Workshop on:

“Frontiers in ocean-atmosphere exchange: Air-sea interface and fluxes of mass and energy”

15 - 18 May, 2017
Cargèse, Corsica, France

On 15 - 18 May 2017 a workshop on “Frontiers in ocean-atmosphere exchange: Air-sea interface and fluxes of mass and energy” took place at the Institut d'Etudes Scientifiques de Cargèse, Corsica, France, which is a unique facility for hosting scientific workshops and summer schools. The motivation behind the workshop derived from the recently-produced SOLAS 2015-2025: Science plan and organisation, which focus is on linking ocean-atmosphere interactions with climate and people. This new science plan is based on five Core Themes, with the workshop focusing on Core Theme 2: “Air-sea interface and fluxes of mass and energy”. Ocean-atmosphere fluxes of momentum, heat, freshwater, gases, and aerosols play a critical role in the regulation of climate and uncertainties in these fluxes constrain our ability to understand and model our changing climate. All exchanges between the ocean and the atmosphere cross the air-sea interface and it is through these fluxes that the ocean and atmosphere are connected. The problem of adequately describing air-sea fluxes is complex and simplistic parameterisations to represent the fluxes in models are not sufficient. A full understanding of the processes at the air-
Event summary

Sea interface will only evolve by interdisciplinary efforts. Thus, twelve speakers from different research disciplines were invited to present their work. The programme should promote strong interaction between the participants and invited speakers, with the presentations in the morning and interdisciplinary breakout sessions in the afternoon, each led by two invited speakers. These sessions were followed by poster presentations, particularly from doctoral candidates and early career scientists.

The initial session was an overview of basic SOLAS themes and presented scientific highlights of the past decade. Additionally, fundamental science topics such as air-sea gas exchange, the microlayer, the role of surfactants and bubbles were discussed, as well as policy-relevant activities like the carbon cycle, the ocean as carbon dioxide sink, ocean acidification, ship emissions, and marine particles were covered. A session on clouds and rainfall as part of the ocean-atmosphere system demonstrated that global warming, which is attributed to anthropogenic climate change, has been linked to changes in the global hydrological cycle. Ocean salinity is a much more reliable indicator of the water cycle than any land-based measurement. Salinity is an important constraint in ocean models and an indicator of freshwater capping. Sea surface salinity is correlated with differences between precipitation and evaporation, and improved knowledge on these differences would provide a better estimation of latent heat flux, and improve the characterisation of stratification of the near-surface ocean layer. Gas exchange is driven by turbulence at the air-sea interface and rain has the effect of modifying the ocean surface turbulence. In addition, has also been shown to enhance near-surface stratification (through buoyancy forcing), which affects sea surface temperature, surface mixing, near-surface currents, as well as communication between the surface and the mixed layer. Most essential for the SOLAS community, rain dampens surface gravity waves (with the potential to enhance capillary waves) and also affects the air-sea gas exchange (enhances the gas transfer coefficient and affects chemistry). Thus, the role and the composition of the sea

Figure 1: Participants of the Workshop.

Back row from left-to-right: Lucia Robles-Diaz, Valentina Giunta, Lucia Gutiérrez-Loza, Graig Sutherland, Magdalena Anguelova, Kyeong Ok Kim, Francesc Peters, Henry Potter, Anoop Mahajan, Nicolas Meskhidze, Sebastian Zeppenfeld, Wade McGillis, Rik Wanninkhof, Evangelos Voyiatzis, Eun Jin Kim, Anna Rutgersson, Anja Engel.

Front row from left-to-right: Leonie Esters, Stéphane Laussac, Joel Sudre, Liselotte Tinel, Christa Marandino, Nathalie Hayeck, Adrian Callaghan, Matt Salter, Tom Bell, Oyvind Breivik, Kai Christensen, Ilan Koren, Peter Liss, Royston Uning, Johnson Zachariah, Luisa Galgani, Anneke ten Doeschate, Brian Ward, Penny Vlahos.

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surface microlayer in the air-sea gas exchange were discussed, as well as sampling methods evaluated. Another major point for discussion during the workshop was the impact of surfactants on surface waves, which has several outstanding issues to be resolved, including rheology (which impacts the remote sensing of slicks); nonlinear wave-wave interactions (which impacts the wave spectrum); and parameterisations of small scale, anisotropic processes (which cause the redistribution of slick material by the wave-induced drift).

To conclude the workshop, a dinner with all participants was organised. We thank the workshop sponsors: SOLAS, the Office of Naval Research Global (ONRG); the World Climate Research Programme (WCRP); and the European Space Agency (ESA), whose support allowed us to provide the facilities for a very fruitful workshop. We also thank the invited speakers, the breakout session leaders, and indeed the participants, all of whom provided a full week of their time to contribute toward the advancement of the SOLAS Theme 2 “Air-sea interface and fluxes of mass and energy”.

Organising Committee:

Brian Ward (bward@nuigalway.ie) and Anneke ten Doeschate (anneke.tendoeschate@nuigalway.ie), AirSea Laboratory, National University of Ireland, Galway, Ireland

Anja Engel (aengel@geomar.de), Christa Marandino (cmarandino@geomar.de), and Emilie Brévière (ebreviere@geomar.de), GEOMAR Helmholtz Center for Ocean Research Kiel, Germany

Link to the event website: https://airsea.nuigalway.ie/cargese/workshop

The outcomes of this workshop contribute to advance our knowledge of the Core Theme 2 of the SOLAS 2015-2025: Science Plan and Organisation.

Figure 2: Ocean, atmosphere and beach near Cargese during the workshop © Anneke ten Doeschate

Event sponsors
Christa Marandino has been a professor of marine and atmospheric chemistry at GEOMAR Helmholtz Centre for Ocean Research Kiel and Kiel University, Germany since 2012. She investigates air-sea interactions, specifically dealing with how trace gases produced and consumed in the ocean influence atmospheric chemistry and climate. Her expertise is in direct air-sea trace gas flux measurements using the eddy covariance technique, as well as mass spectrometric method development and process studies in the ocean’s euphotic zone.

What can we learn from eddy covariance direct flux measurements of multiple gases simultaneously?

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Air-sea exchange is vital for the planet and a crucial component of biogeochemical cycling in the Earth system, as it affects climate through the transfer of heat, momentum, and water, as well as radiatively active trace gas species. Historically, without air-sea gas transfer we would not have terrestrial life on Earth. However, what the future holds, with respect to the ocean and global environmental change, is a serious question. What happens if the carbon dioxide (CO\textsubscript{2}) ocean sink strongly weakens? What impact would a less alkaline ocean have on biogeochemical cycling and climate? What would be the resulting influence on the atmosphere if an increasing fraction of the world’s ocean was made up of oxygen minimum zones? At the centre of all of these questions is gas exchange across the ocean-atmosphere boundary, one of the Earth’s largest boundaries. Research in the last decade has shown that there are already serious changes occurring at the air-sea interface, such as the slowing of the ocean carbon sink (e.g. Watson \textit{et al.}, 2009), possibly due to ocean acidification increasing bacterial remineralisation (e.g. Seg-schneider and Bendtsen, 2013). As the ocean is the largest sink for anthropogenic CO\textsubscript{2} in the atmosphere, its slowing has major implications for climate change. Such major changes and their impacts can only be fully quantified and predicted with a complete understanding of air-sea gas exchange. Unfortunately, our mechanistic understanding of the processes impacting air-sea gas transfer is still lacking in many aspects, especially in the open ocean setting. Two main problems have been identified with traditional, indirect methods to compute gas exchange: oversimplified/unconstrained parameterisations of gas exchange physics and heterogeneity in actual gradients across the interface not represented by gas concentration measurements. Solving these problems requires moving beyond traditional methods to more direct techniques. Eddy covariance is the most direct flux measurement technique and can open doors in gas exchange research. No other technique can directly measure flux on the scales of the forcing parameters, nor reveal the disconnect between calculated fluxes and concentration gradients. However, its wide-
spread use has been hampered by its challenging technical requirements. Direct eddy covariance flux measurements of heat, momentum, carbon dioxide, and dimethylsulphide (DMS) were performed in the Indian Ocean on board the research vessel ‘Sonne’. The cruise took place in July and August, 2014 (Fig. 3a and 4) with the science partnerships for the ‘Assessment of Complex Earth System Processes’ and ‘Organic very short lived substances and their Air sea Exchange from the Indian Ocean to the Stratosphere’. Air-sea distributions of CO$_2$ and DMS were also measured and the gas transfer coefficient ($k$) was directly derived. The cruise took place during the summer monsoon season and air masses were mostly of marine origin. The prevailing winds were northeasterly south of the Equator and southwesterly north of the Equator (up to 16 ms$^{-1}$). The cruise traversed regions with different surface water partial pressure CO$_2$ levels, including areas of strong undersaturation and those at approximately atmospheric equilibrium. The distribution of seawater DMS concentrations was also variable, leading to different flux patterns for the two gases. The directly derived $k$ values can be compared to each other and commonly used parameterisations/models (Fig. 3b). The $k$ values for CO$_2$ are higher than those for DMS, especially at higher wind speeds (U). The functional form of $k$ versus U appears to be linear with U for DMS, whereas the CO$_2$ functional form more closely resembles the Nightingale et al. (2000) parameterisation and is much lower than cubic relationships. A “rollover” in the DMS $k$ values can be seen at wind speeds higher than 11 ms$^{-1}$, which is in agreement with Bell et al. (2013). We hypothesise that the rollover is connected with how waves alter the physics of gas transfer and are currently investigating how to predict this rollover for future calculations. The influence of bubbles on gas exchange at wind speeds above 11 ms$^{-1}$ can also be detected with this dataset. We will calculate the magnitude of this bubble effect and will compare with recently published estimates to assess if the magnitude of bubble mediated gas transfer is universal over different environmental conditions. Interestingly, the rollover seen in DMS $k$ values should be generally applicable to sparingly soluble gases and it occurs at similar wind speeds as bubble mediated exchange. The implications of these findings will be explored in our upcoming publications and Alex Zavarsky’s doctoral dissertation.

Figure 3: a) ‘Sonne’ cruise track plotted on top of the CO$_2$ concentration gradient. Numbers are day of year during cruise. b) The directly derived gas transfer coefficient for CO$_2$ and DMS plotted against wind speed (GM12-DMS). Also pictured are commonly used $k$ parameterisations (LM 86, Liss and Merlivat, 1986; W92, Wanninkhof, 1992; WM99, Wanninkhof and Mc Gillis, 1999; M01, Mc Gillis et al., 2001; N00, Nightingale et al., 2000; H06, Ho et al., 2006; W09, Wanninkhof et al., 2009; P10, Pyrtech et al., 2010; G12-DMS, this study).
References


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Isoprene sea-to-air flux from the sea surface microlayer

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Biogenic volatile organic compounds are climatically-active trace gases in the atmosphere, which can affect the global atmospheric radiation budget. Isoprene (2-methyl-1,3-butadiene, C5H8) is very short lived in the atmosphere and has been shown to be an important precursor to tropospheric ozone (Chameides et al., 1988) and secondary organic aerosol formation (Claeys et al., 2004). C5H8 is released into the atmosphere from the marine environment (Bonsang et al., 1992). The sea surface microlayer (SML) is the boundary layer between the ocean and the atmosphere and covers more than 70% of the Earth’s surface (Cunliffe et al., 2013). The SML is enriched with organic matter (i.e. dissolved organic matter including ultraviolet-absorbing humic substances, amino acids, proteins, lipids, and phenolic compounds) and surfactants (i.e. fatty acids) (Liss and Duce, 1997). Additionally, photosensitised reactions involving the SML lead to production of significant amounts of C5H8 based on field samples and laboratory experiments (Ciuraru et al., 2015) (Fig. 5). Estimating the C5H8 flux is of major importance when determining the impact of marine C5H8 on atmospheric oxidation and organic aerosol particle size distribution in box-, regional-, and global chemistry models. Meas-

Figure 5: Production and fate of C5H8 in the marine boundary layer © Royston Uning

Royston Uning completed his bachelor and master degree in physics at the University of Technology Malaysia, Johor Bahru. In 2015, Royston started his PhD at the National University of Malaysia, Bangi, studying the biogenic volatile organic compound sea-to-air flux at the ocean-atmosphere interface.
ured field datasets are one of the key inputs when using models to estimate the annual global emissions of marine C_5H_8. Existing calculated C_5H_8 emissions, using the current model, achieved comparable results. However, as suggested by Booge et al. (2016), the existing model does not simulate a production of estimated C_5H_8 emissions in the SML. Therefore, the role of the SML on C_5H_8 sea-to-air fluxes remains an open question. Moving forward, future field measurements should incorporate SML C_5H_8 sea-to-air flux measurements to determine marine C_5H_8 emissions to the atmosphere. To fill the knowledge gap, the current study is focusing on method development for in situ sample collection (Fig. 6) and field sampling off the east coast of the Peninsular Malaysia (representing a tropical region). The main objective of this study is to determine the SML C_5H_8 sea-to-air flux. In addition, factors that might influence the sea-to-air flux will be studied (e.g. incoming solar radiation and inorganic nutrients). By using bottom-up measurements, results of this study will provide essential SML C_5H_8 sea-to-air flux data. Consequently, the measured SML C_5H_8 flux is expected to improve the estimation and/or correct the underestimation of total annual marine C_5H_8 emissions from regional to global scales.

Figure 6: Freshly emitted C_5H_8 from the SML, measured using a floating flux chamber. © Royston Uning

References


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Interfacial photochemistry of biogenic surfactants: a major source of abiotic volatile organic compounds

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Air-sea interfaces are ubiquitous in the ambient atmosphere, starting from a single aerosol particle to the surface of the ocean, and cover more than 70% of the Earth’s surface. It was shown that unique photochemical reactions with significant implications for atmospheric processes can occur at such interfaces, leading to the formation of volatile organic compounds (VOC) and secondary organic aerosols (Bernard et al., 2016; Rossignol et al., 2016). This interfacial photochemistry is exclusively due to the presence of surfactants enriched in surface layers with respect to the bulk water. Additionally, the presence of such surfactants increases the propensity of less surface-active compounds to concentrate there as well, creating a unique chemical environment, affecting not only chemistry but also trace-gas exchange (Carpenter et al., 2015). A major source of biogenic surfactants in the ambient environment are so-called biofilms, loosely defined as a population of microorganisms (i.e., fungi, algae, archaea) that accumulate at an interface (Hall-Stoodley et al., 2004) (Fig. 7). Nowadays the global presence of surfactants at air-sea interfaces of aquatic systems is attributed to microbiological activity.

We studied photochemical processes at the air/water interface of biofilm-containing solutions, showing abiotic VOC production from biogenic surfactants under ambient conditions (Brügge-
mann et al., 2017). Online atmospheric pressure chemical ionisation-ion trap-mass spectrometry and proton-transfer-reaction time-of-flight mass spectrometry were used to monitor VOC production. Unsaturated and functionalised VOCs were identified and quantified, giving emission fluxes comparable to previous field and laboratory observations. Interestingly, VOC fluxes increased with the decrease of living cells in the samples, indicating that the cell lysis was the main source for surfactants and VOC production.

Up to now, such VOC emissions were directly attributed to high biological activity in surface waters. However, our results suggest that abiotic photochemistry can lead to similar atmospheric emissions, especially in oligotrophic regions. Furthermore, chamber experiments suggested that oxidation of the produced VOCs by ozone and hydroxyl radicals leads to aerosol formation and growth, possibly affecting atmospheric chemistry and climate-related processes, such as cloud formation and the Earth’s radiation budget. These findings are summarised in Fig. 8, illustrating the impact of photo-induced VOC production on atmospheric chemistry. Due to the large surface area of the oceans, even a small production of VOCs can have important effects on a global scale. However, up to now, abiotic photochemical production of VOCs and their resulting impacts are not included in atmospheric chemistry models.

References


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Kyla Drushka has been a senior oceanographer at the University of Washington Applied Physics Laboratory, Seattle, United States, since 2014. She specialises in understanding processes in the upper ocean and at the air-sea interface from *in situ* and satellite observations.

**The impact of rain on near-surface ocean turbulence**

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Over the tropical oceans, rainfall is characterised by spatial scales of \( O(1-10) \) km and timescales of \( O(10) \) minutes. Rain falling on the ocean forms buoyant surface layers of \( O(0.1-1) \) m thick of relatively fresh, cold water, which are mixed and advected away on time scales of hours to days. The near-surface stratification from rain-formed fresh layers modulates the impacts of heat and momentum fluxes on the upper ocean, affecting surface temperature and currents, air-sea gas exchange, and turbulent kinetic energy dissipation. At the same time, fresh layers can act as a barrier between the atmosphere and the deeper mixed layer. These processes have not been well measured as a result of the transient nature of rain events and the difficulty of making surface measurements in the open ocean. We have recently carried out two experiments designed to characterise the temperature, salinity, and turbulence anomalies associated with rainfall.

The Friday Harbor Rain Experiment, which took place on a dock in Friday Harbor, Washington, United States, was designed to understand the near-surface turbulence generated by rain falling on the ocean. Acoustic Doppler velocimeters, conductivity-temperature-depth sensors (CTD), and a suite of meteorological instruments were deployed on the dock in the northeast Pacific from December 2015 to March 2016, providing a continuous time series of rain rate and raindrop size, wind speed, and vertical profiles of turbulence dissipation rate (\( \varepsilon \)) from 3 to 65 cm depth during different rain and ocean conditions. Figure 9 shows averaged profiles of \( \varepsilon \) under different wind and rain conditions. In non-rain conditions, dissipation rate is dominated by wind forcing at all depths, showing an ~8-fold increase between low (<4 m/s) and moderate (4-10 m/s) winds. The impact of rain is prominent, but depends on wind speed: at low wind speeds, moderate rain rates enhance turbulence (compared to no-rain conditions) by a factor of five and strong rain rates enhance turbulence by a factor of twenty (Fig. 9a). When winds are stronger, however, only the strong rain rates enhance turbulence above non-rain conditions (Fig. 9b). We hypothesise that this occurs because only when winds are relatively weak the kinetic energy input from
rain can exceed that from wind. This has implications for parameterising the impacts of rainfall on air-sea exchange under different wind regimes. The impact of rainfall on near-surface salinity is currently being studied as part of the second Salinity Processes in the Upper Ocean Regional Study (SPURS-2), taking place in the eastern tropical Pacific Ocean from 2016 - 2017. As part of SPURS-2, we deployed the Surface Salinity Profiler (SSP), a towed, surface-following platform to which five CTD sensors in 5 cm to 1 m are mounted (Asher et al., 2014). As the SSP is towed, this gives a continuous time series of temperature and salinity profiles in the upper meter of the ocean. During the SPURS-2 cruise in August 2016, 37 rain events were sampled with the SSP, allowing characterising the impacts of rainfall on the upper ocean. Figure 10 shows an example of a rain event observed during SPURS-2. Strong, steady rainfall up to 40 mm/hr (Fig. 10a) resulted in the formation of an extremely strong salinity anomaly of 9 practical salinity units (PSU) at the ocean surface (Fig. 10c). As a result of very low wind speeds (1 m/s), the fresh signal was trapped above 50 cm: the salinity anomaly is only seen at the 5-20 cm depth instruments until the wind signal picked up at around 13:15 (local time). Statistics from the set of 37 rain events measured with the SSP during SPURS-2 demonstrate that, for a given wind speed, the magnitude of salinity anomalies produced by rainfall is linearly related to the rain rate, meaning stronger rain produces a larger salinity anomaly. For a given rain rate, the salinity anomaly is inversely proportional to the wind speed; thus, under stronger winds, mixing is enhanced and the salinity anomaly is reduced, whereas with weak winds a strong salinity anomaly can form (Fig. 10). These results are consistent with results from a recent modeling study (Drushka et al., 2016). The SSP also carries microstructure temperature and conductivity sensors in order to estimate the turbulence dissipation rate; current efforts are underway to link
Attendees research profiles

wind and rain rate to ε with the SPURS-2 dataset, as it was done with the Friday Harbor data (Fig. 10), in order to understand rain-generated turbulence in the ocean.

References


Figure 10: Rain event observed during the Salinity Processes in the Upper Ocean Regional Study. (a) Rain rate, (b) wind speed, and (c) salinity at five depths measured with the Surface Salinity Profiler.