sup>1</sup>X. Yao <sup>1</sup>Key Lab of Marine Environmental Science and Ecology, Ministry of Education, Ocean University of China, Qingdao, China 2State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Contact: tiangan zh@gmail.com

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TSP samples collected over the Yellow Sea, China, were divided into north continent source (NCS) and non-NCS samples by air mass back trajectory; in which iron solubility values were 5.6±3.9% and 3.1±5.3%, respectively. In the NCS samples, two sub-regimes were

back trajectory; in which iron solubility values were 5.6±3.9% and 3.1±5.3%, respectively. In the NCS samples, two sub-regimes were identified by chemical composition difference using the ratio of SMg/SFe. Cloud processing associated with or without biomass burning was found to have a potential effect on solubility of Fe. No correlation between soluble Fe and secondary inorganic ions was observed in NCS samples. However, in non-NCS samples a good correlation between soluble Fe and secondary inorganic ions was observed likely due to acidification reactions. Enrichment factors indicate the existence of abundant anthropogenic Fe in non-NCS samples. Back trajectories and high enrichment factor of V further implied that part of the anthropogenic Fe could be from marine traffic emissions.

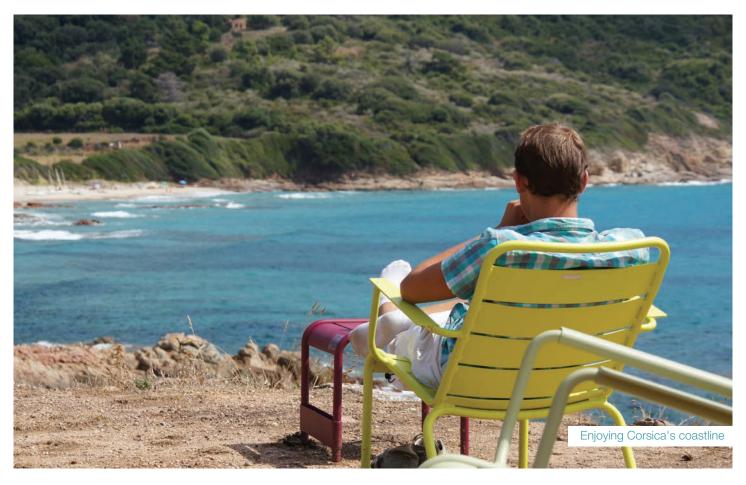
# **SOLAS Summer School 2011**

The SOLAS Summer School was held at the Institut d'Etudes Scientifiques de Cargèse, a picturesque town located on the idyllic French Island of Corsica. Organised and run by Véronique Garçon, and the SOLAS IPO, the 2011 school welcomed 72 PhD students and early career scientists from 25 countries with a wide range of scientific expertise and experience, covering all of the SOLAS scientific areas. The Summer School offers the opportunity to expand and develop knowledge on all aspects of SOLAS science and to meet and strengthen future collaboration with others from around the world researching SOLAS-related topics.

The lectures present an insightful depth of the full breadth of SOLAS science, including an introduction to SOLAS (Véronique Garçon); The carbon and iron cycles (Laurent Bopp and Phil Boyd); Greenhouse and trace gases and their relationship to climate change and its variability (Laurent Bopp, Peter Liss and Alberto Piola); Atmospheric modelling and chemistry (Roland von Glasow and Maria Kanakidou); Air-water gas exchange (Phil Nightingale); Ocean physics and coastal processes (KK Liu and Alberto Piola); Remote sensing and time-series observations (Mike Behrenfeld, Phil Boyd and Eric Saltzman); Marine ecology, aerosols, genomics and macronutrients (Phil Boyd, Phyllis Lam, Maurice Levasseur and Eric Saltzman); and biogeochemical modelling and its changes over long time-scales (Eric Galbraith and Véronique Garçon).









As well as the lectures, special sessions were adopted to deal with issues which arise when working within the world of science. These included sessions on excellent science (Juergen Weichselgartner), the IPCC process (Corinne Le Quéré), ethics in science (Eric Saltzman), the organisation of science (Emilie Brévière) and scientists and the press (Phil Boyd). One of the highlights of these sessions was an introduction to the IPCC Process by Corinne Le Quéré.

During the 2011 Summer School, the students took part in hands-on practicals where they were introduced to techniques used within the field. Ran by lecturers attending the school, these enveloped atmospheric chemistry and carbon cycle modelling, marine genomics, gas exchange, laboratory and cruise work. Communication workshops were also conducted in which the students were given guidance and constructively criticised on maximising opportunities of presenting their research, writing and designing posters and papers. The students were then assigned to develop their own oral and poster presentations.

All the participants made the most of the available free time by dining and socialising within the town of Cargèse, and several made the most of the recuperation time on a day-cruise around the provincial area or hiking in the stunning mountains in the proximity of the Institute. To conclude, the SOLAS Summer School was a pleasure to attend and it was enlivening to observe the development of collaborations and partnerships that are bound to strengthen with time, to the benefit of SOLAS science in the future.

Georgia Bayliss-Brown SOLAS International Project Officer

All photos: Stefan Kontradowitz





# SOLAS Summer School 2011

## Summer school poster competition

The SOLAS Summer School places significant emphasis on the communication aspect of the Summer School. The students attended practical sessions on how to effectively communicate by poster presentation. The lecturers identified the best posters and these are available for download at the SOLAS Summer School website: http://www.solas-int.org/summerschool/welcome.html





### Contribution of ice algae to the water column pool of dimethylsulphoniopropionate (DMSP) during the spring ice melt period in the Arctic

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In the Arctic, dimethylsulphate (DMS) and DMSP are produced by both planktonic and ice microalgae. Maximum DMS and DMSP concentrations are generally measured within the ice edge zone and could partly result from the physiological response of microalgae

Between 1st May and 21st June 2010, we measured the temporal variations in sea ice and water column DMSP concentrations at an ice camp located in the Resolute Passage, Nunavut, Canada. A series of in situ incubations were performed with water collected under the ice, which was exposed to surface (treatment) versus under-ice (control) incident light intensity for 6h. Results show that a large quantity of DMSPp and DMSPd from the ice was released into the water at the end of May. When exposed to surface insolation, microalgae rapidly released their DMSPp pool, which contributed to an increase in the dissolved pool. These results suggest that DMS production in the water column during the melting period could be stimulated by the release of massive amounts of DMSPd from the



### Carbon cycling and air-sea CO<sub>2</sub> exchange in the Californian Upwelling System at a time of change

Giuliana Turi

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Our aim is to investigate the impact of mesoscale eddies on the air-sea CO<sub>2</sub> gas exchange and their contribution to the intraannual variability of pCO<sub>2</sub> in the California Upwelling System. To this end, we use a highly-resolved, physical circulation model (ROMS) coupled to an ecosystem-biogeochemical model (NPZD).

To determine the impact of eddies on the CO<sub>2</sub> gas exchange, we conducted two simulations: one with our standard eddy-permitting configurations and another with modified momentum equations to prevent the formation of eddies. A comparison of these simulations reveals that mesoscale eddies reduce outgassing in the nearshore area by up to 40%.

In a second analysis, we compared pCO<sub>2</sub> variability computed from 2-day and monthly outputs from our standard model configuration to determine the fraction of the total intraannual variability attributable to mesoscale activity. Our model results suggest that up to 60% of the nearshore variability is attributable to mesoscale eddies.



# Diazotroph activity and community structure over an annual cycle under different pCO<sub>2</sub> conditions at Station ALOHA

Daniela Böttjer

<sup>1,3</sup>D. Böttjer, <sup>1,3</sup>M. Church, <sup>2,3</sup>R. Letelier and <sup>1,3</sup>D. Viviani

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The ocean absorbs a considerable fraction of carbon dioxide (CO<sub>2</sub>) emissions from human activities, leading to changes in the seawater carbonate chemistry including increases in surface ocean pCO<sub>2</sub> and concomitant decreases in upper ocean pH. The consequences of these changes for marine life still remain uncertain and are expected to vary between ecosystems and organisms. In the North Pacific Subtropical Gyre NPSG), dinitrogen (N<sub>2</sub>) fixing bacteria (diazotrophs) occupy a key position in the pelagic food web by supplying new nitrogen to the upper ocean, thereby supporting and regulating new production and carbon export. In a series of nearly monthly experiments at Station ALOHA (A Long-term Oligotrophic Habitat Assessment; 22° 45′N, 158° 00′W), we explored the short-term response of natural assemblages of diazotrophs to projected changes in the seawater carbonate chemistry and found that in the oligotrophic waters of the NPSG elevated seawater pCO<sub>2</sub> generally does not enhance rates of N<sub>2</sub> fixation.



# Implementing Calcifiers in a Global Climate Model: A Recipe

Karin Kvale

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This poster described the mid-stage biogeochemical model development process that is forming Kvale's PhD. The basic ecosystem structure had been written and the poster explores some of the production parameter sensitivity as well as the iterative nature of tuning the parameters to achieve stable phytoplankton populations and realistic ocean nutrient distributions. The biogeochemical model is an expansion of an existing ocean biology model in the UVic ESCM, written by Andreas Schmittner at Oregon State University and developed further by David Keller and Andreas Oschlies at GEOMAR. This work adds calcifying phytoplankton to the ecosystem to create more realistic carbon export. Currently, the model development is in the final stages and the model will be submitted for publication in the coming months.



### Active Controlled Flux Technique: Heat Exchange Measurements in the Baltic Sea

Leila Nagel

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Heat is used as a proxy tracer for gas exchange measurements. The water surface was heated by a  $CO_2$ -laser. The temperature response was recorded with an infrared camera. The decay time and therefore the transfer velocity was then determined by Fourier analysis. The measured heat transfer velocities are converted to  $CO_2$ -transfer velocities by Schmidt number scaling.

Combined measurements of heat and gas transfer velocities in the Heidelberg wind-wave-tank "Aeolotron" prove the possibility to use heat as tracer for gas transfer measurements. Field measurements, conducted at two cruises in the Baltic Sea, show good agreement in Schmidt number-scaled heat transfer velocities with empirical parametrisations of gas transfer velocities with wind speed. However, the measured data is seen to scatter up to a factor of three at one wind speed; clearly indicating that wind-speed gas-exchange relations need to be replaced by a better, more complex parametrisation.



# Influence of physical and biological processes on the seasonal cycle of biogenic flux in the Equatorial Indian Ocean

Pottekkat Jayapalan Vidya

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Seasonal cycle of biogenic fluxes obtained from sediment trap at two locations within the equatorial Indian Ocean (EIO), the southern Bay of Bengal trap (SBBT), 5°24′N, 86°46′E, and the equatorial Indian Ocean trap (EIOT), 3°34′N, 77°46′E, were examined to understand the factors that control them. The characteristic of biogenic flux at SBBT was the strong seasonality showing a peak flux in August, while lack of seasonality characterised the flux at EIOT. The enhanced biogenic flux at SBBT during the summer monsoon could be explained with the help of physical processes that controlled chlorophyll biomass through nutrient supply. The mismatch between the lack of seasonality between the biological process that operates in the SBBT with that of the equatorial Atlantic and EIOT with that of the equatorial Pacific, though the physical forcing in these three regions, namely EIO; the equatorial Atlantic; and, the equatorial Pacific, are very different.

# **SOLAS Summer School 2011**

The SOLAS Summer School prides itself in encouraging collaboration and future association between the participants, and, as with the poster presentation workshops, efforts focus on developing the skills required for eloquent oral presentation.

Each participant, after attending this workshop, gained the opportunity to apply the teachings to their own presentations and provided a short demonstration, of their own research, to their cohorts. The students and lecturers identified the best presentations, and these following students gained awards.



# Dinitrogen fixation and nutrient limitation in the eastern tropical South Pacific

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The N budget for the global ocean is poorly constrained, with some reports suggesting that sinks exceed sources (Codispoti, 2007). N<sub>2</sub> fixation (one of the major sources of N) has been commonly studied in large oligotrophic areas depleted in N (Karl et al., 1997). However, a recent geochemical study based on N:P ratios hypothesized that N<sub>2</sub> fixation could be important above N-rich Oxygen Minimum Zones (OMZs), and spatially coupled to N-loss processes (Deutsch et al., 2007). We tested this hypothesis in the Eastern Tropical South Pacific and confirmed the presence of active  $N_2$  fixation organisms along 100°W - 10° & 20°S. Along 10°S, highest rates were associated with the oxycline and the core of the OMZ, and N<sub>2</sub> fixation was iron limited, except in nearer-shore regions, where it was limited by organic carbon availability. These new sources of fixed N need to be taken into account in biogeochemical budgets and models, especially in the context of probable OMZ extension in the future ocean.

## These results will be published in:

Dekaezemacker, J., Bonnet, S., Turk-Kubo, K., Moutin, T., Grosso, O., Bressac, M., Foster, R., Knapp, A., Guieu, C., Zehr, J. and Capone D. (in prep.) Dinitrogen fixation and nutrient limitation in the Eastern Tropical South Pacific.

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Codispoti, L. (2007) An oceanic fixed nitrogen sink exceeding 400 Tg N a–1 vs. the concept of homeostasis in the fixed-nitrogen inventory. *Biogeosciences* 4:233-53.

Karl, D., et al. (1997) The role of nitrogen fixation in biogeochemical cycling in the subtropical North Pacific Ocean. *Nature* 388:533–38.

Deutsch, C., et al. (2007) Spatial coupling of nitrogen inputs and losses in the ocean. *Nature* 445:163–7.

Lecturer's vote winner



# Volcanic ash triggers algal growth in the iron-limited northeast Subarctic Pacific

Josiane Mélançon

Université Laval (Québec-Océan), Québec, Canada. Contact: josiane.melancon.1@ulaval.ca

The Alaska Gyre is a High-Nutrient Low-Chlorophyll (HNLC) area limited by iron. Iron is supplied to the area by processes such as deposition of airborne dust from Asia, vertical mixing and eddies. Another possibly important iron source was highlighted in August 2008: After the eruption of Mt. Kasatochi, in the Aleutian Islands, chlorophyll a concentration in the Alaska Gyre rose by a factor ca. 3. Can volcanic ash deposition trigger phytoplankton growth in the Alaska Gyre? If so, how much ash is needed to trigger a bloom of the magnitude observed in 2008? Is there a threshold where ash has no further effect on phytoplankton growth? To answer these questions, Alaska Gyre water enriched with volcanic ash was incubated aboard the CCGS John P. Tully along Line-P in 2011. We found that an ash concentration as low as 1.2 mg L<sup>-1</sup> was sufficient to stimulate the growth of the key phytoplankton species after a lag phase of ca. four days and that a Michaelis-Menten type relationship linked phytoplankton growth to the concentration of ash added. Overall, our results show that volcanic ash deposition may bring more iron than previously thought to the HNLC waters of the Northeast Subarctic Pacific.

Lecturer's vote winner



∧ Photo : SOLAS' chair, Eric Saltzman, running the oral communication workshop



# The silicon isotope composition of diatoms as a fingerprint for the strength of the biological pump

Florian Wetzel

ETH Zurich, Institute for Geochemistry and Petrology, Zurich, Switzerland. Contact: wetzel@erdw.ethz.ch

The nature of atmospheric CO<sub>2</sub> variations over glacial-interglacial periods is currently a subject of intense research. The sinking of dead organic matter through the oceanic water column, also known as the biological pump, is potentially an important feedback mechanism for setting the ocean-atmosphere CO<sub>2</sub> balance. CO<sub>2</sub> and nutrient consumption by primary producers in the sunlit surface ocean produces an isotope fingerprint that characterises the efficiency of CO<sub>2</sub> and nutrient uptake. To trace this process back in time, ocean sediment cores serve as an archive of biological activity. The sediment contains shell material of dead organisms, like diatoms, that utilise silicon to build a shell around their organic tissue. I measured the silicon isotope fingerprint of such diatom shells and found a strong co-variation with glacial-interglacial conditions. These promising results will enable more in-depth studies that include consideration of other important environmental parameters like iron availability, which influences diatom metabolism.

Lecturer's vote winner



# Diversity of iron-limited diatoms influences silicon cycling

Colleen Durkin

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Diatom production is limited in vast regions of the ocean by the availability of iron. Changes in the way communities in these regions precipitate silica affects biogeochemistry and can be caused by changes in species composition or shifts in the silicon metabolism of individual cells. To disentangle these effects, we conducted a deck-board iron-enrichment experiment at the iron-limited Station Papa in the NE subarctic Pacific Ocean and sequenced the metatranscriptomes of the communities before and after enrichment. Growing diatoms were also labeled with a fluorescent stain that incorporates into newly deposited silica in order to quantify the influence of different species to community silica precipitation. Several genera, including Pseudo-nitzschia, contributed to total community silica precipitation disproportionate to their total abundance, suggesting that the quantity of silica precipitated by the community is particularly sensitive to changes in community composition. A different evolutionary clade of silicon transporters was more abundant in the iron-limited community than in the iron-replete community. This same shift in the transcription of silicon transporters was measured in cultured Pseudo-nitzschia isolates. Pseudo-nitzschia had a large influence in silica uptake and precipitation at Station Papa and these cells may also functional change how silicic acid is utilized when they are iron-limited through the transcription of different silicon transporters.

Student's vote winner



# Small eukaryotic phytoplankton drive the Sargasso Sea's biological pump

Sarah Fawcett

Department of Geosciences, University of Princeton, New Jersey, USA. Contact: sfawcett@princeton.edu

Biologically available nitrogen is an essential phytoplankton nutrient, potentially limiting marine productivity and controlling community composition. In the subtropical ocean, water column stratification impedes the upward flux of nitrate to surface waters such that phytoplankton are assumed to rely largely on ammonium recycled from the breakdown of organic matter. We collected particles from Sargasso Sea surface waters during the summer, used flow cytometry to sort prokaryotic and eukaryotic phytoplankton, and analyzed their respective <sup>15</sup>N/<sup>14</sup>N ratios. We found that prokaryotes (Prochlorococcus and Synechococcus) have uniformly low <sup>15</sup>N/<sup>14</sup>N, consistent with their reliance on recycled nitrogen. In contrast, small eukaryotic phytoplankton have a higher and more variable <sup>15</sup>N/<sup>14</sup>N, similar to that of nitrate in underlying Subtropical Mode Water. For the summertime Sargasso Sea, we estimate that small eukaryotes obtain more than half of their nitrogen from upwelled nitrate. In addition, our data support the view that sinking material derives largely from eukaryotic, not prokaryotic, phytoplankton biomass, suggesting that eukaryotes drive the Sargasso Sea's biological pump.

### Student's vote winner



# Carbonate sediments on Antarctic shelves

Judith Hauck

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As a direct response to ocean acidification, carbonates in sediments on Antarctic shelves will dissolve. But can the dissolution of carbonate sediments from Antarctic shelves constitute a negative feedback to ocean acidification? To quantify this reaction, we analyzed a data set of ca. 400 sedimentary carbonate content mesurements and found an interesting relationship: Initially, CaCO<sub>3</sub> increases in the sediments with increasing primary production due to the coupling of organic matter and CaCO<sub>3</sub> production by organisms. Past the optimum level, CaCO<sub>3</sub> decreases in the sediments with further increasing primary production due to metabolic-CO2 production that subsequently dissolves CaCO<sub>3</sub>. Applying this relationship, CaCO<sub>3</sub> on all Antarctic shelves could be predicted using satellite-derived primary production data. Based on this map, the inventory of CaCO<sub>3</sub> on all Antarctic shelves was calculated to be 4 Pg CaCO<sub>3</sub> or 0.5 Pg C suggesting that sedimentary CaCO<sub>3</sub> will dissolve without releasing a significant alkalinity or buffer signal.

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Hauck, J., et al. (2012) Distribution and mineralogy of carbonate sediments on Antarctic shelves. J. Mar. Systems 90(1):77-87.

Hauck, J., Arrigo, K., Hoppema, M., van Dijken, G., Völker, C. and Wolf-Gladrow, D. (under review) Insignificant buffering capacity of Antarctic shelf carbonates.

Student's vote winner

# SOLAS special reports

# EUR-OCEANS Conference 'Ocean deoxygenation and implications for the marine biogeochemical cycles and ecosystems'

24-26 October 2011, Toulouse, France.

Dewitte, B., Garçon, V. and Paulmier, A.

The organisation of such a conference had been proposed in 2010 by the EUR-OCEANS Consortium, with scientific issues to be defined and detailed. Rapidly, and in the continuity of the international SOLAS workshop on the "Oxygen Minimum Zones - Eastern Boundary Systems (OMZ-EBUES)" which took place on 8-10 November 2010 in Lima, Peru, the ocean deoxygenation and its implication appeared to be very relevant "hot" topics. This Gordon-like Conference held on 24-26 October 2011 was attended by more than 90 scientists from 19 different countries. In addition to the EUR-OCEANS Consortium, the Conference has been financially supported by IRD, CNRS-INSU, Académie des Sciences, LEGOS, OMP, the French embassy in Washington DC (USA), and both international projects IMBER and SOLAS.

The conference aims were to bring together biological, biogeochemical, and physical oceanographers to discuss the issue of deoxygenation in the world ocean and its implications for ocean productivity, nutrient cycling, carbon cycling, and marine habitats. A serious consequence of global warming that is increasingly gaining importance is the decrease of the dissolved oxygen content of the world ocean. Deoxygenation and extension of the OMZs are predicted because oxygen is less soluble in warmer waters and also because the changing oceanic stratification and circulation will reduce the supply of O<sub>2</sub> to the ocean interior. However, the biogeochemical contribution due to the O<sub>2</sub> consumed by the aerobic processes as well as the O<sub>2</sub> ventilation rate by the general circulation remains to be quantified. This deoxygenation in subsurface waters will have widespread consequences due to the role O<sub>2</sub> plays in the biogeochemical cycling of carbon, nitrogen and other important elements. O2 is instrumental to all aerobic



↑ Photo: Attendees of the EUR-OCEANS 2011 meeting.

life and sub-lethal and lethal  $O_2$  thresholds vary greatly between marine organisms. OMZs are also key regions in the climatic gases budgets. The goal of this conference was to provide a science arena where to discuss the state of the art of our knowledge on all topics and in building a unified research agenda across the full range of oceanographic disciplines.

During the three days of the conference, the talks provided a multidisciplinary overview mainly associated with three foci: 1) The description and control mechanisms of the deoxygenation and of the OMZ and hypoxia sites; 2) The deoxygenation impacts on the biogeochemical cycles, climatic gases, microbial activity and ecosystems; 3) The deoxygenation in the past ocean. Inter-comparisons of OMZs systems, and efforts towards new parameterizations for addressing regional and global modeling challenges were also tackled. Poster sessions also took place throughout the 3 days, and a

Round table on the "Respiration Index" controversy in the literature has been experienced. A special issue in the European journal Biogeosciences on the low O2 environment and an ASLO e-Lecture on the conference topics are planned. In perspective, the "ocean deoxygenation" community wishes to keep the ball rolling in maintaining tight scientific exchanges, with the idea of international coordination (objective, approach) for observations (e.g. O2), experiments (e.g. protocols) and modeling efforts (e.g. numerical tools) and intercomparisons of the major OMZs systems.

More details about the conference can be found at:

http://www.eur-oceans.eu/conf-oxygen

Contact: boris.dewitte@cnes.fr

# Joint 6th Workshop on ADOES with Asian SOLAS

### Gao, H., Yao, X. and Uematsu, M.

Joint 6th Workshop on Asian Dust and Ocean EcoSystem (ADOES) with Asian SOLAS was held on October 5-9th, 2011 in Qingdao, China. This workshop was organized by Ocean University of China and SOLAS-ADOES/WESTPAC-ADOES working group with the support by Key Laboratory of Marine Environment and Ecology (Ministry of Education of the people's Republic of China), and Strategic Chinese-Japanese Cooperative Program by MOST/JST. More than 50 participants attended the workshop and 29 scientists from China, Japan, South Korea and US were invited to present their latest research results and findings, with a focus on Asian dust and its potential impact on marine ecosystem. They include: 1) recent experimental results on impact of Asian dust on marine ecosystem, e.g., new techniques developed for measuring air-sea exchange flux and more evidences of ocean acidification, transport pathways and physchemical evolution of dust aerosol in a longdistance transport, and potential impact of biomass burning aerosol on bio-available Fe in China seas; 2) new particle bursts and aerosol optical properties recently observed in the coastal areas; 3) impact of radioactive



materials leakage from the Fukushima nuclear plant on marine environments. Building on these findings, scientists from Ocean University of China, Fudan University, Peking University and Institute of Physical (CAS) also had a group discussion in the workshop for jointly submitting a proposal to deepen current studies on relationship between atmospheric deposition and ocean primary

↑ Photo: Joint 6th Workshop on ADOES with Asian SOLAS participants standing before a quite library in one-week public holiday in China (6-7 October, 2011 taken by Ben Xiaoyu).

activities. The proposal will also attempt to understand the impact of ocean emissions on regional climate.

Contact: hwgao@ouc.edu.cn

# Genesis of global observing network for ocean acidification workshop

### Williamson, P.

The foundations for an international initiative to collate and interpret ocean acidification and its effects have now been established, through a workshop hosted by the University of Washington, Seattle (26-28 June 2012). Over sixty participants from 22 countries attended.

Assessment of the importance of ocean acidification (OA) for organisms, ecosystems and ecosystem services needs observational data on the changes taking place around the world. Making the measurements is only the first step: a structured system is needed to initially ensure their quality and comparability, and then to synthesise the data in order to derive information and knowledge.

Sponsors of the Seattle workshop included the US National Oceanic and Atmospheric Administration (NOAA), the International Ocean Carbon Coordination Project (IOCCP) and the Global Ocean Observing System (GOOS). The initiative also has close links to the newly-announced International Coordination Centre for Ocean Acidification (OA-ICC), to be based in Monaco, and the SOLAS-IMBER Ocean Acidification Working Group.

Such distinguished parentage is important: it not only gave the workshop scientific and political credibility, but also enabled it to build on existing relevant measurements and data synthesis systems (e.g. the Surface Ocean CO2 Atlas, SOCAT). Duplication of effort is thereby avoided, and added value maximised – both key concerns of funding agencies.

Major outcomes from the Seattle workshop comprised a mission statement for the nascent network; identification of standardised measurements (at different priority levels) and potential data products; collation of information of existing and planned OA observing activities (fixed stations, research ships and ships of opportunity); and discussion on gaps and how they might be filled. An interactive map of the current and planned OA observations is in preparation. Its current status is online at www.pmel.noaa.gov/co2/OA2012Workshop, together with other background information on the workshop and relevant contact information.

A Nature News article on the workshop is online at www.nature.com/news/global-network-will-track-acidifying-oceans-1.10922. The full scientific report is expected to be available for wider community discussion at the Ocean in a High CO2 World conference in Monterey in September.

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# Discussion Session Reports

The following reports are brief summaries of the discussion sessions that took place during the SOLAS Open Science Conference.

The full reports can be downloaded from http://www.solas-int.org/news/conferencemeetings/discsess.html

# Climate impact of seasalt-derived Cl atoms

Roland von Glasow (Co-covener). University of East Anglia, Norwich UK. Contact: r.von-glasow@uea.ac.uk Eric Saltzman (Co-convener). University of California, Irvine, CA USA. Contact: esaltzma@uci.edu

Several lines of evidence suggest that that CI atoms resulting from the activation of seasalt can influence tropospheric photochemistry, in particular the lifetime of methane and other hydrocarbons and the cycling of  $NO_x$  and  $HO_x$  (e.g., Allan et al., 2001; Platt et al., 2004; Keene et al., 2009; Lawler et al., 2009; 2011; Thornton et al., 2010). There is increasing observational evidence that this activation occurs, but insufficient data to constrain the rates and geographic extent of this process. As a result, the understanding of CI cycling is currently insufficient to support global models or to assess the impact of CI chemistry on climate and air quality.

The focus of this discussion session was to start developing a coordinated field/laboratory/modelling strategy to answer the following questions:

- 1) Is tropospheric CI chemistry a significant aspect of atmospheric reactivity, and to what extent is this a natural vs anthropogenic effect?
- 2) Do we have to include chlorine chemistry in future climate models to improve the calculation of the radiative forcing and if so, what level of process understanding is required?

During the discussion many ideas for future international field campaigns were brought forward. It was noted that new analytical techniques exist for direct detection of reactive CI compounds, but to date they have only been deployed in ground-based studies at the Cape Verde Islands in the tropical Atlantic. The consensus was that a pilot field study of limited instrumentation and duration should be carried out at other locations to assess whether the Cape Verde results are generally representative of oceanic regions impacted by continental outflow. The discussions included: 1) an inventory of current measurement capabilities; 2) possible study

sites; and, 3) the relative merits of shipboard vs. island platforms for deployment. For logistical and scientific regions, the Bermuda Islands were suggested for the pilot campaign. This would have to be funded through individual grants. The SOLAS/IGAC task Halogens in the Troposphere (HitT) will provide support in terms of communication and fundraising for research will be the responsibility of individual investigators. If the pilot study proves successful in terms of demonstrating active CI chemistry, a larger international experiment would be planned. That effort would focus on the geographic extent of CI cycling and on understanding the photochemical processes involved.

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Keene, W., et al. (2009) Latitudinal variation in the multiphase chemical processing of inorganic halogens and related species over the eastern North and South Atlantic Oceans. *Atmos. Chem. Phys.* 9:7361-85.

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Platt, U., et al. (2004) Hemispheric average Cl atom concentration from <sup>13</sup>C/<sup>12</sup>C ratios in atmospheric methane. *Atmos. Chem. Phys.* 4:2393–9.

Thornton, J., et al. (2010) A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry. *Nature* 464:271-4.

# Ocean-Derived Aerosol: Properties and Climate Impacts

David Kieber (Convener). State University of New York, Syracuse, NY (SUNY-ESF) USA. Contact: djkieber@esf.edu Lynn Russell (Co-convener). University of California San Diego, La Jolla, CA USA. Contact: lmrussell@ucsd.edu Elizabeth Minor (Rapporteur). University of Minnesota, Duluth, MN USA. Contact: eminor@d.umn.edu

The marine aerosol discussion session, with 90+ participants, was introduced with a brief update on the marine aerosol midterm strategy. This included an announcement of an upcoming aerosol workshop (http://www4.ncsu.edu/~nmeskhi/Marine\_Aerosol\_Workshop/WEBSITE.html), mention of recent papers highlighting the importance of marine aerosols (Quinn and Bates, Nature, 2011; de Leeuw et al., Rev. Geophys., 2011), and a reminder of the key research questions and uncertainties in the marine aerosol midterm

strategy outlined in the aerosol white paper http://www.solasint.org/ aboutsolas/organisationaandstructure/ midtermstrategy/whitepapers/aerosols.pdf).

Following the brief introduction, an open discussion ensued that focused on several aspects related to organic matter in marine aerosol during which several important questions were raised and debated. (1) What is the best approach to study primary marine aerosol? Should ambient aerosols be studied directly or should

investigators generate primary marine aerosols? If studying the marine contribution to ambient aerosol, how can the marine source function be teased out since marine aerosols will change rapidly with respect to pH, chemical composition, water content, oxidant concentrations, etc.? (2) How are marine dissolved and particulate organic matter related to the organic matter injected into the atmosphere as primary marine aerosol? Fractionation of marine organic matter (OM) due to bubble bursting is poorly constrained, and there little understanding of how much the surface microlayer impacts marine aerosol organic matter production. This is compounded by the fact that, in general, more than 50% of marine OM is uncharacterized, although this proportion is likely to be significantly reduced due to recent advances in sampling technology (e.g., reverse osmosis/electrodialysis approaches). (3) How can what is likely to be a complex composition of organic matter in marine aerosol be deconvolved, especially in the submicron fraction? This is a critical question that is not expected to be easily resolved because of uncertainties related to the marine source function and the degree to which there is fractionation of marine organic matter during the bubble bursting process. (4) Are oceanographers and atmospheric scientists on the same page with respect to some key terminology including (a) water soluble versus insoluble OM, (b) gels and exopolysaccharides (EPS), and (c) hydrophobic versus hydrophilic. Finally, there was some discussion regarding analytical techniques

associated with generating, collecting and analyzing primary marine aerosol. In particular, (5) is the organic composition chemically altered when collecting ambient aerosol or generating marine aerosol? (6) What are the best approaches to analyze marine aerosol? FTIR, NMR, MS, UV-Vis etc. each have their own advantages and limitations, but together they should render a fairly comprehensive view of organic composition. (7) How much of the observed variability in published number size distributions (de Leeuw et al., 2011) is related to analytical variability versus temporal and spatial variability in the source seawater? (8) What is the equilibration time of surface-active marine DOM with rising bubbles in seawater, and how does this relate to average bubble penetration depths in seawater and in bubble-based aerosol generators? (9) What is the experimental approach that should be used to study the photochemistry of marine aerosol? This is difficult to accomplish, but necessary to understand the aging and atmospheric impact of marine aerosol.

The general consensus of the aerosol discussion session was that we need to move forward on many fronts with both lab-based and field-oriented studies. A systems approach will be needed that involves the international community with many lab groups employing different techniques working on same sample sets to address these questions.

# Genesis of global observing network for ocean acidification

Christoph Heinze (Co-convener). University of Bergen, Bergen Norway. Contact: christoph.heinze@gfi.uib.no
Yukihiro Nojiri (Co-convener). National Institute for Environmental Studies (NIES), Tsukuba-City, Ibaraki Japan. Contact: nojiri@nies.go.jp
Phil Williamson (Rapporteur). University of East Anglia, Norwich UK. Contact: p.williamson@uea.ac.uk

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↑ Photo: In situ studies of the cold-water coral Lophelia pertusa, an organism that may be particularly sensitive to ocean acidification. Credit: Murray Roberts.

# Gas Exchange at high wind speeds: Recent observations and constraints

Rik Wanninkhof (Co-convener). NOAA, Atlantic Oceanographic and Meteorological Laboratory (AOML), Miami, FL USA. Contact: rik.wanninkhof@noaa.gov Bill Asher (Co-convener). University of Washington, Seattle, WA USA. Contact: asherwe@apl.uw.edu Rachel Stanley (Rapporteur). Woods Hole Oceanographic Institution (WHOI), Woods Hole, MA USA. Contact: rstanley@whoi.edu

Quantifying gas transfer at high winds remains challenging and relevant for SOLAS. The breakout session provided a venue to discuss data and theories for gas transfer under these conditions. Several dozen people attended the session, which began with four brief presentations providing theoretical background and an overview of recent results.

- (1) Anna Rutgersson presented the theory of air-sea interaction with emphasis on predicting the behavior of the drag coefficient at high wind speeds.
- (2) David Woolf presented the "direct-flux plus bubble-component" conceptual model for air-sea gas exchange at high winds.
- (3) Mingxi Yang summarized field and laboratory results focusing on showing how diffusivity and solubility affect gas fluxes at high wind speeds.
- (4) Roberta Hamme provided a large-scale oceanographic context for the ideas discussed by David and Minxi, showing how supersaturation of noble gases can be used to understand high wind gas exchange processes.

These overviews were followed by three discussion topics.

- (1) Barry Huebert: The HiWinGS, high wind speed gas exchange field study. Discussion focused on the challenges executing these types of studies, quantifying experimental uncertainties, and possible correlations between uncertainties.
- (2) Rachel Stanley: Gas saturation anomalies as a constraint on high wind gas fluxes. It was concluded that collaboration with groups modeling bubbles in the ocean would be fruitful.
- (3) Christoph Garbe: Laboratory-scale gas transfer studies.

  Discussion focused on the limitations of small-scale experiments but acknowledged that they can be useful for understanding the microphysics of gas transfer.

The attendees concluded that recent advances in measurements and interpretation will improve our understanding of gas exchange at high wind speeds. In particular, new approaches for measuring airside fluxes allow using multiple gases in upcoming field experiments. It was also acknowledged that controlled experiments will remain useful for developing numerical and conceptual models.

# Potential shifts in DMS flux from the ocean due to changing climate

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In a recent review, Quinn and Bates (2011) questioned the impact of ocean-emitted dimethylsulphide (DMS) on global climate. Amongst other issues, they argued that there is a lack of evidence for oceanic DMS production responding to changes in surface temperature and/or incident solar radiation over climate-relevant time scales. This asseveration was made upon the grounds of diagnostic and prognostic models. In this session, the question of what we really know about the production and cycling of the DMS precursor, dimethylsulphioniopropionate (DMSP), and what observational evidence we have about the causes and pace of variability in DMS fluxes, was addressed. Given the fact that, as a general rule, only 1% of total DMSP production by phytoplankton results in a DMS-flux to the atmosphere, shifts of the emission flux by several folds may well occur within natural ranges. In this session, the following topics were discussed:

- 1. What is the potential for changes in regional DMS emission regimes?
- 2. What is the likelihood of such changes upon global climate change?

Several topics were discussed that reflected the large uncertainties about the driving forces of DMS production that still exist. Especially the potential shifts in DMS yield from DMSP as a function of community parameters and environmental stress factors was discussed. What is the potential for regime shifts that can result in several fold changes in DMS flux? Uncertainties discussed were:

- It is still poorly known under what conditions DMSP-production is stimulated. There appears to be a daily rhythm related with the light cycle, and also seasonal variability, most probably related to light and nutrients, occurs. It was concluded that we need to know more about the physiological role of DMSP. In addition, phytoplankton taxonomy is a major factor and deserves more attention.
- The relation between DMSP production and DMS production is not straightforward and can be approached through the DMS yield, which is the amount of DMS produced per DMSP transformed. The DMS yield varies with geography. In the coastal zone, large changes in phytoplankton composition are observed, but no general rule between algal production and DMS yield exists. Observations from the open oligotrophic ocean indicate that the DMS yield is more predictable; with yields increasing in summer.
- Regarding climate change and ocean acidification, it is hard to make predictions. Some mesocosm studies showed a decrease in DMS-yield with increasing pCO<sub>2</sub>. Short-term experimental studies are helpful but climate-relevant patterns can only be addressed with time series studies. The only long-term time series available is station Papa. Here, DMS is recorded in relation to acidification, but no DMSP data are available and therefore no relationship between acidification and DMS-yield can be established.

- The consequences of a decrease in sea-ice cover are also still unknown. Algal blooms appear to be the major vector of DMS-fluxes, but right now it is not possible to predict the development of ice-related algal blooms with global warming. And even so, comparison with developments at the coastal zone shows that an increase in blooms does not necessarily result in an increase in DMSP production.
- In global Earth System Models, major DMS source areas like the coastal zone and the Marginal Ice Zone, are still poorly represented.

In general, it is concluded that the oceans contain a vast pool of DMSP, that may well respond to climate change by changing the rate of transformation into DMS, with subsequent consequences through feedback mechanisms. Even though increased DMS-fluxes will not relate 1:1 with CCN numbers, for the scarcity of observable

particle nucleation in the marine boundary layer, they do affect the growth properties and chemical composition of potential CCNforming particles. As such, the importance of DMS-production for global climate can still not be ignored.

Two recommendations were presented from the discussion:

- 1. To improve insight in the controls of DMS-fluxes, and to serve models, not only a DMS-database is required, but also a DMSP-database. Together these datasets would provide improved means to model the DMS yield (there is evidence that the yield parallels the DMS:DMSP ratio of concentrations); when coupled to ecosystem parameters, the DMS yield concept will give a better insight into the controls of DMS production.
- 2. There is an urgent need for more dedicated time series.

# Improving our understanding of and capacity for model projections of sea ice-ocean biogeochemistry

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The goal of this session was to engage observationalists and modellers in a discussion of model-data scaling issues and approaches, and the hidden problems involved in transferring understanding from fine-scale observations and process measurements to coarse-scale models. One clear outcome was the necessity for networking and collaboration, a main task of the newly established SCOR working group BEPSII (Biogeochemical Exchange processes on Sea-Ice Interfaces). While modellers and observationalists work in the same field, their different approaches warrant skills in mediation and communication, commitment, open mindedness and respect for each others' approaches in addition to the know-how of the other discipline if the collaboration shall be successful.

Significant challenges are involved in scaling knowledge from point and patch measurements up to regional and global scales and in determining their significance to the accuracy of climate change projections. Small-scale sea ice processes such as microphysics, algal response to nutrients, and radiation transfer must be simplified and parameterized in large-scale biogeochemical models. This requires understanding and quantification of simulation-critical processes. Key processes pointed out with respect to exchange at the interfaces were: wind speed, shear at the ice/ocean boundary, buoyant convection, surface roughness, carbon fluxes in brines and under-ice waters, energy budget and snow cover effects; and with respect to the control of gas concentrations in ice: initial entrapment, bubble nucleation, brine movement, and sea-ice permeability.

Within the spatially heterogeneous Arctic, statistics (e.g. means and standard deviations) and syntheses of observations (e.g. budgets) are helpful for modellers.

While a standard run is tuned to a mean value, sensitivity studies explore the influence of the observation-constrained parameter range on the model output. As models are developed in tandem with more observations, standard deviations can be reduced. Nonetheless, understanding of similarities and variability is important to allow the development of simplified parametrisation based on knowledge (of important processes and variables) rather than guesswork.

Building networks and coordinating multi-scale field measurements with complementary modeling facilitates sampling over a broad range of scales, addresses the model-data scaling issue and ensures continuous two-way communication amongst observationalists and modellers. Models are useful to help understand spatial and temporal context and can recommend timing and location of future observations.

The potential development of simple box models for observationalists to use with their own data has been suggested as a possibility.

For observations, temporal and spatial heterogeneity has been identified as a serious barrier. Critical ice ocean exchange processes and algal influences occur during spring and fall transitions, when the ice environment is unsafe and difficult to access, causing knowledge gaps in the annual cycle. Spatial variability is extensive and differences hard to pin down. Many methodological barriers exist, e.g. most methods severely perturb the system, microenvironments are problematic, and automated analysis may come with a loss of precision. Developing consistent methodologies (guide of best practices) is an important task and will be addressed within the SCOR working group.

# The SOLAS science plan and its relevance to society

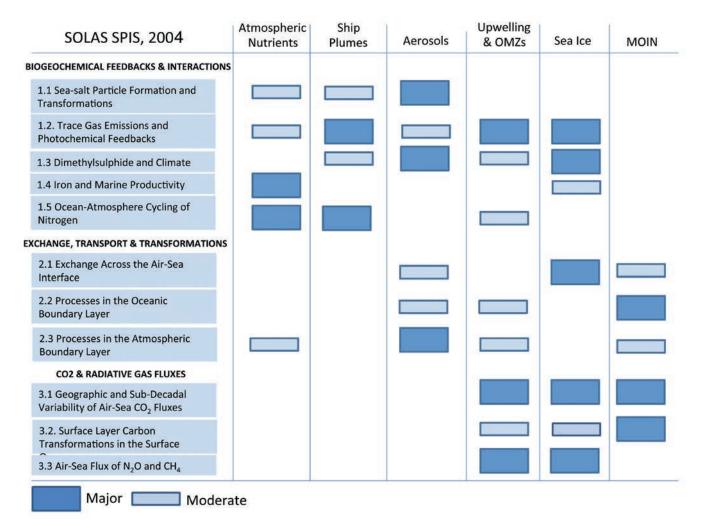
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The 10th anniversary of the SOLAS programme provides an opportunity to consider future directions at a critical time when the international context of environmental science and goals of funding agencies are changing dramatically. The aim of this session was to provide a brief background to these changes and a forum for input to the future development of SOLAS.

The evolution of SOLAS was illustrated by presentation of the original SOLAS Science Plan (SP&IS, 2004), Working Groups, crosscutting activities, and on-going Mid-Term Strategies (MTS; see Fig.1). One of the primary SOLAS sponsors, the International Geosphere-Biosphere Programme (IGBP), is supported by the International Council for Science (ICSU) which is currently undergoing a change in strategic direction towards Earth System Science for Global Sustainability. This directive, known as the Future Earth Initiative (FEI), aims to improve integration of fundamental research and social science, as illustrated by the "Grand Challenges" (Fig.2). A critical issue for SOLAS in this transition is the emphasis

upon societal relevance and what this means for future science directions. SOLAS already contributes to a wide spectrum of issues relating to sustainability, and addresses at least four of the Grand Challenges directly. Relevant SOLAS research directions include anthropogenic forcing, impacts and feedbacks, with direct examples including ocean fertilisation, megacities, and ocean acidification.

However, SOLAS is at a transition point and we need to consider future directions. Does the SOLAS Science Plan require fine tuning, or an overhaul? How do we broaden our mission to include the human dimension and policy-relevant science? For example, should we map SOLAS science priorities onto solutions for societal issues, and engage directly with social scientists in the development of new activities? SOLAS was designed to overcome disciplinary barriers between atmospheric and marine sciences, so can the SOLAS network now be used to transcend disciplinary barriers with social science?



↑ Figure 1: The SOLAS Mid-Term Strategies (top row) mapped against the Foci and Activities of the SOLAS SP&IS, with major relevance indicated by a large dark blue rectangle and moderate relevance by a light blue small rectangle.

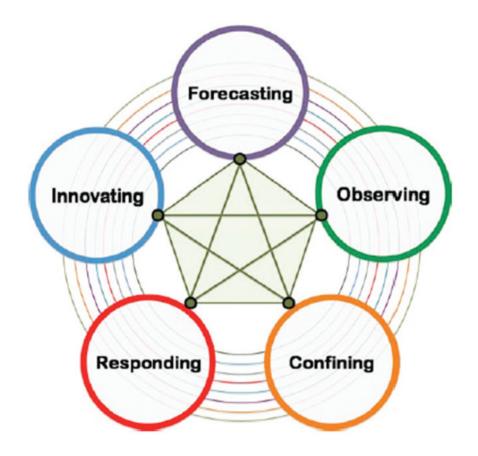
The discussion was lively, with general agreement that SOLAS has much to contribute to global sustainability and a variety of views on how this should be achieved. There was support for proactively communicating the societal/policy relevance of our science, without losing scientific rigor or undue expansion of the scientific scope of SOLAS. Suggested approaches included interacting with the social sciences at a high level by contributing data syntheses and model outputs to other programmes or including societal relevance as a cross-cutting theme in a revised science plan. It was noted that SOLAS is already engaged in policy-relevant issues, an example being the activity around ocean fertilisation which resulted in the Summary for Policymakers and changes in international legislation without moving too far from SOLAS core research.

There was discussion of the pros and cons of the FEI (ie. better articulation of how science benefits society vs. more centralized control of scientific agendas). The move towards greater societal relevance may have its origins in the current governmental focus on econonomic issues. It was commented that legislators and the general public have little appreciation of the economic relevance of SOLAS science such as, for example, the value of Ecosystems Services. However, the FEI could open up opportunities such as greater interaction with industry, with important areas such as marine renewable energy and water quality representing a natural progression toward societally-relevant science.

Developing a new science plan for SOLAS is a challenging undertaking. The science foci in the original SP&IS remain fundamental research frontiers, while many of the specific questions have changed. One approach could be to review the

SP&IS and identify which issues are settled, which remain open, and what new issues have arisen over the past decade. Another approach would be to map stressors (e.g. overfishing and fossil fuel burning) to receptors (e.g. the ocean-atmosphere system). Science communication needs to be at the forefront of any future plan, with the IPCC reports representing a good example of SOLAS science transfer to policy makers. It was felt that the scientific community needs to invest more in communication, in order to justify research and articulate the benefit and excitement behind a scientific discovery. Communication and education should feature more prominently in future SOLAS plans.

Further information was provided by Peter Liss on the FEI transition process. He noted that FEI is an attempt to create a single global change programme and SOLAS has the opportunity to be part of the core group. Programmes will be reviewed for "goodness of fit" and the task team will report on their findings by the end of 2012. The FEI will also include a major component on the social sciences via 'megathemes' or 'integrated research projects' to which SOLAS should contribute. Megacities is one example, but other societalrelevant areas will be developed. At the end of the session it was reiterated that the first stage of the transition to the FEI has occurred, with a letter from the SOLAS Steering Committee to the FEI Transition Team conveying the value of SOLAS research to global sustainability and the interest of the SOLAS community in contributing to the goals of FEI. The transition process should develop over the next two years, with input from the SOLAS community.



↑ Figure 2: The Grand Challenges in Earth System Science for Global Sustainability (ICSU (2010). Earth System Science for Global Sustainability: The Grand Challenges. International Council for Science, Paris.)

# Impacts of dust and ash on ocean productivity

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The SOLAS community has an ongoing interest in the fertilization of ocean ecosystems by continental dust and volcanic ash. Four themes were addressed.

### 1. Relative importance of dust vs. ash

Dust and ash require specific studies because they are potentially different in many respects: iron solubility (ash can release iron more quickly), change in chemical characteristics during atmospheric transport, residence time in the mixed layer, coupling to weather events, and frequency of deposition. Biomass burning and anthropogenic pollution also provide large inputs. Relative contributions from all these sources need to be determined. We must address the coupling of dust and ash events with weather patterns, because this coupling complicates predictability and because weather events may enhance other nutrient sources such as vertical mixing. The importance of macronutrient additions in low nutrient-low chlorophyll (LNLC) regions must be better characterised.

### 2. Bioavailability

A major recommendation was the use of a standardised material by all bioavailability studies, both lab studies of nutrient release and incubation studies of ecosystem effects, to allow better intercomparison of studies using different methods (de-ionised water vs. seawater etc.). A dust standard may become commercially available within a year. Ash is known for poor storage characteristics, complicating production of a reliable standard. The release of other bio-active elements, such as copper, should be included in these experiments.

Mesocosm fertilization experiments should be encouraged in addition to smaller volume incubations to allow for more realistic release of nutrients by sinking particles.

The presence of natural metal-binding ligands and the different chemistry of wet vs. dry deposition should be considered. Measurements of the heterotrophic community are important to assess competition for nutrients and effects on the efficiency of the biological carbon pump and sequestration. Impacts of these events higher up the food chain remain almost entirely unknown.

GEOTRACES is also looking at that the impact of volcanic eruptions on ocean biogeochemistry, with a focus on solubility, and collaboration should be fostered between SOLAS and GEOTRACES on the topic of dust and ash.

### 3. Field measurements strategy

A major recommendation was to improve our capability to measure aerosols and deposition rates in remote areas through automated devices. Information is needed on the mass of material deposited and on the size spectra of the particles. High latitude observations are particularly lacking. Ships of opportunity may provide another sampling platform.

The ocean response to fertilisation events is generally assessed by satellite imagery. Dust/ash can alter the signal and further studies are needed to assess the sensitivity of algorithms to these effects. The potential to mount field expeditions in response to sudden fertilization events was discussed.

### 4. Future changes

In a warmer and highly stratified ocean, aeolian fertilisation could become more important. Both ocean acidification and anthropogenic pollution have the potential to impact iron release from aeolian particles as well as chemical speciation and bioavailability. The climate feedbacks that may be caused by dust and ash remain an open question.

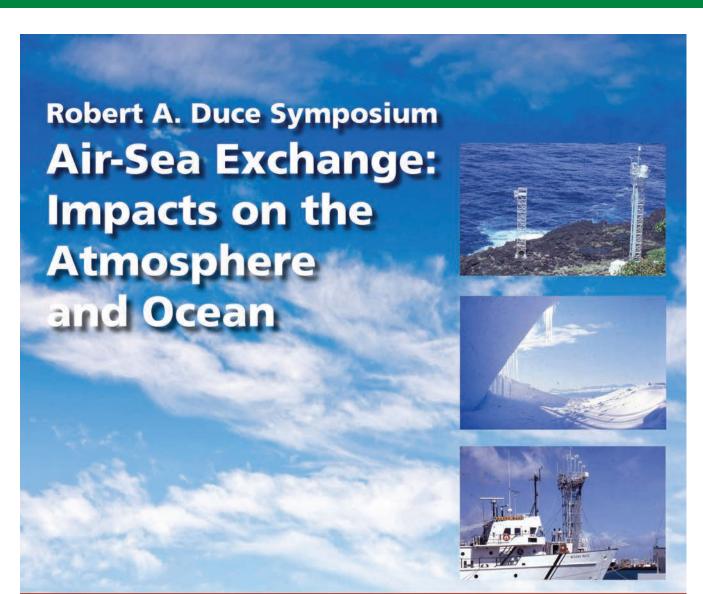
# Good bye Norwich

With the closure of the Norwich office we say goodbye to two long standing members of SOLAS staff Kath Mortimer and Georgia Bayliss-Brown. Kath is moving to a new position as a Web and Communications Project Officer at the UEA whilst also continuing to work on the forthcoming COST publication part time. Georgia begins a new challenge at the Centre for Environment, Fisheries & Aquaculture Science (CEFAS), UK, as Marine Climate Change Scientist.

SOLAS would like to take this opportunity to thank Kath and Georgia for all their work for SOLAS especially for the SOLAS Summer School, Newsletter and Open Science Conferences and wish them luck in their future careers. Thanks go also to all staff who have previously worked in the Norwich office including Casey Ryan, Jeff Hare, Martin Johnson, Justin Ho, Hannah Mossman and Sophie Seeyave.



↑ Photo: Kath Mortimer and Georgia Bayliss-Brown. Credit: Stefan Kontradowitz



# http://annual.ametsoc.org/

The 2013 Robert A. Duce Symposium recognizes Dr. Duce's leadership of the atmospheric and oceanic science community both in the United States and internationally and honors his distinguished contributions to research in Antarctica, the Arctic and all the world's oceans related to



- chemical cycles of pollutant and natural substances in the global atmosphere
- atmospheric transport of chemicals from the continents to the ocean and their impact on marine biogeochemistry
- · atmospheric chemistry and climate

More info on this symposium can be found at annual.ametsoc.org. Sponsors include American Meteorological Society, National Science Foundation, and International Commission on Atmospheric Chemistry and Global Pollution.

# In Focus

As always, in SOLASnews we like to keep you familiar with who is who within the community. In this issue, we would like to introduce our newest National Representatives, Chiara Santinelli (Italy) and Laura Farias (Chile); and, Roberto Benavides and Jasmin Mögeltönder, who are our Project Assistants at the SOLAS International Project Office, Kiel (Germany).

# Chiara Santinelli





Chiara Santinelli, a Biologist by training, carried out her PhD in Chemical Oceanography, at the Pisa University, working on dissolved organic carbon (DOC) and chromophoric dissolved organic matter (CDOM) in the Mediterranean Sea. Since 2005, she is Researcher at the Biophysics Institute of the Italian National Research Council and, in 2009, became Professor of Oceanography at Pisa University. Her research interests focus on dissolved organic matter (DOM) dynamics in both coastal areas and open sea waters, with particular regard to the role of DOM in the global carbon cycle and in carbon export and sequestration in deep waters. She is currently working on carbon fluxes and inventory in the Mediterranean Sea; optical properties (absorption and fluorescence) of CDOM; and, atmospheric deposition of DOM. She has been involved in European and National projects and participated in more than 20 oceanographic cruises in the Mediterranean Sea. She is also working on outreach activity in primary schools (8-10 years old children).

# Roberto Benavides



Roberto Benavides joined the SOLAS International Project Office (IPO) Team in Kiel since August 2011. He is currently studying a masters' in Material Science after graduating with a BSc in Material Sciences from the Faculty of Engineering at the

University of Kiel. After finishing his BSc, he worked for the marine industry in Kiel where he gathered experience in project management. Roberto is helping with the everyday tasks at the SOLAS IPO and is taking care mainly of the new website design and re-launch which is planned for midautumn this year. In his free time, he enjoys playing the bass guitar and training for triathlons.

# Laura Farias





Laura Farias obtained a degree as an Oceanographer at the University Nacional del Sur (Argentina) followed by her Masters and PhD in Oceanography at the University of Concepcion (Chile). Currently, Laura is Associate Professor at the University of Concepcion. Her scientific research has been focused on understanding the nature and extent of the biogeochemical processes involved in the cycling of N<sub>2</sub>O and CH<sub>4</sub>. Her work particularly focuses on how oxygen concentration affects biogeochemical processes, such as denitrification and nitrification, and how oxygen regulates the cycling of N<sub>2</sub>O via both of these processes. She has made scientific contributions relating to N<sub>2</sub>O cycling in the oxygen minimum zones (OMZ) of the eastern South Pacific region.

Having also built and reported one of the first marine time-series of  $\mathrm{N_2O}$  in the world, her observations and experiments were the starting point for questionsother than those traditionally posed—regarding the origin of this gas. The  $\mathrm{N}_2\mathrm{O}$  time series has improved our understanding of processes driving temporal variability (monthly to inter-annual) of  $N_2O$  fluxes across the airsea interface in coastal waters. More recently, she has focussed on the processes involved in  $\operatorname{CH_4}$  cycling and methylated compounds, which offers glimpses into the origin of  $\mathsf{CH}_4$  in surface waters. She also has collected six-years of a (monthly) CH<sub>4</sub> time series, along with measurements of photo- and chemo-synthetic activities. Finally, since the outset of her career, she has strongly strengthened postgraduate education; so far, eight students—primarily from South American countries have graduated under her supervision and successfully returned to their respective countries to disseminate their passion for biogeochemistry.

# Jasmin Mögeltönder



Jasmin joined the SOLAS International Project Office Team in Kiel since July 2012. She studied Political Science, Psychology and International Law at the University of Kiel. Before Jasmin joined our team she made an internship at the federal foreign office in

Berlin and was working as a human rights observer in the Philippines. Now Jasmin wants to enlarge her experience in Project Management.

# New SSC members

We would like to send a very warm welcome, and introduce you, to our newest members of the SOLAS Steering Committee (SSC): Anja Engel (Germany), Michelle Graco (Peru) and Huiwang Gao (China, Beijing). With every welcome comes a goodbye and upon this occasion, on the behalf of the whole SOLAS community, we would like to send a tremendous thank you for all of the hard work and efforts of our departing SSC members, Isabel Cacho (Spain), Sergey Gulev (Russia) and Doug Wallace (Canada); who is currently acting as ex-officio.

# Michelle Graco



Michelle Graco is a Chemical Oceanographer of the Instituto del Mar del Peru (IMARPE). In 1995, she received her degree in Biology and later, in 2002, obtained a PhD in Oceanography from the Universidad de Concepción, Chile, and the

Université Pierre et Marie Curie, France. She worked in the Department of Oceanography at IMARPE from 2005; and, for the past two years has been responsible for undergraduate, oceanography courses at the Universidad Científica del Sur. She also contributes to the masters' programme in Marine Sciences at the Universidad Peruana Cayetano Heredia. Her research interests cover different aspects of the biogeochemistry associated with Ecosystem Boundaries Upwelling systems and Oxygen Minimum Zones. In particular, the response of the nitrogen and carbon cycles to the OMZ spatial and temporal variability, including the greenhouse gases (CO2, N2O), in order to understand the feedbacks between climate change, upwelling ecosystems and OMZs.

# Anja Engel



Anja Engel is a Professor of Biological Oceanography and Head of the Marine Biogeochemistry research division at the Helmholtz Centre for Ocean Research Kiel (GEOMAR), Germany. She also is Adjunct Professor at Stony Brook University, USA.

After receiving her PhD in Biological Oceanography from the University of Kiel, Germany, in 1998, she worked as a Postdoc at UCSB (USA), AWI (Germany) and SUNYSB (USA). In 2005, she became Head of a Helmholtz Young Investigators Group at the Alfred Wegener Institute (AWI) in Bremerhaven, Germany. Her research addresses biogeochemical processes within the upper water column and at the interface with the atmosphere. Her motivation is to better understand the responses of microbial communities to environmental forcing - in particular to ocean acidification, warming and deoxygenation - and the consequences for organic matter cycling and gas exchange. The current focus of her group is on processes involving dissolved organic matter (DOM), such as production, consumption and remineralisation of DOM by marine microbes, and the coagulation of dissolved polymers into gel particles.

# Huiwang Gao



Huiwang Gao obtained his PhD at the Institute of Atmospheric Physics, Chinese Academy of Sciences, China, in 1996, and is currently a Professor and the Dean of College of Environmental Sciences and Engineering at Ocean University of China. His research

interests include air-sea chemical exchanges, marine biogeochemical and ecological modeling, and environmental health assessment.

He has served on some national and international committees, such as the Chinese Society for Environmental Sciences and the Chinese Society for Oceanography and Limnology. As one of the founding members of China SOLAS, he devoted considerable efforts in promoting the initiative on studies of ADOES (Asian Dust and Ocean Ecosystem); and both International SOLAS and UNESCO/IOC/WESTPAC approved the formation of the ADOES task team in 2010. From 2005 to 2011, six international ADOES workshops with Asian SOLAS were held in China, Japan and Korea, and this series of meetings has greatly promoted our understanding of Asian dust and its impacts on the north Pacific ecosystem. Huiwang has published more than 100 papers in Chinese and international journals and was invited to give talks at the 2012 SOLAS Open Science Conference, 2010 AGU Fall meeting and 2010 PICES annual meeting.

# SOLAS endorsed projects

# FLATACOA: Atmospheric dust in South Hemisphere

R. Losno and A. Heimburger. University Paris 7 Denis Diderot, University Paris Est Creteil, LISA, UMR CNRS 7583.

Atmospheric dust concentrations and flux over Southern Oceans is poorly known because of small coverage of South Hemisphere with field experiments. Only few people are living here but all this area is of interest concerning CO<sub>2</sub> sink by the ocean. Trace metal deposition on the oceans can have some impact on its sink. During past years, we have set up a field experiment program combined with a modelisation effort to document deposition flux of continental dust into South Indian Ocean. Two years of continuous flux measurements were performed at Kerguelen (49°S 70°E) and one year at Crozet (46°S 51°E). We have now a database with deposition flux of Li, Na, Rb, Mg, Ca, Sr, Ba, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, REEs, U, Al, P, S, As and Pb on both locations on a monthly or 2 weeks basis. For example, the total deposited iron flux measured is about 500 nmol/m²/year at Kerguelen and Crozet (Figure 1), in good agreement with models.

One of the major sources of dust seems to be Patagonia and we have got funding to extend our investigations to this area in order to explore dust emissions ("Dust From



↑ Figure 1: Deposition sampler ready to be sent from the clean room to the field at Kerguelen or Crozet.

# Accumulated Flux of Iron Flux J Average Flux /12/06 06/02/09 28/03/09 17/05/09 06/07/09 25/08/09 14/10/09

↑ Figure 2: Accumulated iron flux at Kerguelen from December 2008 to January 2010. The slope of the line represents an average flux obtained by linear regression.

Dates (d)

Patagonia", INSU/CNRS). We have set up from beginning 2012 a sampling station at Rio Gallegos (Argentina, 51°S 69°W) where atmospheric aerosol is collected on a weekly basis for 2 years. An aerosol LIDAR is about to be installed giving vertical profiles on an hourly basis. Chemical analyses of collected aerosols will be performed next year, including bulk elemental composition and solubility. Soil samples are also collected to serve as raw material for aerosol generation in laboratory. Chemical properties of these aerosols would be carefully studied. Thanks to kindness of colleagues, we also benefit of soil samples from South Africa and Australia and therefore have a complete panel of possible sources of atmospheric dusts in South of South Hemisphere. One of our goals is to use elemental ratio to track the origin of dust in our total deposition measurements at Kerguelen and Crozet.

The main difficulty we had to overcome is the logistics very complicated with long delays, about one year but sometimes two, between preparation of sampling and return of samples. We have developed specific washing and preservation protocols to keep stable the chemical composition of our samples. We hope to significantly improve our knowledge of dust cycles in South Hemisphere and give constraints values for global modelization of trace metals deposition into the Ocean. This will certainly improve our knowledge of biogeochemistry in South.

For further information, please visit (http://www.solasint.org/science/research endorsements/resendprojects/endorsed projects.html#flatocoa



↑ Figure 3: Atmospheric sampling station set up at Rio Gallegos.

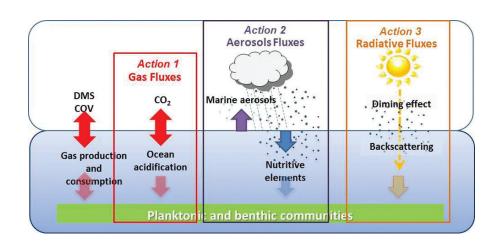
# MERMEx (Marine Ecosystems Response in the Mediterranean Experiment)

MERMEx is a component of the MISTRALS (Mediterranean Integrated STudies at Regional And Local Scales) decennial program dedicated to the understanding of the Mediterranean Basin environmental process under the planet global change (www.mistrals-home.org/). MERMEx aims to study the response of Mediterranean ecosystems and biodiversity to climate changes and anthropogenic pressure in order to better anticipate their upcoming evolution. It is focusing on the response of ecosystems to modifications of physicochemical forcing at various scales, both in time and space, linked to changing environmental conditions and increasing human pressure. It proposes a comprehensive, integrated approach considering the continuum between the coastal zone and the open sea and its interfaces, including ocean-continent, oceanatmosphere and water-sediment. MERMEx White Book was published in 2011 in Progress in Oceanography. The project is divided into several thematic approaches that were grouped into five work packages (WP): WP1- Impact of hydrodynamic changes on Mediterranean biogeochemical budgets; WP2- Ecological processes; biogeochemistry and food web interactions; WP3- Land-ocean interactions including extreme events; WP4- Natural and anthropogenic air-sea interactions; and, WP5- Ecosystem based management. In each WP several actions are currently funded or submitted for funding through different funding agencies [MISTRALS, ANR, EU...].

As MERMEx, via the WP4 objectives, directly addresses the 3 science issues from the International SOLAS Science Plan and Implementation Strategy, it was endorsed by SOLAS in August 2011.

In the various proposed actions, ongoing projects are the following:

- CALIBORON past pH reconstructions in the Mediterranean Sea based on the boron isotopic signature in biogenic carbonates – calibration using Mediterranean mussels and corals; started in 2011, eric.douville@lsce.ipsl.fr;
- CARBORHONE pCO<sub>2</sub> and DIC dynamics in the Rhone river estuary and the Gulf of Lions; started in 2011; bozec@sb-roscoff.fr;
- ANR Blanc SAM MERMEx-ChArMEx, Quantification and determination of marine organic aerosol fluxes as a function of trophic conditions; started in 2012; barbara.danna@ircelyon.univ-lyon1.fr); and,



↑ Figure 1: Main MERMEx activities relevant to SOLAS (WP4 objectives and actions): The assessment of gas fluxes (CO₂) and acidification and the impacts on ecosystems and biogeochemical cycles is strongly connected to the FP7-MedSeA project. The study of aerosol fluxes at the air-sea interface is coupled with the component ChArMEx of MISTRALS (Chemistry-Aerosol Mediterranean Experiment) and considers both the formation of marine aerosol (in collaboration with FP7-MedSea project also) and the atmospheric deposition of nutrients. The influence of solar radiations on biogeochemical cycles includes the potential effect of aerosol and tropospheric ozone attenuation on marine ecosystems.

• PHOTOMED - Metabolic and structural changes of the bacterial community in response to the phototransformations of dissolved and particulate organic matter in Mediterranean Sea; started in 2011, joux@obs-banyuls.fr).

There are also several other relevant projects with strong links to MERMEx:

- MedSeA EU FP7, started in February 2011, Mediterranean Sea Acidification in a changing climate with in particular a joint experiment using large pelagic mesocosms in Corsica (Summer 2012) to assess the effects of ocean acidification on planktonic communities in oligotrophic areas (see article in this issue);
- eFOCE BNP-Paribas, started in 2011, European Free-Ocean Carbon dioxide Enrichment experiments: development of benthic experimental systems to study the effects of ocean acidification of benthic communities in the field (Bay of Villefranche, Mediterranean Sea); started in 2011; gattuso@obs-vlfr.); and,
- The instrumented site at Frioul for the radiative measurements in the air and in the sea (Regional funding; richard.sempere@univ-amu.fr).

Another action will concern the setting up of a proposal for a field cruise entitled PEAcEtIME "ProcEss studies at the Air-sEa

Interface: a Mediterranean Experiment" (joint experiment between MERMEX and ChArMEx planned in 2015). This project was presented at the 2012 OSC to call for international collaboration on that "SOLAS cruise" in the Mediterranean.

For further information please visit, http://mermex.com.univ-mrs.fr/

### Reference:

Mermex Group, 2011. Marine Ecosystems Responses to climatic and anthropogenic forcings in the Mediterranean. Progress in Oceanography 2(91):97-166

### Coordination:

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# ADEPT - Aerosol deposition and ocean plankton dynamics

Peters, F. Institut de Ciències del Mar (CMIMA, CSIC), Pg. Marítim de la Barceloneta 37-49, 08003 Barcelona, Catalunya, Spain. Contact: cesc@icm.csic.es

ADEPT is a research project funded by the Spanish Ministerio de Economía y Competitividad to study the effect of atmospheric aerosol deposition on the dynamics of the Mediterranean Sea, a marine LNLC (low nutrient low chlorophyll) system.

Over geological time scales, dust of mineral origin seems to be crucial in driving oceanic biogeochemical fluxes. The objective of ADEPT is to investigate whether dust deposition can also be reflected in Mediterranean ecosystem dynamics at an ecological time scale. Basinwide, the input of nutrients to the Mediterranean Sea from atmospheric deposition is roughly equal to the land-based input. The potential ecosystem effects of such inputs, however, must be necessarily different as land-based sources are concentrated in coastal areas, while atmospheric inputs are distributed over large areas of the basin. The Saharan and Sahel regions are two of the most active areas in terms of dust export. A large portion of this dust travels across the LNLC Mediterranean Sea and is deposited within its basin. In addition, there is deposition of aerosols from anthropogenic origin, mainly from the more industrialized northern Mediterranean shore and with a large potential impact near the coastal areas. Increased ocean temperature and stratification and increased land erosion and anthropogenic emissions point to an increased future sensitivity of the Mediterranean ecosystem to atmospheric deposition.

ADEPT uses a multiscale and complementary approach to evaluate possible ecosystem responses to deposition. We relate satellite chlorophyll data with modeled Saharan dust deposition at the basin scale. We also measure deposition at several locations across the NW Mediterranean and simultaneously sample chemical and biological parameters of the water column in order to find relationships between both sets of variables. We count with non-scientists for sample collection in a socialized science approach. In addition, we conduct laboratory experiments with aerosol amendments to seawater to study plankton stimulation dynamics, utilization of organic matter by bacteria, and changes in bacterial composition and diversity, all for a better mechanistic understanding of the processes involved.

ADEPT (www.icm.csic.es/bio/adept) held a kick-off meeting in Barcelona on Feb. 2, 2012. Among the first issues that are being addressed is the setup of bulk deposition measurement stations at the Institute of Marine Sciences in Barcelona and at the Center of Advanced Studies of Blanes both in Spain. A third collector will be placed at the Stazione Zoologica Anton Dohrn in Naples, Italy. We analyze mainly inorganic nutrients and organic carbon. A pollen collector has also been placed at the Blanes site. Daily water column sampling efforts are being started at several locations along the Spanish coast with the help of a range of collaborators. The project benefits from the

added logistics and manpower. Stakeholders appreciate the proximity of scientific efforts to their environmental concerns and the bonds that develop between scientists and society at large should benefit everyone. We have started to find significant correlations between modeled deposition data (BSC-DREAM: Barcelona Supercomputing Center - Dust REgional Atmospheric Model) and satellite derived chlorophyll in large areas of the Mediteranean. The potential influence of Saharan deposition on ecosystem dynamics is largest for the Central and Eastern Mediterranean. We will be happy to collaborate/network with parties interested in studying the potential effects of atmospheric deposition on biogeochemical cycles and ecosystem dynamics in the Mediterranean or other LNLC areas.



↑ Figure 1: Ph.D. student Rachele Gallisai sampling the bulk deposition collector on the roof of the Marine Sciences Institute in Barcelona, Spain.

# MedSeA project

The MedSeA project is assessing ecological and economic impacts from the combined influences of anthropogenic ocean acidification<sup>1</sup> and warming, while accounting for the unique characteristics of this region. MedSeA is funded by the European Commission 7th Framework Programme from 2011 to 2014. To date, MedSeA has examined existing data of the Mediterranean Sea and has obtained new observational and experimental data of the region.

The project is developed in four main themes:

# 1. Dynamics of the Mediterranean carbonate chemistry from interannual to millennial timescales

The MedSeA project is characterizing the Mediterranean seawater carbonate chemistry and quantifying the rate of pH decrease in the Mediterranean waters. It will ultimately



provide maps identifying regions expected to be most affected by acidification.

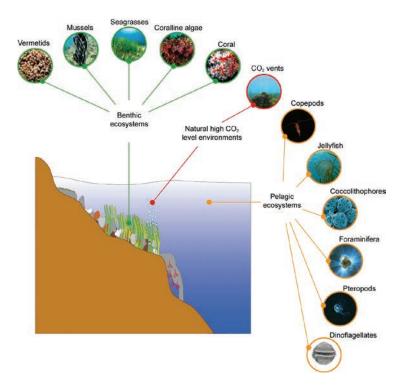
We are performing new field studies on the seawater carbonate system variables and have been collecting time-series measurements in order to trace the seasonal and spatial variability. MedSeA is also looking into providing proxy-based reconstructions of seawater pH, carbonate ion concentrations, and pCO $_2$  along with the response of key marine calcifiers during target intervals of the Late Quaternary (e.g. last interglacial period).

# 2. Mediterranean key-stone species and ecosystem responses

We are defining the susceptibility and resilience of key-stone species and endemic ecosystems (Figure 1) to Mediterranean acidification and warming. Analysis of the experimental results will allow projections of changes to the services that these ecosystems and species provide.

Laboratory experiments have been undertaken to study the individual and dual impacts of acidification and temperature on key pelagic and benthic organisms.

A first mesocosm experiment has been performed off Corsica this summer (June-July 2012) and has gathered data to identify the impact of acidification on the planktonic community, including biodiversity and species succession as well as the role of the



Λ Figure 1: Evolution of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in the nine mesocosms. C refers to control mesocosms (x3), P refers to perturbation mesocosms (x6) and OUT refers to outside ambient levels in the bay of Calvi. Atm is the atmospheric pCO<sub>2</sub> equilibrium (around 400 ppm during the time of the experiment).

microbial loop. A second experiment is planned for next year in the eastern Mediterranean to test the effect of high CO<sub>2</sub> conditions in a more alkaline and oligotrophic seawater environment.

Study the responses of benthic community is vital to our understanding of the ecological effects of ocean acidification, as 98% of all described marine species live on the sea floor. MedSeA researchers characterized the current state of selected fragile ecosystems, identifying possible risks under ocean acidification and climate change. Our results reveal major changes in community structure following environmental change. This was strikingly evident around CO<sub>2</sub> vents, but also in carefully manipulated laboratory and mesocosm experiments. Of special importance are changes in the well-being of engineering species such as seagrass and vermetids which build the ecosystem frame-work. In their absence, many other organisms and ecological services are detrimentally affected.

### 3. Socio-economic effects of Mediterranean Sea acidification and potential adaptation strategies and policy tools

The MedSeA project examine the direct and indirect socio-economic (welfare) impacts of ocean acidification. Economic impacts of ocean acidification on red coral, mussels, aquaculture, and ecosystem regulating services such as carbon sequestration are examined. This includes productive and nonuse values, and effects on tourism

demand and satisfaction. The approach takes into account different factors and economic mechanisms like costs, prices, labour demand, trade, and income effects. In addition, indirect effects are studied through interactions between marineresource based and other economic sectors.

### 4. Moving ahead

In the coming months, MedSeA scientists will be looking into projecting future changes and related uncertainties. We will be expanding projections of acidification to include the Mediterranean Sea by relying on modelling tools, which will aid to bridge experimental results with socio-economic studies. As a practical outcome, the project will propose policy measures for adaptation and mitigation that may geographically vary and at the same time require coordination between regions or countries.

<sup>1</sup> 'Ocean acidification' refers to the ongoing decrease in ocean pH directly caused by the ocean's uptake of carbon dioxide (CO<sub>2</sub>) from human-induced atmospheric CO<sub>2</sub> emissions.

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↑ Photo: Bottom view of the mesocosms (© Stareso)



↑ Photo: Sampling of the mesocosms (© A. Rees, PML)

# BIOACID ready to start its second 3-year phase

Riebesell, U. GEOMAR, Helmholz-Zentrum für Ozeanforschung Kiel, Germany



The German research project BIOACID (Biological Impacts of Ocean ACIDification) is about to complete its

first 3-year phase. Funded by the German Ministry for Education and Science (BMBF), BIOACID brings together 15 research institutes and universities across Germany to jointly work on aspects ranging from organism responses to ocean acidification and their underlying mechanisms to ocean acidification impacts on marine biogeochemical cycles and feedbacks to the climate system. BIOACID has established close collaboration with its sister projects EPOCA (European Project on Ocean Acidification; ended in April 2012), the UK Ocean Acidification Research Programme (UKOA) and the EU-project Mediterranean Sea Acidification in a Changing Climate (MedSeA). BIOACID supports the activities of the Ocean Acidification International Coordination Centre (OA-ICC) launched in July of 2012 and works closely with the OA International Reference User Group (OA-iRUG). BIOACID phase 1 will complete its work in August 2012.

During its first funding period BIOACID research provided evidence that

 OA negatively affects many (but not all) calcifying organisms

- OA stimulates primary production by some benthic and various pelagic autotrophic organisms
- OA stimulates nitrogen fixation by diazotrophic cyanobacteria
- less severe responses to OA occur after long-term acclimation in some groups
- some groups will be capable to adapt to OA
- OA will change marine community composition

A follow-up proposal for a second phase of BIOACID has been evaluated positively and is now recommended for funding by the BMBF. If successful, BIOACID will continue its research on the impacts of ocean acidification (OA) until 2015.

The growing evidence of potential biological impacts of ocean acidification affirms that this global change phenomenon may pose a serious threat to marine organisms and ecosystems. Despite a wealth of knowledge on specific effects of acidification and the related changes in seawater chemistry on the physiology of individual marine taxa, many uncertainties still remain. Because the majority of studies are based on single species experiments, little is presently known about possible impacts on natural communities, food webs and ecosystems. Moreover, few studies have addressed

possible interacting effects of environmental changes occurring in parallel with ocean acidification, such as warming, deoxygenation, and changes in surface layer stratification and nutrient supply. Almost completely unknown at present is the potential for evolutionary adaptation to ocean acidification. To pave the way for a more encompassing assessment of future biological responses to ocean change and their possible socio-economic consequences phase 2 of BIOACID will

- strengthen the integration within the BIOACID community to allow for more realistic community-level experimentation and field observation
- focus more strongly on interacting affects through multiple stressors
- expand evolutionary biology to assess the potential for adaptation of key taxa
- integrate socio-economic assessments and stakeholder involvement

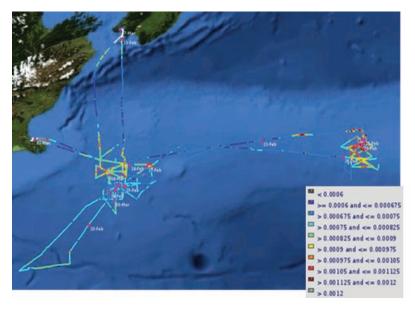
The overarching focus of BIOACID II will be to address and better understand the chain from individual organism responses and their underlying mechanisms, to community and ecosystem changes and their consequences for food webs and biogeochemical cycling, to economic impacts and feedbacks to the climate system.

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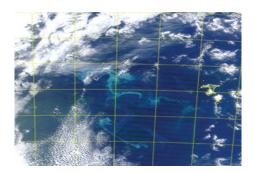
# Surface Ocean Aerosol Production (SOAP) in the South-West Pacific Ocean

Law, C.S., Harvey, M., Smith, M. and the SOAP Team\*National Institute of Water and Atmospheric Research (NIWA), Wellington, New Zealand

Biologically-active regions of the surface ocean support the production of a range of compounds that influence the production, composition and properties of aerosols in the marine boundary layer. The SOAP voyage in February-March 2012 examined biotic influences on aerosol production in a productive frontal system in the south-west Pacific Ocean. Sampling took place along the Sub-Tropical Front east of New Zealand, primarily in three phytoplankton blooms with different characteristics (Figure 1 and 2). Bloom 1 was dominated by dinoflagellates with high chlorophyll-a, low surface pCO<sub>2</sub> (minimum 260 µatm) and high DMS (maximum 20 nmol/l), whereas Blooms 2 & 3 were dominated by coccolithophores with lower Chl-a, moderate pCO<sub>2</sub> (minimum 305 µatm) and lower DMS.



 $\Lambda$  Figure 1: The SOAP voyage track with the colours indicating  $\beta$ 660 backscatter, which was used as a proxy for coccelithophore abundance



↑ Figure 2: MODIS AQUA image of Bloom 2, west of the Chatham Islands, indicating the presence of coccolithophores.

Work–package 1 examined the relationships between the distribution of DMS and pCO<sub>2</sub>, and phytoplankton biomass & species composition, and related spatial variation in aerosol number distribution and composition properties of the surface microlayer. Underway measurements showed regional covariance between atmospheric and surface water DMS. Process measurements indicated that a significant proportion of dissolved DMSP in surface waters was consumed by bacteria and cleaved into DMS; however, there was little evidence of near-surface or microlayer enrichment or depletion of DMS.

Work–package 2 measured DMS & CO<sub>2</sub> flux to and from the atmosphere, and examined relationships between gas transfer velocity and physical drivers, such as near-surface turbulence, sea-state and whitecap coverage. Different DMS flux measurement approaches were employed, including eddy correlation measurements from the ship's bow and gradient flux measurements at distance from the ship on a catamaran (Figures 3 and 4). Preliminary data from the latter, augmented by measurements on the foredeck and crows–nest showed a consistent gradient of decreasing DMS with height.

Work-package 3 addressed the relative importance of primary and secondary organic sources to nuclei production. Aerosol size range was well-characterised by a range of instruments (see Fig. 4), which facilitated the study of interactions between sea salt aerosol, precursor gases and nucleation. In addition to DMS, other candidate aerosol precursor gases were measured in the atmosphere, including methyl halides, halogen oxides and VOCs. Instances of particle nucleation were observed, with nucleation (10 nm and 15 nm) and Aitken mode sized particles (50 nm) typically including a significant secondary organic component.



↑ Figure 3: Autonomous catamaran deployment

This generally occurred during periods of high solar radiation in biologically active regions, whereas the organic contribution to particles was lower during cloudy conditions. In vitro bubble bursting chamber measurements also indicated a moderately oxidised primary organic fraction in the produced particles.

SOAP are currently in the initial data analysis phase, with a data workshop planned for 2013. SOAP is a SOLAS endorsed project, and a NZ SOLAS contribution to the SOLAS Mid-Term Strategy Ocean-derived aerosols: production, evolution and impacts. For further information, please visit

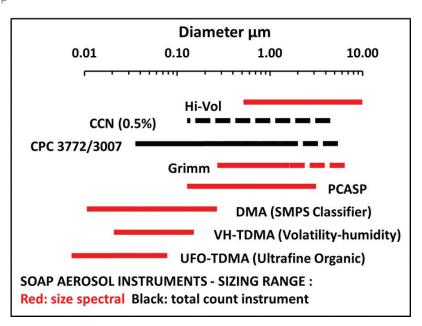
https://www.niwa.co.nz/atmosphere/project s/soap



↑ Figure 4: Gas sampling mast

\*K. Currie, F. Elliot, S. George, P. Johnston, J.McGregor, A. Marriner, G. Olivares, G. Olsen, K. Safi, N. Talbot, C. Walker (NIWA, NZ); T. Bell, C. McCormick, E. Saltzman (UCI, USA), W. deBruyn (U Chapman, USA), S. Landwehr (NUIG, Ireland), C. Marandino (IFM-Geomar, Germany), M. Lizotte. M. Levasseur (Uni. Laval, Canada); S. Miller, (SUNY, USA), L. Cravigan, M. Mallet, Z. Ristokski (QUT, Australia); P. Vaattovaara (U Eastern Finland), S. Lawson, M. Keywood, J. Ward (CSIRO, Australia), N. Harris, A. Robinson (U Cambridge, U.K.).

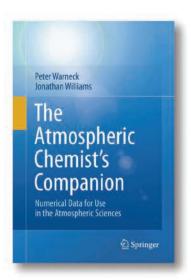
Contact: cliff.law@niwa.co.nz



A Figure 4: Aerosol size characterisation during SOAP (Hi-Vol - Lear Sieglar flowset high volume sampler, fitted with 6 stage cascade impactor); CCN - Cloud condensation nuclei monitor; CPC - condensation particle counters; Grimm dust monitor; PCASP - Passive Cavity Aerosol Spectrometer; DMA - Differential Mobility Analyser (Scanning mobility particle sizer); VH-TDMA Volatility/Humidity - Tandem DMA; UFO-TDMA - Ultrafine organic Tandem DMA.



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P. Warneck, Max Planck Institute for Chemistry, Mainz, Germany; J. Williams, Max Planck Institute for Chemistry, Mainz, Germany

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Peter Warneck, a physical chemist specializing in atmospheric chemistry, received the diploma in 1954 and the doctorate in 1956 at the university in Bonn, Germany. In 1959, following several postdoctoral assignments, he joined the GCA Corporation in Bedford, Massachusetts, where he explored elementary processes in the atmospheres of the earth and other planets. He returned to Germany in 1970 to head the chemical kinetics group in the Air Chemistry Division of the Max-Planck-Institute for Chemistry in Mainz. In 1974 he also became professor of physical chemistry at the university in Mainz. In 1991, following German reunification, Warneck was appointed the founding director of the new Institute for Tropospheric Research in Leipzig. He served in this position parallel to his activities in Mainz until official retirement. Warneck's research included laboratory studies of chemical mechanisms and photochemistry as well as the development of analytical techniques for field measurements. Since 1990, his interests are focused on chemical reactions in clouds. Jonathan Williams is an atmospheric chemist. He received his BSc in Chemistry and French and his Ph.D. in Environmental Science from the University of East Anglia, England. Between 1995-1997 he worked as a postdoctoral researcher at the NOAA Aeronomy laboratory in Boulder, USA, and from 1998 to present as a member of staff at the Max Planck Institute for Chemistry, Mainz, Germany. He has participated in many international field measurement campaigns on aircraft, ships and at ground stations. Dr Williams is currently an editor on three atmospheric chemistry journals.



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