

# Air-sea Gas Flux Climatology; Progress and Future Prospects

Science Workshop - 24-27 sept. 2013

## 1. Abstracts for oral presentation

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Dr ARDHUIN Fabrice, IFREMER, France

### **Dissipation source terms and whitecap statistics**

F. Ardhuin, F. Leckler, J.F. Filipot, A. Mironov

Whitecaps are the main sink of wave energy and their occurrence has been related to the steepness of the waves. Recent parameterizations of the wave dissipation in numerical models are based on this property, but wave models have seldom been verified in terms of whitecap properties. Here we analyze and adjust the breaking statistics used in two recent wave dissipation parameterizations implemented in the spectral wave model WAVEWATCH III® and now used operationally at NOAA/NCEP. For dominant breaking waves, the reduction of breaking probabilities with wave age is well reproduced. Across the spectrum, the parameterizations produce a reasonable distribution of breaking fronts for wave frequencies up to three times the dominant frequency, but fail to reproduce the observed reduction in breaking front lengths for the shorter waves. Converted to whitecap coverage, the breaking parameterizations agree reasonably well with the classical empirical fits of whitecap coverage against wind speed and the global whitecap coverage estimated from space-borne radiometry.

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Dr ASHER William, University of Washington - USA

### **The effect of surfactants of near-surface concentration fluctuations due to turbulence and wind stress**

W. Asher, M. Tavakolinejad, A. Jessup

Experimental evidence has shown that increasing divergence of the flow field very near the air-water interface is correlated with increases in the air-water transfer velocity of sparingly soluble gases. Additionally, it has been shown that the rate at which near-surface concentration fluctuations of carbon dioxide occur is also correlated with the surface divergence. This suggests that conceptual models for air-water gas exchange based on surface divergences might provide a reasonably correct physical picture of the near-surface hydrodynamics governing gas transfer. However, in order to develop surface divergence-based conceptual models into a general framework for estimating air-sea gas transfer velocities, it must be determined if the correlations are dependent on surface cleanliness, and whether the same relationship can be used for mechanically forced turbulence and turbulence generated at the surface by the wind stress. Here, we present experimental results from a small-scale wind-water tunnel that link depth-dependent near-surface concentration fluctuations of carbon dioxide to surface divergence estimated from surface velocity measurements. The data are used to explore whether there is a universal relationship between statistics of the concentrations fluctuations, the surface divergence, and gas transfer.

Dr BAKKER Dorothee , School of Environmental Sciences, University of East Anglia  
-United Kingdom

**Effect of mixing and stratification on the summertime carbonate chemistry of the northwestern European shelf**

D.C.E. Bakker, G. Lee

The northern North Sea is an efficient pump for carbon from the atmosphere to the deep ocean (Thomas et al., 2004). Stratification of the water column is an important factor in separating production and atmospheric carbon dioxide (CO<sub>2</sub>) uptake in the mixed layer from subsurface respiration, with subsequent subsurface carbon export to the Atlantic Ocean. Here we investigate the effect of stratification on the carbonate chemistry on the UK and Irish shelves in June-July 2011. Strongly stratified profiles with uptake of atmospheric CO<sub>2</sub> by surface waters and high subsurface dissolved inorganic carbon are found in the Celtic Sea. By contrast, fully mixed profiles with little CO<sub>2</sub> air-sea transfer occur in the northern Irish Sea.

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Mr BARITEAU Ludovic, CIRES and NOAA - USA

**Progress on Direct Air/Sea CO<sub>2</sub> Flux Observations: results from DYNAMO2011 and TORERO2012.**

L. Bariteau, B. Blomquist, C. Fairall -NOAA Earth System Research Laboratory, J.B. Edson - University of Connecticut, W. McGillis -Columbia University/LDEO, J. Hare, B. Huebert- University of Hawaii

The exchange of CO<sub>2</sub> between the atmosphere and ocean is a major process in the global carbon cycle. Many uncertainties still remain in our understanding of the CO<sub>2</sub> air/sea gas exchange, partly due to instrumentation technology not being able to precisely resolve the flux signal (water vapor and motion interferences). Traditional methods for direct CO<sub>2</sub> flux measurement from ships require favorable conditions ( $\Delta p\text{CO}_2$  of at least 50  $\mu\text{atm}$ ) for a reasonable signal to noise ratio on 1-hr time scale. However new technical innovations offer significant improvements in both precision and detection limit for eddy correlation flux measurements. In this presentation we investigate flux data from two recent field programs using infrared (IRGA) and high precision cavity-ringdown (CRDS) analyzers. The data are used to compare the relative performance of the analyzers and discuss recommended procedures in EC flux estimates to correct or minimize the most significant bias error resulting from instrumental and meteorological causes.

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Dr BELL Tom, Plymouth Marine Laboratory - UK

**Concurrent measurements of DMS and CO<sub>2</sub> air/sea gas transfer by eddy correlation in the North Atlantic**

T.G. Bell, S. Miller, W. De Bruyn, B. Ward, K.H. Christensen, E.S. Saltzman

Air/sea dimethylsulphide (DMS) and carbon dioxide (CO<sub>2</sub>) fluxes and gas transfer coefficients (kDMS, kCO<sub>2</sub>) were measured by eddy correlation over the western North Atlantic Ocean during June/July 2011 aboard the R/V Knorr. Atmospheric and seawater DMS were measured using atmospheric pressure chemical ionization mass spectrometry.

CO<sub>2</sub> levels in seawater and air were measured using commercially-available infra-red gas analysers (LiCor). Seawater concentrations were measured continuously from the ship's underway system using a porous membrane equilibrator (DMS) and a showerhead equilibrator (CO<sub>2</sub>). The cruise included regions of high biological productivity, which created strong CO<sub>2</sub> and DMS air/sea concentration gradients. Data were collected at wind speeds from 0 to 18 m/sec and whitecap areal extent from 0 to 5%. Four stations were occupied during the cruise for periods of 24-36 hours. Significant variations in the relationship between kDMS and wind speed were observed at different stations. Differences in the observed relationships between wind speed and kDMS and kCO<sub>2</sub> at intermediate to high wind speeds will be discussed.

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Dr BENTAMY Abderrahim , IFREMER -France

### **Enhancement of the oceanic turbulent fluxes estimated from remotely sensed data**

A. Bentamy; B. Blanke; F. Desbiolles; S. Grodsky; J. Hanafin; K. Katsaros ; A. Mestas-Nuñez; R. Pinker;

This study aims at using and investigating the quality and the content of the newly-estimated long time series of momentum, latent and sensible heat fluxes as well as associated bulk variables: surface wind speed and direction, air and sea surface temperatures, and specific air and sea humidities from several satellite missions the period: 1999 - 2009. For this release, remotely sensed data from the scatterometer onboard QuikScat, and from radiometers onboard several Defense Meteorological Satellite Program (DMSP) satellites (Special Sensor Microwave/Imager [SSM/I] F11, F13, F14 and F15), are matched in combination with new NOAA daily sea surface temperature analyses. This new release includes several improvements. For instance QuikScat rain-free winds are selected with respect to the most recent published study results. The calibration of the model relating brightness temperature to the specific air humidity is improved. It is performed at the global scale based on the use of the new ICOADS daily data. The fluxes are estimated over satellite swaths, and daily and monthly-averages are calculated over global ocean with a spatial resolution of 0.25° in longitude and latitude. The calculations of air-sea fluxes from satellite observations are accomplished using bulk formulas (COARE-3.0 model) that take atmospheric stability into consideration. The quality of the retrieved satellite fluxes is determined through comprehensive comparisons with moored buoy and field experiment estimates in different ocean basins. At regional and global scales, satellite gridded fluxes are compared to ship data analyses (ICOADS) and to numerical model estimates provided by the numerical weather prediction (NWP) centers such as Météo France (Arpege, Aladin), ECMWF (operational analysis and re-analysis (ERA Interim)) and NOAA/NCEP (CFSR). Using the error analysis of the resulting flux fields, their contents are investigated in terms of monthly, seasonal, and inter-annual signals averaged over the Atlantic, Pacific, and Indian ocean basins. The results are illustrated by investigating the spatial pattern of latent heat flux variability associated with El Niño-Southern Oscillation (ENSO).

Pr CHEN Ge, Ocean University - China

### **Impact of climatology data geometry on the results of empirical orthogonal function analysis**

G. Chen

Locality (or regionality) is a fundamental feature of most geophysical modes in the ocean/atmosphere system. Meanwhile, nonlocality (or globality) is an intrinsic characteristic of the empirical orthogonal function (EOF) technique which is widely used to extract principal modes from complex spatiotemporal variability. Obviously, there is a natural mismatch between the “head” and “cap”. As a result, localized signals may not be properly resolved by applying such methodologies. In this study, the geographic effects on the results of EOF analysis are examined using the Global Precipitation Climatology Project (GPCP) dataset for the period of 1979-2011, leading to two main conclusions. First, as far as precipitation is concerned, most of the mode-active zones are located over the ocean, and the global EOFs are mathematically “tuned” by oceanic variabilities. A land/ocean separation strategy significantly releases such a constraint, allowing more detailed and contrasted spatial and temporal patterns to be revealed, and should therefore be recommended when EOF is applied. Second, when a zonal or meridional division is adopted, major consequences in the montage of an EOF mode include a considerable increase in spatial contrast around dipoles and a certain degree of discontinuity near boundaries. The level of discontinuity depends not only on dividing scheme but also on mode order. In the temporal domain, regional time series are found to be more sensitive and dispersive with respect to latitude than to longitude. Thus, disproportional zonal/meridional divisions may introduce severe distortion in the derived regional EOFs, and should therefore be avoided. Such a complex relationship implies that the use of a single pair of space pattern and time series to represent the geophysical variability of the entire domain is inevitably insufficient and very often misleading.

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Dr CZERSKI Helen , Institute for Sound and Vibration Research, Univ. of Southampton-UK

### **The effect of temperature, salinity and natural ocean surfactants on bubble fragmentation and coalescence**

H. Czerski

The plumes of bubbles generated by breaking waves in the ocean are thought to influence marine aerosol production, air-sea gas transfer, and both the optical and acoustical properties of the upper ocean. One of the major uncertainties in the current understanding of these bubbles plumes is the effect of natural surfactants. These chemicals are produced by marine life and will accumulate on surfaces, including the surfaces of bubbles, changing the surface physical properties. It is thought that the presence of surfactants may change bubble plumes significantly, by altering bubble formation processes and by slowing bubble dissolution. However, there is not currently enough information to predict these changes or their importance. This study is a step towards understanding the effects of natural surfactants on ocean bubble plumes, and the consequences for gas exchange and aerosol production. Using very clean apparatus, individual bubbles of different sizes were either fragmented or smashed together by turbulence in different water conditions. Fragmentation is known to be the main mechanism generating new large bubbles underneath breaking waves, so studying the effects of surfactant on this process should provide insight into the generation of natural bubble plumes.

Dr FAIRALL Chris – NOAA - USA

### **High Wind Gas Exchange Study, HiWinGS Measuring Air-Sea Gas Exchange in High Winds for Improvement of Physics-Based Air-Sea Transfer Parameterizations**

B. Huebert, J. Hare, University of Hawaii  
C. Fairall, S. Pezoa, NOAA, Earth System Research Laboratory  
L. Bariteau, B. Blomquist, University of Colorado/CIRES  
I. Brooks, ICAS University of Leeds  
S. Miller, SUNY Albany  
E. Saltzmann, UC Irvine  
J.B. Edson, University of Connecticut  
C. Zappa, Columbia University/LDEO

HiWinGS is a collaboration between groups from the U. Hawaii, U. Colorado, NOAA/ESRL, LDEO, U Conn, SUNY Albany, UC Irvine, UC San Diego, U Leeds UK, U Southampton UK, PML UK, and NOC UK. The R/V Knorr will conduct a dedicated cruise just south of Nuuk, Greenland from 10 Oct to 15 Nov 2013. Eddy-covariance fluxes will be measured for gases of very different solubilities (CO<sub>2</sub>, DMS, acetone, methanol, isoprene, monoterpenes, and SO<sub>2</sub>), to quantify the impact of chemistry on gas exchange. We will derive exchange velocities ( $k$ ) for each gas from measured fluxes and concentrations. The heart of the experiment is to then identify the chemical and physical factors that control  $k$ . Groups measuring the physical variables controlling gas exchange and stress apportionment are thus critical to the experiment. These variables include directional wave spectra, wave breaking, bubble dynamics, and water-side turbulence. Our goal is to measure air-sea gas exchange in winds above 17 m/s alongside the physical factors controlling that exchange, to improve physics based air-sea transfer parameterizations.

We will use, compare and contrast a range of outputs from the OceanFlux Greenhouse Gases processing system and uncertainty analyses to aid in the evaluation and interpretation of the in situ data from the cruise in 2013 (e.g. air-sea CO<sub>2</sub> fluxes, significant wave heights, wind speeds, SST foundation, impact of SSTskin on the CO<sub>2</sub> fluxes, rain frequency and intensity, existence of SST fronts). We will also use the historical Earth observation data to evaluate (for our region of study and temporal period) the uncertainties introduced from ignoring vertical temperature gradients when calculating the in situ air-sea CO<sub>2</sub> flux.

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Dr FAIRALL Chris – NOAA - USA

### **Theoretical and numerical analysis of carbonate reaction time scales on thermal effects of air-sea CO<sub>2</sub> flux**

C. Fairall, L. Bariteau

Several recent papers have discussed the so-called cool-skin effect on the net CO<sub>2</sub> flux over the oceans. The thermal effects are complicated by temperature-dependent carbonate reactions. In a dynamic system, the departure of the CO<sub>2</sub> concentration profile (ocean side) will depend on both the air-side concentration, turbulent-molecular conductivity, and the reaction rate (time scale). In this paper we use a conservation equation approach originally developed for the deposition of ozone to water. The equations are applied to a simple CO<sub>2</sub> system with an assumed linear temperature cool-skin profile. An analytical solution is obtained that allows estimates of the cool-skin effect on CO<sub>2</sub> flux as a function of the carbonate reaction time. We also examine a more accurate system where the turbulent transfer coefficient decreases non-linearly towards the interface. This system cannot be solved analytically, but numerical solutions are discussed.

Dr FIEDLER Björn, GEOMAR Helmholtz Centre for Ocean Research Kiel - Germany

### **When Chemical Oceanographers Go Robotic – Towards Accurate pCO<sub>2</sub> Measurements on Novel Autonomous Platforms**

B. Fiedler<sup>1)</sup>, P. Fietzek<sup>1,2)</sup>, P. Silva<sup>3)</sup>, N. Vieira<sup>3)</sup>, T. Steinhoff<sup>1)</sup>, H. Bittig<sup>1)</sup>, J. Karstensen<sup>1)</sup>, A. Körtzinger<sup>1)</sup>

1) GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

2) CONTROS Systems & Solutions, Kiel, Germany

3) Instituto Nacional de Desenvolvimento das Pescas (INDP), Mindelo, Cape Verde

Detailed knowledge about the air-sea gas exchange between ocean and atmosphere plays a key role in understanding the past and present state of the global carbon cycle and predicting its future. Despite a growing data base, the present global uptake rate of the world ocean for anthropogenic CO<sub>2</sub> still has an uncertainty of 50 % ( $+2.0 \pm 1.0$  Pg C yr<sup>-1</sup>) which to a major extent is due to limited temporal and spatial coverage of CO<sub>2</sub> measurements within large parts of the oceans. This calls for an improvement.

Vertical profiles of pCO<sub>2</sub> can currently only be assessed indirectly through laborious sampling of other carbonate system parameters. Furthermore, high accuracy surface measurements of pCO<sub>2</sub> can only be conducted with complex and comparatively large instrumentation setups that rely on large platforms (e.g., research or merchant vessels, moored buoys).

Recently developed small-sized and submersible pCO<sub>2</sub> sensors can be used to overcome these constraints. Thus, new platform technologies such as profiling floats or gliders come now into reach, leading to a more sophisticated approach to measure pCO<sub>2</sub> in the world's oceans. This approach greatly facilitates the improvement of spatial and temporal coverage of pCO<sub>2</sub> measurements even in remote parts of the oceans and thus leads to a better understanding on carbon cycle dynamics.

In order to demonstrate the feasibility of this approach we present a pilot study in which a typical profiling Argo float was equipped with a pCO<sub>2</sub> sensor and an optode O<sub>2</sub> sensor for high resolution measurements in the water column and at surface. Consecutive deployments of the prototype profiling float were carried out at the Cape Verde Ocean Observatory (CVOO) in the eastern tropical North Atlantic. The profiling float performed upcasts every 31 h while measuring pCO<sub>2</sub>, O<sub>2</sub>, salinity, temperature and hydrostatic pressure in the upper 200 m of the water column. Measurements are in good agreement with conventional time-series measurements and derived air-sea CO<sub>2</sub> fluxes match climatological data for this region.

Furthermore, we present ongoing developments for the extension of other autonomous platforms towards direct pCO<sub>2</sub> measurements at CVOO. A moored profiler attached to an underwater winch deployed in May 2013, as well as sensor integration work into a wave glider platform will be presented. These platforms will significantly enhance data coverage at CVOO on temporal and spatial scales.

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Ms FOURNIER Séverine, IFREMER, France

### **Large tropical river plume monitoring with SMOS to better estimate Land-Sea Freshwater fluxes**

S. Fournier, N. Reul, B. Chapron, D. Vandemark, J. Salisbury

Rivers are important variables in oceanography as their fresh water affects SSS and the buoyancy of the surface layer and vertical stratification which in turn can affect air-sea interactions. As well, they represent a source of materials exotic to the ocean and important

to biological activity. Obviously, they are key hydrologic components of the fresh water exchanges between land and ocean. Despite this importance, tracing major tropical river water (e.g. Amazon, Congo, Ganges) over large distances has not been straightforward previously principally because of a lack of SSS observations. Tracing those very large rivers over great distances now become an important endeavor, as sufficient data are available from surface salinity sensors placed aboard satellites. In this talk, we will first illustrate these new monitoring capabilities for some of the world largest oceanic fresh water pools generated by the discharge of very large tropical rivers. In particular, we show how SMOS SSS traces the fresh water signals from the Amazon-Orinoco and Congo river plumes during the period 2010-2013. The spatial extent of the Amazon river plume over the ocean is thus shown to be an excellent proxy for the river discharge, as measured at Obidos gauge. In addition, quasi-linear seasonally varying conservative mixing laws are derived from the satellite SSS and Ocean color properties. These empirical laws are further used to estimate the salinity at high spatial resolution from the absorption coefficient of colored dissolved organic matter (aCDOM) from satellite ocean color data. These high-res SSS products (~4 kms) are validated against Thermosalinograph data and reveal details in oceanic structures not well captured by the microwave sensors. These new salinity observation tools will definitively help better constraining the freshwater fluxes between land and ocean in the tropics.

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Dr GARBE Christoph, IWR / University of Heidelberg - Germany

### **Extracting fluxes of GHGs at the air-water interface from satellite remote sensing**

C. Garbe, J. Vihharev, A. Butz, J. Sudre, H. Yahia, B. Dewitte, A. Paulmier, S. Illig, I. Dadou, R. Sabia, V. Garçon

In this contribution, we present a technique based on optimal control theory for computing interfacial fluxes of GHGs. Improved techniques are applied to retrieving vertical column densities (VCDs) of GHGs from glint measurements of GOSAT. A simplified transport model is solved using the Galerkin finite element method. On uniformly refined meshes this method leads to the same algebraic systems as the discretization using finite differences. However, the Galerkin discretization offers the possibility for the systematic a priori and a posteriori error analysis. Moreover, the a posteriori error analysis gives the opportunity to optimize the meshes used in the solution process and in the error control. Grid adaptivity is performed using the Dual Weighted Residual Method. The method provides reliable a posteriori error estimators based on local residuals weighted by sensitivity factors computed with respect to a given quantity of interest. This leads to the concept of the goal-oriented adaptivity. The approach makes it feasible to compute fluxes from VCDs very efficiently.

We present results of this approach in both the Benguela upwelling and the Humboldt system. The presented analyses were performed within the ESA STSE Oceanflux project "Upwelling".

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Dr GARBE Christoph, IWR / University of Heidelberg - Germany

### **Interfacial transport and turbulent statistics from thermography**

C. Garbe, J. Schnieders

The transport of mass across the air-water interface strongly depends on small scale processes, such as interfacial turbulence induced by microscale wave breaking.

Thermography makes it possible to measure fine temperature fluctuations induced by turbulence directly at the interface. Linking transport models with thermographic measurements, transfer velocities can be computed. Through the high temporal and spatial resolution of these types of measurements, the influence of different interfacial processes can be analyzed. In this contribution, we will present measurements of spatial turbulent statistics and transfer velocities with respect to friction velocity. This gives new insights into different factors influencing interfacial transport and may lead to physically based parameterizations of transfer.

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Dr GARCON Véronique, CNRS/LEGOS - FRANCE

### **Towards super resolution of air-sea CO<sub>2</sub> fluxes at the air-sea interface in the EBUS**

V. Garçon, J. Sudre, H. Yahia, S. Illig, I. Montes, B. Dewitte, A. Paulmier, I. Dadou, A. Butz and C. Garbe

Within the Support to Science Element project OceanFLux, the Upwelling theme was exploring the potential of inferring from atmospheric vertical columns of CO<sub>2</sub> derived from space (GOSAT,..) , together with an atmospheric chemical transport model and multiplicative cascades on oceanographic turbulent signals (SST, ocean color,..), the flux of CO<sub>2</sub> at the air-sea interface at very high (super) resolution. In order to accurately quantify the contribution of the Eastern Boundary Upwelling fluxes and OMZs in the net global ocean-atmosphere CO<sub>2</sub> fluxes, there is an urgent need to assess the fluxes through satellite, earth observation data, outputs of coupled models in addition to the classical in situ observations. Results of super-resolution reconstruction of oceanic pCO<sub>2</sub> signals and air-sea CO<sub>2</sub> fluxes obtained from outputs of numerical models off southern hemisphere EBUS indicate a mean absolute error of 2.5 uatm on the oceanic pCO<sub>2</sub> retrieval over a 10 years simulation (1990-2000) off Benguela. First results obtained with Carbon Tracker data over the year 2008 will be presented and discussed.

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Dr GODDIJN-MURPHY Lonneke, Environmental Research Institute -Scotland

### **Using satellite altimetry to measure air-sea gas transfer velocity**

L. Goddijn-Murphy, D. Woolf

The relationship of gas transfer velocity to satellite-derived backscatter, or wind speed, is useful to provide retrieval algorithms. Gas transfer velocity is controlled by both the individual water-side and air-side gas transfer velocities. In practice, for insoluble gases the rate limiting step is transfer through the water side and water-side gas transfer velocity is often taken as an adequate estimation of gas transfer velocity. We calculated air-side transfer velocities using a numerical scheme, in order to estimate water-side gas transfer velocities from measurements of the total transfer velocity for DMS (dimethyl sulphide). Relationships between water-side transfer velocity and altimeter-derived variables are derived; using Ku-band backscattering or altimeter derived wind speed give equally good results. Using the difference between the Ku-band and C-band signals, and thus reducing the contribution from longer waves, improves the gas transfer velocity estimates. Since DMS was used to calibrate the relationship, and DMS is sufficiently soluble to neglect bubble-mediated gas transfer, the relationship could be applied to estimate water-side gas transfer velocities through the unbroken surface of any other gas. For less soluble gases, such as CO<sub>2</sub>, the contribution of



breaking waves to water-side air-sea gas transfer velocity has to be taken into account. An option is to use satellite observations or models of whitecapping, and apply a relation between whitecap fraction and bubble mediated gas transfer.

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Dr IAFRATI Alessandro, INSEAN-CNR - Italia

### **Numerical modelling of the air-sea interaction in wave breaking and consequences in terms of the air-sea gas exchanges**

A. Iafrazi, A. Babanin, M. Onorato

It is well known that the wave breaking plays a key role on the exchanges at the air-sea interface. In wind generated waves, the form drag associated to the breaking occurrence significantly enhances the momentum and energy transfer from air to water and, at the same time, it governs the dissipation of the wave energy and affects the spectrum. Both these effects are modelled in wave forecasting models but the community recognizes that additional effort toward the development of more accurate models is deserved (e.g. Cavaleri et al., 2012; Babanin, 2011). From the fluid dynamic viewpoint, the breaking is a complicated phenomenon involving a strong air-water interaction, with entrainment of air bubbles, and ejection of sprays and droplets in the lower atmosphere layer. Of course, the air entrainment and the subsequent fragmentation process, the rise up of the bubbles and the bursting of the bubbles at the ocean surface, as well as the droplets released in the atmosphere contributes to the gas exchanges across the ocean surface. These phenomena can be numerically simulated at a certain level of detail, although still limited at smallest scales (e.g. Iafrazi, 2009; Iafrazi, 2011). Recent studies on the breaking generated by modulational instability have shown that a significant air-flow can be generated by the breaking occurrence. It has been found that the breaking occurrence triggers the formation of large vortical structures in the atmosphere, which propagates upwards at heights up to about half of the fundamental wavelength (Iafrazi et al., 2013). It is believed that such structures, beside contributing to the momentum transfer, enhance the vertical transport of aerosols.

At the Workshop, the results obtained which can have a role in the air-sea gas exchanges will be discussed. Although presently limited to small scale problems, with not all the subscales properly resolved, future developments of the numerical model can help in understanding and quantifying some of the basic phenomena taking place at the ocean surface.

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Pr de LEEUW Gerrit, FMI & UHEL - Finland

### **A new sea spray aerosol source function (OSSA) and application to estimate direct and indirect radiative effects using ECHAM**

G. de Leeuw, J. Ovadnevaite, A. Manders-Groot, H. Korhonen, A. Partanen, C. O'Dowd

A new sea spray aerosol (SSA) source function (SSSF), termed Oceanflux Sea Spray Aerosol or OSSA, was derived based on in-situ sea spray measurements along with meteorological/physical parameters. Submicron sea spray fluxes derived from particle number concentration measurements at Mace Head, at the west coast of Ireland, were used together with open-ocean eddy correlation flux measurements from the Eastern Atlantic (SEASAW cruise). In the overlapping size range, the data for Mace Head and SEASAW were found to be in good agreement, which allowed deriving a new SSSF from the combined dataset which covers the dry diameter range from 15 nm to 6  $\mu\text{m}$ . The sea spray production

was parameterized in terms of the Reynolds number instead of the more commonly used wind speed to include information on wave height, friction velocity and viscosity.

Different flux- Reynolds number relationships were derived for 5 different size modes. This formulation removes the different effects of rising and waning wind speeds on the SSA production flux since these are included in the Reynolds number. Furthermore, the Reynolds number incorporates the kinematic viscosity of the water, thus the SSSF includes sea surface temperature dependence. The temperature dependence of the resulting SSSF is similar to that of other in-situ derived source functions and results in lower production fluxes for cold waters and enhanced fluxes from warm waters as compared with SSSF formulations that do not include temperature effects.

The OSSA SSSF is currently implemented in a global transport model (LOTOS-Euros) and in a global climate model including transport and deposition (ECHAM-HAM). ECHAM-HAM will be used to calculate aerosol optical depth (AOD) and for the evaluation of direct and indirect radiative effects of SSA. The results serve further to evaluate the OSSA SSSF from comparison with independent data sets.

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Dr MCGILLIS Wade, Columbia University - United States

### **Air-Sea Gas Exchange at Ice Surfaces**

W. McGillis, C. Zappa, B. Loose

Quantifying gas exchange across air-water-ice surfaces has become increasingly important. We have explored gas exchange across frozen surfaces in a range laboratory wind-wave-ice facilities to determine baseline rates and the nature of fundamental ice-flow processes. Ice growth and flow in leads has profound effects on the gas exchange rate. The interactions of turbulence, waves, and ice is a central mechanism for the physical control of air-water-ice gas transfer. The results and relationship between ice and gas exchange will be presented and discussed.

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Dr MCNEIL Craig, APL/UW – Seattle - United States

### **Comparison of air-sea gas flux data from three tropical cyclones**

C. McNeil, E. D'Asaro

We will review dissolved N<sub>2</sub> and O<sub>2</sub> data sets collected using gas sensing floats air-deployed into the paths of Hurricane Frances (2004), Hurricane Gustav (2008), and Typhoon Megi (2010). Some inorganic carbon system measurements were also made in the wake of Typhoon Megi during the recovery cruise. Comparison of observed and predicted gas saturation levels using available models will be presented and discussed.

Dr MIRONOV Alexey, IFREMER - France

### **Statistical properties of breaking waves in field condition: A Gaussian field approach.**

A. Mironov, B. Chapron, V. Dulov

Breaking of the wind waves play a dominant role in the dynamics of upper ocean layer, air-sea interactions and energy dissipation of wind waves. Modeling of physical and statistical properties of breakers still remains poorly described.

In this work, we present an new analysis of statistical properties of video-detected breaking waves. More precisely, the analysis is based on the use of a near-Gaussian statistical assumption applied to the filtered wave field within a given velocity interval and a given propagation direction. Whitecaps, as associated to regions of the field exceeding some critical threshold, can be described with high-level statistics (e.g. Adler, 1981). For a Gaussian field, high excursions shall be well approximated with elliptical paraboloid whose centers follow a Poisson process. Accordingly, individual foam patches are also approximated with ellipses with a mean eccentricity connected to the directional mean square slopes of the filtered waves. Within a given velocity range, whitecap surface sizes are also randomly distributed to closely obey an exponential distribution. Individual breaking crest lengths must thus be Rayleigh distributed.

These theoretical predictions were validated with a massive experimental data set. Field video observations of wavebreaking statistics were obtained during filed campaign at the Black sea platform in Katsiveli, Ukraine. Validation was performed for wide range of wave and wind conditions.

The present results can be used to provide realistic statistical properties of wavebreaking field, as well as to provide some imprved means to efficiently model the whitecap coverage and thickness for different wind and wave conditions.

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Dr OCAMPO-TORRES, Francisco, CICESE, Physical Oceanography Department - Mexico

### **On the atmosphere-ocean exchange of carbon dioxide in coastal waters.**

F. J. Ocampo-Torres(1), G. García-Rubio(1), P. Osuna(1), H. García-Nava(2)

1 CICESE, Oceans Division, Physical Oceanography Department, Ensenada, BC, México

2 IIO-UABC, Ensenada BC, México

Field measurements are being carried out in order to better determine the ocean surface waves influence on carbon dioxide exchange between ocean and atmosphere. Preliminary direct determination of fluxes have been performed from detailed observations and the use of the eddy correlation method, with a data set obtained during a pilot experiment at a rocky point near Ensenada, in the Northwest of Mexico. While our analysed results are limited to onshore wind conditions, they still reveal some variations associated with local weather and the oceanic background signal. New measurements are being acquired in Todos Santos Island and at a station 2 km offshore where an ASIS buoy has been deployed.

This research mainly deals with the determination of space and time exchange processes variability, which would be a decisive piece of information when building budgetary estimates and climatology.

The challenge of obtaining detailed and continuous ocean-atmosphere fluxes as well as sea state information is dealt with in the context of air-sea interaction processes influencing upper ocean dynamics, hence weather and climate.

Dr OLSEN Are , Geophysical Institute, University of Bergen -Norway

### **SOCAT - A Global Data Product for Quantification of Air-Sea Exchange of CO<sub>2</sub>.**

A. Olsen, D. Bakker, B. Pfeil, S. Hankin, K. Smith, C. Sabine, S. Alin, C. Cosca, B. Hales, S. Harasawa, S. Jones, A. Kozyr, N. Metz, Y. Nojiri, K. O'Brien, U. Schuster, M. Telszewski, B. Tilbrook, C. Wada, N. Lefevre, J. Mathis, D. Pierrot, R. Wanninkhof, and all other SOCAT contributors

The Surface Ocean CO<sub>2</sub> Atlas, SOCAT, is a major community effort to make surface ocean CO<sub>2</sub> (carbon dioxide) data openly available for scientists, stakeholders and policymakers worldwide. The data themselves are gathered from data centers and individual scientists, and subjected to extensive quality control, involving fCO<sub>2</sub> recalculation, data consistency checks, and checks for completeness of community-agreed metadata documentation. Whenever quality issues are identified, we seek to resolve these in collaboration with the data contributor, if this is practically possible. Following the quality control, data from each cruise is flagged according to its quality and level of documentation.

SOCAT was initially released in 2011, and consisted of two products (i) the uniform format fCO<sub>2</sub> database (Pfeil et al., 2013) and (ii) a gridded atlas at a resolution of one degree in latitude and longitude and a time step of one month, prepared by averaging the data in each grid box with no spatial and temporal interpolation (Sabine et al., 2013).

The second version of SOCAT will be released in June 2013 at the 9th International Carbon Dioxide Conference taking place in Beijing, China. SOCATv2 includes approximately 4 more million fCO<sub>2</sub> data points than SOCATv1 did, bringing the total number up to 10.1 million fCO<sub>2</sub> data. It will include data from the late 1960s through 2011 and includes data from all of the world oceans, including the Arctic and the Coastal Seas.

SOCAT is available through a Live Access Server hosted by NOAA/PMEL (National Oceanic and Atmospheric Administration/ Pacific Marine Environmental Laboratory), as concatenated regional and global files at the Carbon Dioxide Information Analysis Centre, and as individual cruise files including original data at PANGAEA.

We will present the SOCAT data product, including aspects of the underlying work, file contents and structure, access points, future plans and provide some examples of SOCAT science.

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Dr PAGET Aaron, , Brigham Young University -United States of America

### **Estimating global active and total whitecap coverage for air-sea gas exchange using satellite-derived winds.**

A.C. Paget, M.A. Bourassa

Whitecaps, which form by entraining air into the water on breaking, plunging, and crashing waves, increase the rate of gas transfer from the atmosphere to the ocean. A global estimate of the local active and total whitecap fraction is required to accurately estimate the effects of whitecaps on air-sea gas exchange globally. Wind speed is frequently used to estimate the active and total whitecap fraction. For the past 50 years, the whitecap fraction has been estimated using a power law and the 10-m wind ( $u_{10}$ ). The parameters used to estimate the whitecap fraction using the  $u_{10}$  have not been modified for global satellite 10-m winds, reported as equivalent neutral winds ( $u_{10EN}$ ). The notable differences between  $u_{10}$  and  $u_{10EN}$  are magnified when estimating whitecap coverage with a power law.

This study presents new parameterizations for estimating the whitecap fraction using  $u_{10EN}$ . The Whitecap Database developed by Anguelova and Webster provides microwave emissivity-based whitecap fraction from WindSat's 10 and 37 GHz channels. The Whitecap

Database provides daily whitecap fraction on a  $0.5^\circ \times 0.5^\circ$  global grid with values representing the active and total whitecap fraction. Whitecap fraction is matched to QuikSCAT, SSML, and GDAS u10EN and coefficients to the power law are determined using the u10EN and the active and total whitecap fraction from the Whitecap Database. Error between the estimated and observed whitecap fraction is shown, and new coefficients for a power law are presented.

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Dr PARAMPIL Sindu, Department of Earth Sciences, Uppsala University-Sweden

### **Impact of coastal upwelling on the air-sea exchange of CO<sub>2</sub> in a Baltic Sea basin**

S.R. Parampil, M. Norman, A. Rutgersson, E. Sahlée

In this study, we use in-situ and satellite data to investigate four upwelling events off the east coast of Gotland and their impact on the air-sea exchange of CO<sub>2</sub>. In-situ measurements show strong correlations between sea surface temperature and partial pressure of CO<sub>2</sub> in the water (pCO<sub>2</sub>) during upwelling and we use this relation with the satellite SST to calculate fluxes of CO<sub>2</sub> in the upwelling region. Comparison of the CO<sub>2</sub> budget for the region between upwelling cases and an 'idealized non-upwelling' scenario yields relatively large differences: There is a 19-250% reduction in the uptake of CO<sub>2</sub> by the water or increased emission of CO<sub>2</sub> into the atmosphere during upwelling. Our calculations also suggest that upwelling events may have a profound impact on an annual time scale too, that is, they decrease the annual mean CO<sub>2</sub> uptake by the Baltic Sea by 25%. In addition there is a significant difference between directly measured fluxes and those calculated from measurements using a standard bulk formula. This discrepancy may be due to the fact that pCO<sub>2</sub> is not representative of the footprint area of the measured flux during upwelling.

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Dr PARARD Gaëlle , Uppsala University Department of Earth Science -Sweden

### **Remote sensing algorithms for sea surface CO<sub>2</sub> in the Baltic Sea**

G. Parard, A. Rutgersson

Carbon dioxide is the most important anthropogenic green house gas, the global emissions of CO<sub>2</sub> from fossil fuel combustion and cement production were of  $9.5 \pm 0.5$  PgC yr<sup>-1</sup> in 2011 (Le Quéré et al., 2012). One important sink is the ocean CO<sub>2</sub> uptake, which absorbed 26% of the anthropogenic emission,  $2.5 \pm 0.5$  PgC yr<sup>-1</sup> (Le Quéré et al. 2012; Global Carbon Project 2012). The uncertainty of this estimation is still significant and in the ocean the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) is mostly estimated from a sparse network of surface observations in space and in time. Remote sensing products would give significant new information as they potentially can cover the ocean surface with relatively high resolution in time and space. We focus here on the semi-enclosed Baltic Sea in the Northern Europe. It is a brackish sea with a surface area of about 377,000 km<sup>2</sup>. The goal of our work is to develop and validate remote sensing based method for estimating pCO<sub>2</sub> in Baltic Sea. In first part, we work on data of pCO<sub>2</sub> mooring at 57.45°N, 18.98°E, closer to the coast, measures Sea Surface Temperature (SST) and pCO<sub>2</sub> at 4 m depth semi-continuously since 2005 (Rutgersson et al., 2008) near the coast to construct relationship with satellite data and after apply this at the Baltic Sea scale. We used remote sensing SST, chlorophyll, mixed layer depth and primary production for the period 2005–2011. At the mooring during November to March the pCO<sub>2</sub> measuring show strong correlation with SST measurements with a positive relationship

between pCO<sub>2</sub> and SST which correspond to the thermodynamical effect defined by Takahashi et al, 1993 in ocean. We have typically this relationship during the winter months, the pCO<sub>2</sub> variations follow the SST variations with an increase of 3,98%/°C, which is close to the thermodynamic relationship of 4,23%/°C. During the spring-summer period, we have two types of relationship, the presence of upwelling event impact the pCO<sub>2</sub> variability and the chlorophyll gives more information during this period. In a second part, the relationship found to compute pCO<sub>2</sub> at the mooring is apply on all Baltic Sea and improve at spatial scale.

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Dr RASCLE Nicolas, IFREMER, France

### **Vertical and horizontal distributions of wave-induced turbulence**

N. Rasclé

The air-sea gas exchange is strongly related to the upper ocean turbulence and to surface wave breaking. We highlight here some characteristics of the coupled ocean-wave-atmosphere system, with special emphasis on the upper ocean turbulence.

First we consider an horizontally homogeneous ocean-atmosphere system. The turbulence in the upper ten meters of the ocean is mostly generated by breaking surface waves. The amount of turbulent kinetic energy (TKE) as well as the depth it reaches must therefore be related to the size and frequency of breaking waves. We discuss here the agreement between available measurements of TKE dissipation underneath the surface and available measurements of size distribution of breaking waves. To lowest order, the upper ocean turbulence is believed to depend on the wave age but the sign of that dependency is still a matter of debate. We conclude that the general picture of the upper ocean turbulence and of its link to surface waves is still not complete.

Second, the ocean is seldom horizontally homogeneous, with the presence of mesoscale eddies and submesoscale fronts and turbulence. We investigate with a numerical wave model how those meso/submesoscale currents modify and reorganize the horizontal distribution of breaking waves. We evaluate the importance of such redistribution for air-sea interactions and exchanges. We discuss how high resolution roughness images (e.g. from synthetic aperture radar) at times represent direct observations of such reorganization of wave breaking by surface currents.

We finally discuss how such findings on the vertical and horizontal distributions of wave-induced turbulence are relevant for air-sea gas exchange studies.

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Dr REUL Nicolas, IFREMER, France

### **A perspective of the high surface-wind remote sensing capability with SMOS sensor**

N. Reul, J. Tenerelli, B. Chapron, D. Vandemark, Y. Quilfen, Y. Kerr

The Soil Moisture and Ocean Salinity (SMOS) mission provides multi-angular L-band (1.4 GHz) brightness temperature images of the Earth. Because upwelling radiation at 1.4 GHz is significantly less affected by rain and atmospheric effects than at higher microwave frequencies, the SMOS measurements offer unique opportunities to complement existing ocean satellite high wind observations that are often erroneous in these extreme conditions. In this talk, we shall provide an overview of the results of the first phase of the SMOS+STORM STSE project which aimed to exploit the identified capability of SMOS L1 Brightness Temperatures to monitor wind speed and whitecap statistical properties beneath

Tropical Cyclones and severe storms. Such new capability at the core of the project was recently demonstrated by analysing SMOS data over the category 4 hurricane IGOR that developed in September 2010. Without correcting for rain effects, the wind-induced components of SMOS ocean surface brightness temperatures were co-located and compared to observed and modelled surface wind speed products. The evolution of the maximum surface wind speed and the radii of 34, 50 and 64 knots surface wind speeds retrieved from SMOS were shown to be consistent with hurricane model solutions and observation analyses. During the project this feature has been extensively verified in other cases (such as for hurricane SANDY in 2012), with the aim of producing a SMOS-derived storm catalogue. The SMOS sensor is thus closer to a true all-weather ocean wind sensor with the capability to provide quantitative and complementary surface wind information of great interest for operational hurricane intensity forecasts but also to improve air-sea fluxes estimates in extreme events.

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Dr ROEDENBECK Christian, MPI Biogeochemistry - Germany

### **Ocean-atmosphere CO<sub>2</sub> flux variability estimated from SOCAT pCO<sub>2</sub> observations**

C. Rödenbeck, D. C. E. Bakker, N. Metz, A. Olsen, C. Sabine, N. Cassar, R. F. Keeling, and M. Heimann

A temporally and spatially resolved estimate of the global sea-air CO<sub>2</sub> flux is presented, obtained by fitting a data-driven diagnostic model of ocean mixed-layer biogeochemistry to surface-ocean CO<sub>2</sub> partial pressure data from the SOCAT data base. The estimated seasonality is well-constrained from the data in most regions, and compares well to the widely used monthly climatology by Takahashi et al. (2009). Comparison to independent data tentatively supports the slightly higher seasonal variations in our estimates in some areas. The estimated interannual variations are largest in the Tropical Pacific, and tied to ENSO.

Extending the diagnostic model to link carbon variability to variability in nutrients and oxygen, it offers a way to implement multiple data constraints on sea-air CO<sub>2</sub> fluxes. As a prerequisite towards this goal, we demonstrate that the seasonality estimated from the pCO<sub>2</sub> data is consistent with an independent seasonal climatology of the surface-ocean PO<sub>4</sub> concentrations. Likewise, tropical interannual signals estimated from SOCAT data are compatible with signals from atmospheric oxygen data. Sea-air CO<sub>2</sub> flux variability is also estimated from pCO<sub>2</sub> data by other groups using a range of complementary methods (interpolation, regression, neural networks, data assimilation). An international intercomparison project is underway.

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Pr RUTGERSSON Anna, Uppsala University -Sweden

### **Do we need to consider water-side convection when calculating air-sea gas transfer?**

A. Rutgersson, M. Norman, E. Sahlée, A. Andersson, E. Podgrajsek

Combination of surface water cooling and a deep ocean mixed layer generates convective eddies scaling with the depth of a mixed layer that enhances the efficiency of the air-sea gas transfer. This enhancement is explained by the convective eddies disturbing the molecular diffusion layer and inducing increased turbulent mixing in the water (Rutgersson et al 2011). The enhancement can be introduced into existing formulations for calculating the air-sea

exchange of gases by using an additional resistance, due to large-scale convection acting in parallel with other processes. The additional resistance is expressed by the convective velocity scale of the water and the friction velocity and characterizes the relative role of surface shear and buoyancy forces. Calculated fluxes from the Baltic Sea basin shows an altered seasonal cycle in surface gas fluxes of CO<sub>2</sub> and O<sub>2</sub> when introducing the convection (Norman et al., 2012).

This is of particular interest for the low to moderate wind-speed regime, when spray and bubbles have less dominance of the efficiency of the transfer. It is also possible that gases of different solubility shows a different response to various forcing mechanisms. Lake data of methane fluxes exhibits a stronger diurnal cycle than CO<sub>2</sub> as a response to the strong diurnal cycle of water-side convection (Podgrajsek et al., 2013).

The potential need of taking processes into account generating turbulence of a larger scale, such as water-side convection or Langmuir circulation (Belcher et al, 2013) introduced larger requirements on the remote sensing products used for air-sea gas flux climatologies.

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Mrs SANNA Valentina, Fluid Solutions -alternative srl - Italy

### **Assessment of a sea-air modeling system in the Adriatic Sea using a nested approach.**

V. Sanna, G. Savino, D. Crinò, A. Ciarravano, E. Binotti

The main objective of the present work is to study the field dynamics around the southerner coastal area of the Adriatic Sea applying a cyclic modeling system for the period 2001-2010, in order to obtain accurate results, needed to master the sea-air transfer processes.

The cyclic modeling system was chosen to carry out this study and better correlate air-sea interactions. The atmospheric model WRF (Weather research and Forecasting model) was applied to obtain predicted wind data which were included as input in the ocean circulation model sbPOM (Stony Brook Parallel Ocean Model). Afterwards, wind fields and current velocities were used to force the sea surface wave model SWAN (Simulating WAVes Nearshore) in order to obtain the corresponding wave pattern for the whole Adriatic Sea. The spatial resolution of the predicted wind field was 6.5 km with a mean hourly temporal resolution. Two other numerical simulations were carried out on a nested domain in order to evaluate the real contribution on the results using a nested approach and to investigate the importance of the wind field resolution. The two calculations differ to each other for an increase in the predicted wind field resolution from 6.5 km to 3 km.

Numerical predictions of wind, currents and waves were compared with experimental data. The importance to apply a fine wind field resolution (3 km), especially near the coastline, is confirmed by the results, which present more accuracy in the wave field prediction compared with the coarse wind field resolution (6.5 km). Finally, one more calculation was carried out with WRF model, taking into account current and wave results. This approach permitted to achieve high consistency in the forecasting of sea surface temperature, humidity, and carbon dioxide concentration.



Dr SCHUSTER Ute, University of East Anglia - UK

### **The northern hemisphere air-sea CO<sub>2</sub> flux - its variability and uncertainty**

U. Schuster, S. Nakaoka, A.J. Watson, Y. Nojiri, P. Landschutzer

Measurements of sea surface pCO<sub>2</sub> and related parameters have been done in the North Atlantic and North Pacific for over a decade, using Voluntary Observing Ships, offering the unique opportunity of studying northern hemisphere variability.

Changes in the North Atlantic Oscillation (NAO) are known to induce shifts in the path of the Gulf Stream, leading to changes in sea surface temperature (SST) in the vicinity of such shifts. SST changes can be expected to thermodynamically lead to changes in sea surface pCO<sub>2</sub>, as seen in the vicinity of 26.6N/62.5W in the Atlantic between 2002 and 2007 (Figure 1a). However, a similar relationship between sea surface pCO<sub>2</sub> and the NAO index is not found here. In the North Pacific, the influence of changes in the Pacific Decadal Oscillation (PDO) on sea surface pCO<sub>2</sub> are different, and no change in the correlation between sea surface pCO<sub>2</sub> and SST is found.

Using Neural network and geostatistical techniques, regional and basin-scale maps of sea surface pCO<sub>2</sub> and air-sea CO<sub>2</sub> flux are being produced, together with the uncertainties being identified. We will present the total northern hemisphere air-sea CO<sub>2</sub> flux and its variability over the last decade, and the mechanistic biological, chemical, and physical, and climate mode drivers of identified variability.

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Dr SMYTH Tim, Plymouth Marine Laboratory- UK

### **The Observational Platforms of PML for air-sea exchange**

T. Smyth, V. Kitidis, H. Findlay, T. Bell, M.X. Yang, F. Hopkins, I. Brown, R. Beale

Regular high-quality measurement of air-sea exchange parameters are essential for sea-truthing Earth Observation products. The Plymouth Marine Laboratory leads the Atlantic Meridional Transect and Western Channel Observatory, and these efforts have contributed significantly to our understanding of air-sea exchange of many different gases. PML's observational expertise and strengths in remote sensing and modelling allow us to work seamlessly from in situ data to EO algorithm implementation. As well as presenting on some of the more novel results of our air-sea exchange work, some of the future directions that we plan to take in the next few years will be highlighted.

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Pr SOLOVIEV Alexander, Oceanographic Center, Nova Southeastern University - USA

### **Air-sea gas exchange and bio-surfactants: low and high wind speed extremes**

A. Soloviev

Bio-surfactants play important role in air-sea gas exchange. Under low wind speed conditions, bio-surfactants suppress ocean gravity-capillary waves. This effect results in slicks on the sea surface. Slicks alter direct (interfacial) component of the air-sea gas exchange. Under high wind speed conditions, bio-surfactants affect the bubble-mediated component of air-sea gas exchange by altering surface properties of air-bubbles. Surfactants are often associated with the presence of surfactant-producing bacteria. The bacterial

composition and its functional importance in the near-surface layer of the ocean are still understudied due to sampling complexities. A new sampling technology has been developed by Kurata et al. (2012) to identify surfactant-producing bacteria in the sea surface microlayer and water column, using DNA analysis. A 47 mm polycarbonate membrane filter was deployed outside the ship distorted area to obtain snapshots of the bacterial community structure in the sea surface microlayer. Water column samples were taken with a peristaltic pump. A high-throughput sequencing technology was employed to compensate for the small sample size from the microlayer. A case study in the Straits of Florida, involving SAR satellite imagery, revealed substantial presence of surfactant-producing marine bacteria (*Acinetobacter*, *Bacillus*, *Corynebacterium*) in the water column below the slick area and in the sea surface microlayer. Under high wind speed conditions, sampling of the microlayer is complicated. In this case, the presence of surfactant-producing bacteria is detectable from DNA analysis of the water column samples. The challenge of identification of surfactant-producing bacteria from color satellite measurements is discussed in the context of parameterizing global CO<sub>2</sub> uptake by the oceans.

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Dr TORRES Ricardo, Plymouth Marine Laboratory - UK

### **Sensitivity of CO<sub>2</sub> fluxes in a shelf environment to the assimilation of EO in a 1D Ecosystem model**

R. Torres, S. Ciavatta, M. Ruiz-Villareal, J. Shutler

We will present results from data assimilation experiments at the coastal station L4 (10 nm south of Plymouth, 50°15.00'N, 4°13.02'W, depth of 51 m) using the 1D coupled hydrodynamic-ecosystem model GOTM-ERSEM. The European Sea Regional Ecosystem Model (ERSEM, Baretta et al., 1995; Blackford et al., 2004) is a biomass and functional group based biogeochemical model that resolves the time evolution of the pelagic ecosystem including the nutrient and carbon cycle within the planktonic trophic chain of primary producers (picophytoplankton, nanoflagellates, dinoflagellates and diatoms), consumers (meso- and micro-zooplankton and heterotrophic nanoflagellates) and decomposers (heterotrophic bacteria). ERSEM includes a comprehensive carbonate system (Blackford & Gilbert 2007, Artioli et al. 2012) and explicitly simulates the production of dissolved organic carbon (DOC) and organic matter (DOM).

The data assimilation system implemented in this work is the 1D version of the Ensemble Kalman Filter (EnKF) as described in Torres et al., 2006 and Ciavatta et al 2011. The data used in the assimilation experiments consist of EO data from MERIS and MODIS sensors for the L4 station. The variables include both Chlorophyll-a and SST for 2010.

These experiments provide the sensitivity of in water partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) and resulting air-sea fluxes of CO<sub>2</sub> to assimilating either SST or Chl-a. The EnKF provides additional information on the structure and time evolution of the covariances of all the model variables and allows the discrimination of the ERSEM variables that have the largest impact on the variability of pCO<sub>2</sub>. We will present results obtained during the simulation of year 2010.

Dr TOURNADRE Jean, IFREMER - France

**Altimeter sigma0 bloom and surface slick**

J. Tournadre, B. Chapron

Sigma0 blooms are zone of the ocean where the backscatter measured by an altimeter reaches extremely high values. This corresponds to no winds zone where the ocean surface is completely flat. The presence of these highly reflective patches on the ocean surface that might results from natural or anthropogenic surface films distorts the altimeter waveforms. A method based on the analysis of altimeter waveform has been used to estimate the distribution of probability and length of the slicks.

We present a new method based on the inversion of waveforms in term of high resolution (300m) surface backscatter that allows a precise determination of the flat ocean surface. The method is validated using the large database of SAR and visible image collected during the Deepwater Horizon oil spill.

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Dr VANDEMARK Doug - UNH/EOS/OPAL - United States

**Prediction of oceanic carbon dioxide levels at observational time series nodes using satellite ocean remote sensing products**

D. Vandemark, T. Moore, S. Salisbury

This study focuses on building predictive models for ocean pCO<sub>2</sub> based on several satellite and ocean model inputs, and doing so at selected ocean time series measurements sites. These sites are the STRATUS, PAPA, and WHOTS nodes, chosen because of multiyear daily pCO<sub>2</sub> measurements. Several empirical least squares inversions were devised and tested for pCO<sub>2</sub> prediction with fairly impressive success in terms of root mean square differences of less than 10 uAtm. Sensitivity of the model to choice of inputs was assessed and mixed layer depth, SST and SSS are found to be dominant in explaining variance, whilst ocean color data are less so but are still providing some additional information. While success in local algorithm development and validation was achieved, these locally-trained models did not fair well in predicting ocean pCO<sub>2</sub> levels as one moved away from the sites beyond 200-1000 km – i.e. they were not globally useful. The work points to pros and cons of working with the long-term time series sites as opposed to the climatological databases of, for example, SOCAT and Takahashi.

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Dr VLAHOS Penny, , University of Connecticut - USA

**Parameterizing the bubble-mediated air-sea flux of a non-ideal gas, DMS**

P. Vlahos<sup>1,2</sup>, J. Liang<sup>3</sup> and E.C. Monahan<sup>1</sup>

<sup>1</sup>Departments of Marine Sciences and <sup>2</sup>Chemistry, University of Connecticut – Groton

<sup>3</sup>Oceanography, University of Washington - Seattle

Air sea gas exchange parameterization is critical for an accurate partitioning of climatically and environmentally important non-ideal gases (e.g., DMS) between the ocean and atmosphere, yet is still poorly constrained primarily because the effect of physio-chemical mechanisms and gas bubbles is insufficiently studied. Bubbles provide additional pathways

for air-sea gas transfer, and gases inside bubbles can dissolve even at supersaturation because of surface tension and hydrostatic pressure. The effect of bubbles on the transfer of an ideal gas is the enhancement of the total gas transfer rate and an equilibrium supersaturation condition. Those two bubble effects increase rapidly with wind speed for an ideal gas. For a non-ideal gas, however, the fugacity may be reduced when the amount of near-surface bubbles increases with wind speed, because amphiphilic molecules are more attracted to bubble-water interfaces than to either the liquid or gas. The increase in gas transfer rate with wind speed for these gases is therefore much smaller than for ideal gases [Vlahos and Monahan, 2009]. Furthermore, the bubble-induced supersaturation due to the complete dissolution of bubbles for these gases is expected to be larger than for ideal gases. Combining the theory of Vlahos and Monahan [2009] and the bubble distribution calculated by a coupled large eddy simulation – bubble population model [Liang et al., 2012], we here improve the bubble-mediated gas flux parameterization for the non-ideal gas DMS. While bubble-induced supersaturation due to completely dissolved bubbles is negligible for a highly soluble ideal gas, it is important for DMS because of the reduced solubility and the subsequent reduced gas flux through the ocean surface.

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Dr WANNINKHOF Richard , NOAA/AOML -USA

### **The Relationship between Wind Speed and Gas Exchange over the Ocean Revisited**

Wanninkhof, R.

Relationships between gas exchange and wind speed are used extensively for estimating bulk fluxes of atmospheric gases across the air-sea interface. Here I provide an update on a frequently used relationship proposed in Wanninkhof (1992). The update reflects the advances that have occurred over the past two decades. The general principle of obtaining a relationship constrained by the globally integrated bomb  $^{14}\text{CO}_2$  flux into the ocean remains unchanged. The improved relationship is determined using revised global  $^{14}\text{C}$  inventories and improved wind speed products. Empirical relationships of the Schmidt number necessary to determine the fluxes are extended to  $40\text{ }^\circ\text{C}$  to facilitate use in models. The focus is on gas exchange of carbon dioxide but the suggested functionality can be extended to other gases at intermediate (from  $\approx 4\text{ m s}^{-1}$  up to  $\approx 12\text{ m s}^{-1}$ ) winds.

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Dr WATSON Andy, University of East Anglia

### **Key note talk**

Dr YANG Mingxi , Plymouth Marine Laboratory -United Kingdom

### **Air-sea Exchange of Oxygenated Volatile Organic Compounds over the Atlantic Basin**

M. Yang, P. Nightingale, R. Beale, P. Liss, B. Blomquist, C. Fairall

Oxygenated Volatile Organic Compounds (OVOCs), such as methanol, acetone, and acetaldehyde, are important for atmospheric chemistry and climate by influencing the cycling of ozone and the hydroxyl radical. OVOCs are emitted from natural and anthropogenic sources, (photo)chemically produced and destroyed in the atmosphere, and removed from air via deposition. Due to the scarcity of air-sea flux and concentration measurements, the role of the ocean in the cycling of these compounds remains poorly quantified. Here we present direct flux measurements of these OVOCs by eddy covariance and their near surface dissolved concentrations from a recent cruise in the Atlantic. Constrained by the aerodynamic limit, the transfer of methanol from air to sea appears to be effectively a depositional process, independent of the seawater methanol concentration. Acetone varied from influx in high latitudes to efflux in the subtropical gyre of the North Atlantic to near saturation in the South Atlantic. For acetaldehyde, a small oceanic emission was observed, but at a lower magnitude than predicted based on the two-layer model.

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Pr ZAPPA Christopher J, Lamont-Doherty Earth Observatory of Columbia University - USA

### **Precipitation and the global air-sea CO<sub>2</sub> flux**

C.J. Zappa, W. R. McGillis

Rain is one process unrelated to wind forcing that is known to enhance the gas transfer velocity [Harrison et al., 2012; Ho et al., 2000; Takagaki and Komori, 2007; Zappa et al., 2009]. Rain also plays a significant role in the exchange of CO<sub>2</sub> between the ocean and atmosphere, through surface layer chemical dilution and via export of carbon from the atmosphere by wet deposition. Recently, we have determined that these effects play a significant role in the uptake of CO<sub>2</sub> in the western equatorial Pacific [Turk et al., 2010]. However, global bulk estimates of air-sea CO<sub>2</sub> flux have to date ignored these effects [Takahashi et al., 2002; Takahashi et al., 2009].

Here, we use monthly global precipitation measurements from the Global Precipitation Climatology Project Version 2.1 Combined Precipitation Data Set, a global monthly climatology of the atmosphere-ocean surface p(CO<sub>2</sub>) difference [Takahashi et al., 2009] and a surface dilution model to provide an estimate of the enhanced transfer, chemical dilution and deposition effects of rain on the global air-sea CO<sub>2</sub> flux. Our results show that during high rainfall events, chemical dilution from the rain can lower the surface ocean p(CO<sub>2</sub>) in these regions by more than 30 microatm. This increases the air-sea  $\Delta p(\text{CO}_2)$  in ocean sink regions, while in ocean source regions  $\Delta p(\text{CO}_2)$  is lowered and can potentially turn a weak source into a sink. As this effect is confined to a very near-surface layer it is neglected in surface mixed layer and climate models as well as by standard measurements of surface p(CO<sub>2</sub>) that are normally made at 3-5 m depth. During rain, the gas transfer velocity is also increased which embellishes the increase in  $\Delta p(\text{CO}_2)$  and further enhances the sink potential, but this effect is smaller. Depending on the region, the annual net air-sea CO<sub>2</sub> flux can change by more than 100%. In this study, the precipitation results in making chemical dilution, enhanced gas transfer, and wet deposition significant contributions to the ocean CO<sub>2</sub> sink.

Dr ZHAO Dongliang  
Ocean University of China - China

**On the relationships of gas transfer velocity with turbulent kinetic energy dissipation rate and wind waves**

D. Zhao, Z. Li, S. Li, Z. Song

The exchange of carbon dioxide across the air-sea interface is an important component of the atmospheric CO<sub>2</sub> budget. Understanding how future changes in climate will affect oceanic uptake and release of CO<sub>2</sub> requires accurate estimation of air-sea CO<sub>2</sub> flux. This flux is typically expressed as the product of gas transfer velocity, CO<sub>2</sub> partial pressure difference in seawater and air, and the CO<sub>2</sub> solubility. As the key parameter, gas transfer velocity has long been known to be controlled by the near-surface turbulence in water, which is affected by many factors, such as wind forcing, ocean waves, water-side convection and rainfall. Although the wind forcing is believed as the major factor dominating the near-surface turbulence, many studies have shown that the wind waves and their breaking would greatly enhance turbulence compared with the classical solid wall theory. Gas transfer velocity has been parameterized in terms of wind speed, turbulent kinetic energy dissipation rate, and wave parameters on the basis of observational data or theoretical analysis. However, great discrepancies, as large as one order, exist among these formulas. In this study, we will systematically analyze the differences of gas transfer velocity proposed so far, and try to find the reason that leads to their uncertainties. Finally, a new formula for gas transfer velocity will be given in terms of wind speed and wind wave parameter.

## 2. Abstracts for poster presentation

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Dr ARCHER Stephen, Bigelow Laboratory for Ocean Sciences - USA

### **Investigation of the influence of the sea surface microlayer on ozone deposition rates**

S. Archer, K. Moore, P. Matrai

O<sub>3</sub> deposition into the ocean surface represents a significant loss from the atmosphere with current best estimates, based on chemistry transport model analyses, being about one third of the global annual O<sub>3</sub> deposition of 600–1000 Tg O<sub>3</sub> yr<sup>-1</sup>. Such deposition likely represents the net flux to the physical ocean surface, chemical interactions in the presence or absence of a surface microlayer and bidirectional reactions between O<sub>3</sub> and reactive iodine dependent on the environmental light regime. A laboratory-based experimental approach is used to further explore controls on the rates of O<sub>3</sub> deposition to seawater. We quantify rates of O<sub>3</sub> deposition to natural seawaters and address the causes of the variability in relation to dissolved organic matter and iodide concentrations. Experimental results are presented showing the influence of artificial surfactants, specific micro-algal exudates and natural microlayers on O<sub>3</sub> deposition rates.

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Dr BOZEC Yann, UMR 7144 CNRS-UPMC, Station Biologique de Roscoff – France

### **High Frequency Monitoring of pCO<sub>2</sub> using a CARIOCA sensor on a Marel buoy in a temperate coastal ecosystem: The Bay of Brest (2003-present)**

Y. Bozec (1), L. Beaumont (2), S. Blain (3), E. Bucciarelli (4), E. Grossteffan (5), A. Guillot(2), S. L'Helguen (4), L. Merlivat (6), M. Répécaud (7), P. Rimmelin (5), P. Tréguer (5)

- 1) UMR 7144 CNRS-UPMC, Station Biologique de Roscoff, Place Georges Teissier 29680 Roscoff, FRANCE (bozec@sb-roscoff.fr)
- 2) Division Technique INSU-CNRS
- 3) UMR 7621 CNRS-UPMC, Observatoire Océanologique de Banyuls sur Mer
- 4) UMR 6539 CNRS-UBO, IUEM, Brest
- 5) UMS 3113 CNRS-UBO, Institut Universitaire Européen de la Mer (IUEM), Brest
- 6) LOCEAN, Université Pierre et Marie Curie, Paris
- 7) IFREMER, Centre de Brest

The constraint of air–sea CO<sub>2</sub> fluxes and their variability at various time and spatial levels remain a central task in global carbon and climate studies. Over the past decade, the coastal oceans have been the focus of several studies highlighting the key role of these ecosystems in the global budget of air-sea CO<sub>2</sub> fluxes. The CARbon Interface Ocean Atmosphere (CARIOCA) sensor allows for both long term and high frequency measurements of the partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>). The CARIOCA sensor is therefore an excellent tool for investigating the high variability and the evolution of air-sea CO<sub>2</sub> fluxes in coastal environments. Here we present high-frequency pCO<sub>2</sub> data recorded since 2003 during the first deployment of a CARIOCA sensor on a MAREL buoy in the surface waters of a temperate coastal ecosystem, the Bay of Brest (IFREMER site), which is impacted by both coastal and oceanic variability. High frequency measurements allowed for the quantification of the diurnal, tidal and seasonal variability in the assessment of the annual CO<sub>2</sub> air-sea fluxes. Biological activities were the main process controlling the pCO<sub>2</sub> variability in surface waters on a seasonal time-scale. On a shorter scale, the tidal and diurnal cycle are shown to

be responsible for high pCO<sub>2</sub> variability. Our investigation revealed that the surface waters of the Bay were near equilibrium with the atmosphere and that the inter-annual variability was rather small.

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Ms BRION Emilie, ALTRAN Ouest - FRANCE

### **Estimating the CO<sub>2</sub> fluxes over the North Atlantic subtropical basin**

E. Brion, F. Guinot, P. Karleskind, L. Richier

In collaboration with the Laboratory of Spatial Oceanography (IFREMER, Brest), we addressed the air-sea CO<sub>2</sub> fluxes over the North Atlantic subtropical basin. We have calculated the CO<sub>2</sub> fugacity (fCO<sub>2</sub>) from the sea surface temperature (SST), using the empirical relation developed by Lefebvre & Taylor (2002) over the region and satellite temperature data (AVHRR/AMSRE). We have shown that results are in good agreement with in-situ data (SOCAT database), as soon as the data density is high enough. Air-sea CO<sub>2</sub> fluxes are then estimated from fCO<sub>2</sub>. We have used different gas transfer velocities in order to assess their impact on the computed air-sea CO<sub>2</sub> fluxes. For this work, we remotely processed our data from the OceanFlux-GHG project tool that relies on the Cersat Cloud Facility, about which we have tested the features and usability.

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Mr HADDADI MOGHADDAM Kouros, International Sturgeon Research Institute, Iran

### **Seasonal changes of biogenic substance and bioproductivity of water in the northern part of the Caspian Sea**

K. Haddadi Moghaddam

The Caspian Sea is the unique water body : it gives 80% of the total fish catch in internal water bodies of the country and it has 90% of the world sturgeons stock. So the study of processes of water quality formation in the Caspian Sea has the scientific and practical significance. Features in the formation of hydrological –hydro chemical regime of the Caspian Sea are defined by the closure, the inland position, the river runoff impact and by other factors. In connection with possible consequences of variations of the Caspian Sea level and anthropogenic pollution of marine environment. It is necessary to establish the mechanisms in dynamics of water ecosystem state, to reveal the most important internal water processes determining the water quality and water self- purification, to establish main processes of the transformation of polluting substances. To study the behavior of the Caspian Sea ecosystem, the model of organogenic substance transformations was used. This model considers interconnected biogeochemical cycles on N and P as well as major fluxes in transformations of Si, dissolved organic C and O<sub>2</sub> in two layer water ecosystem. Using the modeling data, the total inputs of biogenic substances with river waters are estimated and the primary forms of biogenic substances entering the northern part of the sea are identified. Volga waters carry to Caspian Sea 50.2-58.6% of N compounds and 56.5% of DSi. These assessments agree reasonably with the data available in the literature on the intra annual distribution of a biogenic load from the Volga runoff.

The values of hydrobion production were evaluated for all considered groups on the basis of calculated internal fluxes of substances (in units of biogeochemical elements – C, Si, N, P). Production was calculated by summation of positive fluxes of substances, spent on the construction of biomass (consumption of nutrients) and its unavoidable losses (excretion



of metabolic products, biomass dying off, grazing by organisms of higher trophic levels, output into the adjacent areas by a water flow). So with the help of mathematical modeling the mean multi annual biohydrochemical portrait of the northern shallow water and the most productive part of the Caspian Sea ecosystem is received. The modeling results on the annual dynamics of organogenesis

Substance concentration inputs of biogenic substances due to the river run off internal fluxes of compounds bioproduction and balance between production and destruction processes in the area of the North Caspian comprehensively characterize an ecological state of a marine environment as well as expose features of development of biotransformation processes and circulation of biogenic substances.

### **Climatology of the Caspian Sea in present circumstances**

K. Haddadi Moghaddam

The Caspian Sea basin is the most important fisheries water body in the country. Over 70% of the world catch of sturgeon are harvested here. This Sea is the biggest enclosed body of water on Earth, having an even larger area than that of the American Great Lakes or that of Lake Victoria in East Africa. It is situated where the South-Eastern Europe meets the Asian continent, between latitudes 47.07'N and 36.33N and longitudes 45.43 E and 54.20E. It is approximately 1,030 km long and its width ranges from 435 km to a minimum of 196 km. It has no connection to the world's oceans and its surface level at the moment is around -26.5 m below MSL. At this level, its total coastline is some 7,000 km in length and its surface area is 386,400 km<sup>2</sup>. The water volume of the lake is about 78,700 km<sup>3</sup>. Approximately 130 large and small rivers flow into the Caspian, nearly all of which flow into the north or west coasts.

The fisheries in the basin develops under the influence of complicated interactions of natural and anthropogenic factors which necessitated the elaboration of a system of purposeful measures providing conservation and rational exploitation of bioresources. Transgression of the Caspian Sea level, radically changed the conditions of bioresources formation and exploitation and determined the need for assessment of changes. In order to stabilize the sea level and to provide conditions for natural fish reproduction under conditions of regulated flow of rivers a number of measures was proposed:

- Reduction of loss of consumed share of the Caspian water balance (construction of a dividing dam between the Northern and Middle Caspian, isolation of eastern shallow waters of the Northern Caspian)
- Rational utilization of the Volga water (elaboration of operation regime of the cascade of the Volga reservoirs, construction of a dividing dam in the Volga delta, amelioration of spawning grounds, dredging and cleaning of fish way canals)
- Replenishment of water resources of the basin through supplies from the other regions (transfer of part of flow of the northern rivers and the Black Sea water).
- Regulation of fishing and pass of breeders to the spawning grounds

The present study was supported by the Iranian Fisheries Research Organization (IFRO) and was a part of scientific project "Study on feeding Habits of Sturgeon in the Caspian Sea conducted at the Ecology Department of the Caspian Sea international sturgeon research institute. I would like to thank Dr. Motalebi (Director of IFRO) and Dr. Poukazemi.

Mr HAMILTON Bryan, Nova Southeastern University - United States

### **DNA Analysis of Surfactant Associated Bacteria in the Sea Surface Microlayer in Application to Satellite Oceanography**

A. Soloviev, M. Shivji, A. Tartar, B. Hamilton

Natural surface active materials result from biochemical and biophysical processes in the near-surface layer of the ocean. These processes involve bacteria. Identifying the surfactant-associated functional group of marine organisms and its relation to marine organisms contributing to ocean color will help us to establish a connection between remote sensing of color and temperature and SAR satellite remote sensing. The primary objectives of this study are to conduct a pilot experiment in the Straits of Florida and perform DNA analysis of the biological organisms in the near surface layer of the ocean that contribute to ocean color and the production of surface active materials; to develop the initial study design to contribute to a future field campaigns; to coordinate the implementation concept to the schedule of future satellite launches by NASA and other space agencies. We will conduct a pilot experiment in the Straits of Florida in order to identify a possible connection between marine organisms contributing to ocean color and surfactant associated marine organisms. The new sampling technique will involve taking the in situ DNA samples during color and SAR satellite overpasses. We will then be able to quantitatively analyze the communities at these sites, using the bacterial samples taken from the sea surface microlayer and near surface layer of the ocean under different wind wave conditions including slicks as well as formation of climate active aerosols by bubbles.

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Dr HANAFIN Jenny, CNRS-UBO and IFREMER, France

### **Comparison of WAVEWATCH-III ® model output whitecap fraction with in situ observations**

J. Hanafin, F. Ardhuin, B. Chapron, M. Yelland, B. Moat

Recently, modeling of whitecap properties was implemented in the spectral wave model WAVEWATCH-III ® (WW3). The two different wave breaking parameterizations which have been developed for WW3 were implemented in special hindcasts over the period 2006-2009 for comparison with in situ observations in the context of the OceanFlux-GHG project.

The model parameterizations use different approaches related to the steepness of the carrying waves to estimate breaking wave probabilities. That of Ardhuin et al. (2010), denoted as T451 in the following, is based on the hypothesis that breaking probabilities become significant when the saturation spectrum exceeds a threshold, and includes a modification to allow for greater breaking in the mean wave direction, to agree with observations. In the second, denoted as T570 (Filipot and Ardhuin, 2012), breaking probabilities are defined at different scales by using wave steepness and then the breaking wave height distribution is integrated over all scales. A further adaptation of the latter to make it self-consistent is described in (Leckler et al, 2012, manuscript in review by Ocean Modelling) which was also implemented in the hindcasts.

Comparisons were made with in situ data collected during research cruises in the North and South Atlantic, and the Norwegian Sea in 2007, 2008 and 2009. The model values follow the Monahan and Woolf (1989) parameterisation for combined static and dynamic breakers quite well, with a tendency to overestimate at wind speeds up to 16m/s and underestimate at higher wind speeds. The error due to the fact that model winds may have a wind speed dependent bias compared to the in situ winds, and have less spatial and temporal variability will be presented.

Ms HARTMAN Susan, NOC -UK

### **Controls on CO<sub>2</sub> flux variation at a sustained observatory (PAP-SO) in the northeast Atlantic Ocean**

S.E. Hartman, D. Turk, Z.P. Jiang, R. S. Lampitt, H. Frigstad, D. J. Hydes

We present high-resolution year-round autonomous measurements of pCO<sub>2</sub> taken in situ at the Porcupine Abyssal Plain sustained observatory (PAP-SO) in the Northeast Atlantic (49°N, 16.5°W; water depth ~ 4850 m) for the period 2010 to 2012. There is a persistent under saturation of CO<sub>2</sub> in surface waters throughout the year which gives rise to a perennial CO<sub>2</sub> sink. pCO<sub>2</sub> measurements, made at 30m depth on the sensor frame are compared with other autonomous biogeochemical measurements at that depth (including fluorescence and nitrate data) to analyse daily to seasonal controls on pCO<sub>2</sub> flux in the inter-gyre region of the North Atlantic. Comparisons are also made with in situ regional time-series data from a ship of opportunity, mixed layer depth measurements from profiling Argo floats and Meteorological measurements made on site through collaboration with the UK Met office. Comparison with an earlier dataset collected at the site confirms year-to-year variability in pCO<sub>2</sub> flux due to variation in primary production and changes in the mixed layer depth and supply of DIC and nitrate to the surface.

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Dr HO David, University of Hawaii - USA

### **Rain-induced gas exchange: When and where does it matter?**

D.T. Ho, F. Veron, M. Kelley, E.L. Harrison, S.S. Eggleston

There is considerable interest in rain and its influence on air-sea gas exchange, as rain has been shown in laboratory experiments to enhance gas exchange in the absence of wind, and rain is one of the variables that can be sensed remotely from space. In preliminary studies on the combined effects of wind and rain on gas exchange, the two processes were found to be linearly additive. However, in follow-up studies with different experimental setups, it was found that the effect of rain was only significant when the kinetic energy flux delivered by rain exceeded that of the wind. Hence, at low wind speeds, rain has a noticeable effect on gas exchange but the effect quickly disappears as wind speeds increase. These findings in the laboratory suggest that over the ocean, the effect of rain on air-water gas exchange could be significant if: a) the rain rate is high, and/or b) the wind speed is low.

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Dr JONES Steve, University of East Anglia -UK

### **Decadal trends in surface ocean pCO<sub>2</sub>**

S.D. Jones, C. Le Quéré, C. Rödenbeck, A.C. Manning

We use the newly released SOCAT v2 data set to assess the decadal trends in surface ocean pCO<sub>2</sub> during the 1990s and 2000s. Such long term trends are inherently valuable in understanding changes in the global carbon budgets as published by the Global Carbon Project. Additionally, a significant change in the trend of atmospheric CO<sub>2</sub> concentrations occurred around the year 2000 which does not reflect the continued increase in

anthropogenic CO<sub>2</sub> emissions. This study assesses the potential role of the ocean carbon sink in the observed change in atmospheric CO<sub>2</sub> trends.

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Mr LECKLER Fabien, Laboratoire d'Océanographie Spatiale, IFREMER - France

### **Wave breaking analysis using stereo video system.**

F. Leckler, F. Ardhuin, A.Mironov, V. Dulov, A. Benetazzo, F. Fedele

Images of the ocean surface in the visible range of the electromagnetic spectrum provide quantitative information on a number of physical parameters. Recently, Mironov and Dulov (2008) used video records to analyze wave breaking. Their study provided statistics over a large range of breaking events. On the other hand, Benetazzo et al. (2008) proposed a method to reconstruct the elevation maps of the ocean waves from spatial-widespread and non-intrusive stereo video system. The main problem in stereo analysis is how to find, given a point in the first image, the corresponding point in the second image. Benetazzo et al. (2008) proposed a classical cross-correlation method. When image texture in correlation window and correlation coefficient exceed thresholds, matching is kept. However, in presence of foam patches, texture and correlation coefficient can be brought up the thresholds by few very white points. When these white points are on extremities of the correlation window, obtained matched point pairs leads to aberrant surfaces. Thereby, we first improve the point matching method to reconstruct sea surface with foam patches. Four sequences of elevation maps are used to investigate distribution of breaking over wave scales and directions. Moreover evolution of the breaking wave shape is investigated, in particular the critical slope of the incipient breaking waves is estimated. Obtained sea surfaces are also used to analyze directional shape of the wavenumber spectrum.

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Dr LOURANTOU Anna, Laboratoire des Sciences du Climat et de l'Environnement - France

### **On the assignment of prior ocean flux errors in CO<sub>2</sub> atmospheric inversions**

A. Lourantou, F. Chevallier, P. Ciais

Inferring the space-time distribution of CO<sub>2</sub> surface fluxes (FCO<sub>2</sub>) over the globe from atmospheric CO<sub>2</sub> measurements is a mathematically ill-posed problem that can be regularised with prior information about the fluxes. This prior information is typically provided by model outputs, inventories or observation climatologies. To a large extent, the weight between the prior fluxes and the observations in the inversions depends on the uncertainty assigned to the prior. Conversely, the skill of the inversion critically depends on the quality of the assigned uncertainty statistics. Multivariate Gaussian probability density functions usually model this uncertainty and there is an increasing need to strengthen their realism in order to avoid empirical suboptimal choices. Previous work has anchored the parameters of one of these statistical models over land based on the comparison between simulations of a process-based terrestrial ecosystem model with FCO<sub>2</sub> measurements from the FLUXNET network (Chevallier et al, 2006).

The present paper extends this study to the ocean. We build statistics of the misfits between pCO<sub>2</sub> measurements and typical prior ocean FCO<sub>2</sub> databases. Our pCO<sub>2</sub> measurements are onboard observations gathered either in the LDEO (Lamont Doherty Earth Observatory Takahashi et al., 2012) database or in the latest SOCAT (Surface Ocean CO<sub>2</sub> Atlas) database, from 1968 up to 2007. We convert the pCO<sub>2</sub> measurements into FCO<sub>2</sub> by using two different wind speed datasets, a climatological one (Takahashi et al, 2009) and one

issued from the ECMWF (European Centre for Medium-range Weather Forecasts) reanalyses. Our prior ocean FCO<sub>2</sub> databases come from either the Takahashi climatology or the IPSL- PISCES model (Levy et al., 2012). The statistics are drawn within each ocean basin and then aggregated at the basin and annual scale using correlation information. This approach allows assessing the uncertainty of the prior carbon budgets per basin and per year. We proceeded as such, considering the TransCom basins configuration (DeFries et al, 1994).

We show that for all possible data/model couples, the calculated uncertainty budgets are comparable for each basin. The new SOCAT database suggests smaller budget errors than LDEO, with the exception of the N. Atlantic. Overall, this study shows the necessity of distinguishing ocean basins and prior databases when entering prior flux information to atmospheric inversions.

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Dr MARANDINO Christa, GEOMAR - Germany

### **Interpretation of eddy covariance measurements of CO<sub>2</sub> and DMS fluxes and gas transfer coefficients using outputs from the OceanFlux Greenhouse Gases project**

C. A. Marandino, T. Steinhoff, A. Zavorsky

Eddy covariance air-sea fluxes and concentration gradient measurements for CO<sub>2</sub> and DMS (perhaps also acetaldehyde and acetone) will be measured along the equator, starting in Fortaleza, Brazil and ending in Walvis Bay, Namibia, in the Atlantic Ocean in July 2013. We will derive gas transfer coefficients (k) from this data and correlate with wind speed (U) and other parameters measured on board. The functionality of k vs. U will be compared for the suite of gases to investigate the influence of solubility, invasion, and evasion on the gas transfer coefficient. In addition, we will use a range of outputs from the OceanFlux Greenhouse Gases processing system and uncertainty analyses to assist the interpretation of the in situ data (e.g. significant wave heights, existence of diurnal warming, impact of SST skin on the CO<sub>2</sub> fluxes, rain frequency and intensity, existence of SST fronts). The correction of CO<sub>2</sub> k values for the ocean skin temperature and the effect of rain on gas transfer processes are of special interest in this region. We will also use the historical Earth observation data to evaluate the uncertainties introduced from neglecting vertical temperature gradients when calculating the air-sea CO<sub>2</sub> flux.

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Mr MARREC Pierre, Station Biologique de Roscoff – France

### **Spatio-temporal dynamics of air-sea CO<sub>2</sub> fluxes in the Western English Channel (WEC) based on FerryBox measurements**

Marrec P., Cariou T., Latimier M., Macé E., Morin P., Vernet M., and Y. Bozec.

The constraint of air-sea CO<sub>2</sub> fluxes and their variability at various time and spatial levels remain a central task in global carbon and climate studies. In coastal ecosystems high-frequency and extended pCO<sub>2</sub> data are presently relatively sparse regarding the diversity of these systems. Voluntary Observing Ships (VOS) allow covering regularly extended areas at a lesser cost. We installed in December 2010 a FerryBox system on the VOS Armorique to study the processes controlling air-sea CO<sub>2</sub> fluxes in the Western English Channel (WEC). The Ferry crosses 2 times a day the WEC between Roscoff (France) and Plymouth (UK) and measures temperature, salinity, dissolved O<sub>2</sub>, fluorescence and partial pressure of CO<sub>2</sub> (since April 2012) continuously along the ferry track. We will present the main physical,

biological and chemical properties of the area controlling the spatio-temporal variability of air-sea CO<sub>2</sub>. These high-frequency data provide new insights into the CO<sub>2</sub> system dynamics and the air-sea CO<sub>2</sub> fluxes variability from diurnal to inter-annual time scales in the WEC.

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Dr WANNINKHOF Richard, NOAA/AOML -USA

### **The NOAA Ship of opportunity pCO<sub>2</sub> project**

R. Wanninkhof, D. Pierrot, G. Goni, T. Takahashi, R. Feely, N. Bates, K. Sullivan, C. Cosca

Relationships between gas exchange and wind speed are used extensively for estimating bulk fluxes of atmospheric gases across the air-sea interface. Here I provide an update on a frequently used relationship proposed in Wanninkhof (1992). The update reflects the advances that have occurred over the past two decades. The general principle of obtaining a relationship constrained by the globally integrated bomb <sup>14</sup>C flux into the ocean remains unchanged. The improved relationship is determined using revised global <sup>14</sup>C inventories and improved wind speed products. Empirical relationships of the Schmidt number necessary to determine the fluxes are extended to 40 °C to facilitate use in models. The focus is on gas exchange of carbon dioxide but the suggested functionality can be extended to other gases at intermediate (from ≈ 4 m s<sup>-1</sup> up to ≈12 m s<sup>-1</sup>) winds.

In this project funded by the NOAA Climate Observations Division, four NOAA investigators and three academic principal investigators have outfitted 17 research and commercial vessels with automated carbon dioxide analyzers as well as thermosalinographs (TSGs) to measure the temperature, salinity and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) in surface water and air in order to determine the carbon exchange between the ocean and atmosphere. The effort started in 1990 by outfitting two NOAA research ships. It has recently expanded to coastal ships with a focus on ocean acidification. The data is served from local participant sites and provided to global databases and synthesis efforts such as the Takahashi pCO<sub>2</sub> climatology effort and the surface ocean carbon atlas (SOCAT).