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CH_4 and CO_2 emissions and carbon imbalance in a 10-years old tropical reservoir (Petit-Saut, French Guiana)

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In recent years, there has been an increasing concern on greenhouse gas emissions from artificial reservoirs, particularly in the tropics where the flooding of large amounts of primary forest together with high temperatures lead to high methane emissions. In this study, the emissions of carbon dioxide (CO_2) and methane (CH_4) from the Petit Saut hydroelectric reservoir (Sinnamary River, French Guiana) to the atmosphere were quantified for 10 years since impounding in 1994. Diffusive emissions from the reservoir surface were computed from direct flux measurements in 1994, 1995 and 2003 and from surface concentrations monitoring. Bubbling emissions, which occur only at water depths lower than 10 m, were interpolated from funnels measurements in 1994, 1997 and 2003. Degassing at the aerating weir downstream the turbines was calculated from the difference in gas concentrations upstream and downstream the dam and the turbined discharge. Diffusive emissions from the Sinnamary tidal river and estuary were quantified from direct measurements in 2003. Total carbon emissions were 0.33±0.01 $MtC.y^{-1}$ (CO_2: 0.26±0.02; CH_4: 0.07±0.01) the first 3 years after impounding (1994-1996) and then decreased to 0.12±0.01 $MtC.y^{-1}$ (CO_2: 0.10±0.01; CH_4: 0.016±0.006) since the year 2000. On average over the 10 years, 67% of the CO_2 emissions occurred by diffusion from the reservoir surface, 25% from the estuary, 8% by degassing at the weir and a negligible fraction by bubbling. CH_4 diffusion and bubbling from the reservoir surface were predominant (respectively 40 and 44%) only the first year after impounding. Since 1995, degassing downstream the turbines has become the predominant pathway for CH_4 emissions, reaching 60-70% of the total CH_4 flux. A carbon budget of the whole system for the year 2003 that considers riverine inputs and outputs and gaseous emissions reveals that the carbon pool flooded initially is the predominant contributor to the gaseous emissions. In 10 years, about 20% of the 10MtC flooded was lost to the atmosphere. The carbon lost showed a decreasing trend with time typical for a decomposition kinetics of organic matter. A simple model with three fractions of organic matter (one rapidly decomposing, one slowly decomposing, one refractory) fitted well to the data. Our results confirm the significance of greenhouse gas emissions from tropical reservoir but stress the importance of (1) considering all the gas pathways upstream and downstream the dams; (2) taking into account the reservoir age when upscaling emissions rates at the global scale.

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Carbon Dioxide Evasion from Large Tropical Rivers: Measurements from the Amazon and Mekong River Basins

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We measured air-water fluxes of carbon dioxide (CO_2) in riverine environments at a variety of spatial scales in two of the ten largest river systems in the world: the Amazon and the Mekong. Fluxes of carbon dioxide were quantified using a floating chamber equipped with a fan and an air pump to circulate the air within the chamber and through a portable infrared gas analyzer to measure CO_2 concentration continuously as it accumulated within the chamber. In addition, data were collected at all sites for pH, dissolved inorganic carbon, dissolved oxygen concentration and saturation, water temperature, weather conditions (wind speed, relative humidity, air temperature), and partial pressures of carbon dioxide (P_{CO2}) in both air and water.

Partial pressures of CO_2 measured in rivers and streams of the Amazon basin are, on average, approximately ten times more concentrated than atmospheric equilibrium values ($pCO_{2\text{-water}}$=3620±2540 ppm). Preliminary air-water flux measurements made with the floating chamber indicate that CO_2 fluxes in most rivers and streams of the Amazon basin are effluxes, as expected (average CO_2 evasion=20±21 mmol CO_2 m^{-2} hr^{-1}).

P_{CO2} values in the Mekong River basin are also several-fold more concentrated than atmospheric saturation levels ($pCO_{2\text{-water}}$=2150±1430 ppm). In the Mekong as well, estimated gas exchange rates generally represented evasion fluxes and were lower than in the Amazon (average CO_2 evasion=4.8±4.1 mmol CO_2 m^{-2} hr^{-1}).

On average, pH values were higher in the Mekong river system than in the Amazon (7.41±0.65 vs. 6.23±1.05, respectively), suggesting an explanation for the higher average pCO_2 values observed in the Amazon. However, percentage saturation of dissolved oxygen was higher on average in the Mekong basin than in the Amazon (96±23% vs. 65±20%, respectively), which suggests that the balance between productivity and respiration differs between the two river systems on the whole.

These preliminary results suggest that previously published estimates of basin-wide CO_2 outgassing in the Amazon are probably conservative [*Richey et al.,* 2002]. In addition, it appears that different ecological dynamics within the rivers and the surrounding forests, different geological settings, and different land-use regimes may lead to substantially different CO_2 evasion rates for these two large tropical river systems.

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The Role of Air-Water Gas Exchange in the Source Apportionment of Volatile Organic Compounds in Streams

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The National Water-Quality Assessment (NAWQA) Program of the U.S. Geological Survey seeks to understand the sources and processes that determine the concentrations and behavior of contaminants in the natural waters of the United States [*Gilliom et al.*, 1995]. Contaminant groups of interest include volatile organic compounds (VOCs), pesticides, nutrients, trace elements, and major ions. For perennial urban streams, NAWQA results indicate the frequent presence of multiple dissolved VOCs [*Gilliom et al.*, 1995; *Lopes and Price*, 1997]. An adequate understanding, however, does not exist of the identities and relative roles of the typical contaminant sources that lead to the observed VOC concentrations, or of the coupled manners in which physical, chemical, and biological processes in streams act on those contributions to yield observed position- and time-dependent concentrations. The NAWQA Program is interested in the continued development of "source apportionment" (SA) models for use in tracking how multiple VOC sources and sinks can combine to yield a given observed concentration at some stream point (x,y,z,t). Reasons for interest in the relative and absolute contributions of different sources to VOC concentrations include the need to apportion: 1) the origins/responsibility for observed contamination; and 2) the associated human and ecosystem risks posed by various sources.

This study describes the development and testing of a model to predict the time- and position-dependent concentrations of volatile organic compounds (VOCs) in streams as well as the SA of those concentrations. The model estimates the relative contribution of sources and sinks to a given observed VOC concentration. For VOCs, sources include the atmosphere (by absorption), as well as point and non-point inflows of VOC-containing water. Loss processes include volatilization to the atmosphere, degradation, and outflows of VOC-containing water from the stream to local groundwater. This paper presents: 1) the details of StreamVOC, a SA model for VOCs in streams; and 2) comparison of model output with measured concentrations for eight VOCs found in the Aberjona River (Winchester, Massachusetts). Input data for the model were obtained during a synoptic study of the stream system conducted July 11-13, 2001 as part of the NAWQA Program. The input data included a variety of basic stream characteristics (e.g. flows, temperature, and VOC concentrations). The StreamVOC model output agreed moderately well with the measured concentration data for a number of the VOCs, and provided compound-dependent SA estimates as a function of longitudinal distance down the river. For the compounds where the stream was a source of the VOC to the atmosphere, the quality of the agreement between the predicted and observed concentrations could be improved by simple adjustments of the model input parameters. Furthermore, these adjustments were the same for all VOCs in this class, demonstrating the need for careful characterization of the sources when using the StreamVOC model.

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An Application of a Surface Penetration Model to Air-Water Gas Transfer

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Previously, we reported on laboratory results from a wind-wave tunnel comparing transfer velocities of heat and gas measured at a wavy air-water interface using an active infrared technique and two gas tracers, respectively [*Atmane et al.*, 2004]. Surface renewal model formalisms [*Danckwerts*, 1951] indicate that the transfer velocity of heat, k_H, will be related to the transfer velocity of a sparingly soluble non-reactive gas, k_L, by the ratio of their Schmidt numbers raised to the ½ power. However, in our previous data when k_H and k_L were referenced to Sc = 660 using relationships derived from surface renewal, k_H was found to be several times higher than k_L. Potential origins of such a discrepancy such as lateral patch dispersion were not found to be able to account for the observations.

Surface renewal theory relates k_H or k_L to the timescales of renewal events in the thermal or concentration boundary layers, respectively, near the air-water interface. However, there are other conceptual models describing how aqueous-phase turbulence affects heat and gas transfer. For example, in surface penetration theory eddies that impinge upon the air-water interface do not necessarily renew the entire surface layer. In the random eddy modification to the surface penetration framework, k_H or k_L depend on both a timescale for the renewal event and the depth in the boundary layer at which this renewal event occurs [*Harriott*, 1962]. An important consequence of including eddy approach distances into the calculation of the transfer velocity is that heuristic arguments based on diffusive length scales can be used to explain how heat and gas might not scale with diffusivity as predicted by a pure surface renewal model.

Numerical simulations performed by *Atmane et al.* [2004] using the random eddy model of *Harriott* demonstrated that in the general case one would not expect k_H and k_L to scale as the square root of the ratio of their diffusivities. Furthermore, these simulations showed that the scale factors observed in the wind-tunnel data sets could be explained in terms of a surface penetration conceptual framework. These results suggested that both the timescales and depths of surface renewal events are required in order to unambiguously calculate heat and gas transfer rates at air-water interfaces. However, it was not possible to directly test surface penetration models using the wind tunnel data set because measurements of eddy approach distances were not available.

Asher and Pankow [1986] measured k_L for carbon dioxide (CO_2) as a function of aqueous-phase turbulence in a grid-stirred tank. They also measured surface renewal timescales [*Asher and Pankow*, 1991b] and eddy approach distances [*Asher and Pankow*, 1991a] under the same turbulence conditions. Here, we use these data to calculate the air-water flux of carbon dioxide using the random eddy surface penetration model of *Harriott* [1962]. These fluxes are compared to carbon dioxide fluxes measured directly by *Asher and Pankow* [1986] in order to provide further evidence that surface penetration provides a more complete conceptual picture of air-water transfer processes than surface renewal theory.

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Southern Ocean blooms promote atmospheric CO_2 uptake

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Large parts of the Southern Ocean have low primary productivity, often due to lack of sufficient iron. Seasonal algal blooms occur locally, eg. in the wake of islands, in ice-free waters near Antarctica and near frontal systems. Surface iron concentrations in these blooms are relatively high [De Baar et al., 1995; Buccarielli et al., 2001]. Here we will discuss how such algal blooms influence the CO_2 air-sea gradient and CO_2 air-sea exchange relative to waters outside the bloom. The presentation will include results from the Crozet Plateau, the Polar Front at 6°W, and the Weddell Sea.

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Oxygen fluxes and new production between the Northwest European shelf and the open ocean : results from a ship of opportunity

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We present preliminary estimates of oxygen fluxes and new production calculated from continuous, high-frequency and monthly sampled sea surface waters (5m) from a ship of opportunity (SOO) operating between the UK (Portsmouth) and northern Spain (Bilbao). The purpose of this ongoing work is to quantify the air-sea exchanges along the shelf-margin-open sea continuum and the degree to which different hydrographic sections act as atmospheric carbon sinks or sources. Monthly sampling of oxygen, nutrients, chlorophyll, temperature and salinity occurred between February and July 2004 alongside continuous unmanned CTD and chlorophyll fluorescence measurements. The route was subdivided into different hydrographic sections that were analysed separately.

Oxygen was under-saturated with respect to the atmosphere in all sections in winter. Oxygen fluxes calculated from standard parameterisations and averaged across the different sections, varied in magnitude between – 3.6 and 5.2 moles m^{-2} $month^{-1}$. Fluxes were greatest in the Ushant frontal area and lowest in the harbours and the Bay of Biscay. Between April and July all areas were sources except for Portsmouth Harbour. Conversion of these fluxes into seasonal new production using the Redfield ratio yielded estimates of between 115 g C m^{-2} $season^{-1}$ (Ushant) and 29 g C m^{-2} $season^{1}$ (Portsmouth Harbour). This is the first time a ranking has been attempted across a shelf.

Continuous Optode® measurements were added in December 2004 with a view to improving flux estimates and their relationship with contemporaneous measurements of skin temperature, near surface temperature, salinity, chlorophyll a/fluorescence and wind speed. Data from this work will be presented with a view to providing improved detail of the role of the Northwest European oceanic margins to the marine carbon cycle.

How significant are tropical coastal zones in Global trace gas emissions and what role will the Asian Tsunami play?

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Sub tropical coasts are dominated by mangrove ecosystems which cover ~ 75% of the coastline. Other major influences on coastal biogeochemistry in these regions are estuarine inputs. Recent studies indicate that mangroves could be a large source of climatically active gases, including carbon dioxide (CO_2)**,**nitrous oxide (N_2O) and methane CH_4. Waters surrounding mangroves are predominantly heterotrophic whereas the mangrove forests are considered to demonstrate net autotrophy. The balance between these processes will govern the net radiative forcing effect of mangroves and their potential influence on climate. Thus far no studies have taken a holistic approach with integrated studies of trace gas emissions and data from these environments are especially scarce. The global emission of CO_2 from mangrove creeks to the atmosphere has been calculated as ~ 50 10^6 tC year $^{-1}$. Globally oceans behave as a net sink for CO_2 of ~ 2.2 GtC year $^{-1}$, however subtropical and tropical open oceanic waters behave as net source of ~ 0.43 GtC year $^{-1}$ (between 32^0 N and 32^0 S. The calculated additional CO_2 source from mangroves would add 12% to this figure from a surface area of about a thousand times smaller. Moreover this figure probably represents a significant underestimation as the areas influenced by mangrove runoff is unknown and the calculated fluxes are based on few data with an order of magnitude of variation.. It is clear from these observations that on a regional scale mangroves are important vectors in CO_2 cycling and could be globally significant. Our own data have shown N_2O and CH_4 concentrations, in a highly polluted sub tropical Indian estuary (Adyar, Chennai), in excess of 9000 % saturation (530 nmol l^{-1}) and 18964133 % saturation (370708 nmol l^{-1}) respectively which quantitatively represents 1-3 orders of magnitude higher than comparable values found in studied temperate estuaries. These data illustrate that such estuaries could contribute disproportionately large atmospheric N_2O and CH_4 fluxes especially in the context of global estuarine trace gas fluxes. Data are also presented illustrating mangroves as moderate sources of atmospheric N_2O and large sources of CH_4.

The recent Asian Tsunami had a profound impact on the physical hydrology of Indian estuaries and Mangroves. Prior to this natural disaster these estuarine environments were predominantly hyposynchronous with correspondingly low tidal ranges, whereas after the event tidal ranges increased significantly. The relevance of this to observed trace gas emissions, before and after the Tsunami is discussed.

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Shifting constraints on carbon dioxide exchange and carbon cycling in the Arctic: a case study of the Barents Sea

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The Barents Sea marginal ice zone exhibits high, seasonal planktonic productivity and carbon uptake resulting in mixed layer $f\mathrm{CO}_2$ values of down to 135 μatm and a 150 $\mu\mathrm{mol.kg}^{-1}$ reduction in total inorganic carbon from wintertime values. Stoichiometric carbon consumption ratios are far in excess of Redfield and specific alkalinities indicate that the waters are almost totally of North Atlantic origin. The temporal balance between stratification, mixed layer depth and ice cover controls the extent of air-sea carbon dioxide equilibria. The northwards transport of Barents Sea Water into the Arctic Ocean, including the formation of Arctic Intermediate water through cooling and brine formation, is an effective surface to depth carbon pump. We have developed a model to estimate centennial changes in this transient rectification process - the Barents Sea carbon pump - using predictions of ice cover, hydrography and rising atmospheric carbon dioxide and we discuss the implications of changing controls on gas exchange and carbon cycling on the Arctic shelves as a whole.

Measuring Gas Exchange Rates in Upland Streams: Challenges and Solutions

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Upland streams present a different set of challenges than open oceans or lakes for quantifying gas exchange between the water surface and the atmosphere. Peatland streams are typically supersaturated with CO_2 and CH_4, which in specific parts of the drainage system is lost to the atmosphere by evasion. Recent work in the UK [*Billett et al. 2004 ; Hope et al. 2001*] has shown that streams draining peatlands act as important conduits of CO_2 transport to the atmosphere; initial results suggest that the evasion flux may be a significant term in the overall C budget of the catchment. A range of methods exist for estimating vertical gas transfer, although some are more appropriate for lakes rather than streams. The incised nature of many upland stream channels will generally decrease the impact of wind shear on water surfaces; water turbulence being generated primarily by streambed roughness, water gradient and channel flow constriction. A transportable method is required to make rapid measurements under various flow conditions in remote parts of catchments, where vertical emission rates are typically highest.

This paper compares a number of potential methods (floating chamber, propane tracer, mass balance and an indirect approach) for quantifying gas exchange rates of CO_2. The work has been carried out in 2 small contrasting peatland streams (Rough Sike and Cottage Hill Sike) in the Trout Beck catchment in N England. The streams exhibit a wide range in pH (3.8-7.6) and DOC concentrations (3.1-58.2) typical of upland, flashy UK catchments. Comparative measurements were made on 12 separate occasions over a 12-month period, to cover a range of stream flow and temperature conditions. These include both physical (water depth, flow, temperature, wind speed, reach length travel time and area) and chemical (pH, conductivity, dissolved O_2, DOC, DIC, Ca, free CO_2 and CH_4) measurements. On each occasion gaseous evasion was measured by the simultaneous release of a conservative gas (propane) and a soluble (NaCl) tracer over a 20m long study reach. Gas exchange was also measured over a 15-minute period using floating chambers by (1) continuous monitoring of CO_2 build up using an IRGA or (2) sub-sampling the chamber headspace. In addition, a mass balance approach, which makes various assumptions about the consumption/production of CO_2 along the study reach was evaluated, as well as an indirect approach using wind speed to estimate surface boundary layer thickness.

This comparative study shows that under certain stream conditions significant differences exist in instantaneous evasion rates calculated using the 4 different methods. For example, at low/moderate flow the propane tracer and chamber method produce comparable results, although at high flow the former produces much higher values. Overall it is concluded that floating chambers are an appropriate method for evasion flux measurements in remote, high elevation drainage systems, associated with a high degree of natural spatial and temporal variability.

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Diversity of Ecosystems and Coastal Ocean CO2 Fluxes

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Annually integrated air-water CO_2 flux data in 44 coastal environments were compiled and gathered in 8 major ecosystems (inner estuaries, outer estuaries, whole estuarine systems, mangroves, salt-marshes, coral reefs, upwelling systems and open continental shelves), and up-scaled in the first attempt to integrate air-water CO_2 fluxes over the Coastal Ocean, taking into account its geographical and ecological diversity. If estuaries and salt-marshes are not taken into account in the up-scaling, the Coastal Ocean behaves as a sink for atmospheric CO_2 and the uptake of atmospheric CO_2 by the Global Ocean increases by 24%. If estuaries and salt-marshes are taken into account in the up-scaling, the Coastal Ocean behaves as a source for atmospheric CO_2 and the uptake of atmospheric CO_2 from the Global Ocean decreases by 12%. A rigorous up-scaling of air-water CO_2 fluxes in the Coastal Ocean is hampered by the very poorly constrained estimate of the surface area of inner estuaries. However, the present estimates clearly indicate the significance of this biogeochemically highly active region of the biosphere in the global CO_2 cycle.

Variability of the gas transfer velocity of CO_2 in a macrotidal estuary (The Scheldt)

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We report a large data-set of 295 interfacial CO_2 flux measurements obtained in the Scheldt estuary (November 2002 and April 2003), using the floating chamber method. From concomitant measurements of the air-water CO_2 gradient, we computed the gas transfer velocity of CO_2. The gas transfer velocity is well correlated to wind speed and a simple linear regression function gives the most consistent fit to the data. Based on water current measurements, we estimated the contribution of water current induced turbulence to the gas transfer velocity, using the conceptual relationship of O'Connor and Dobbins (1958). This allowed us to construct an empirical relationship to compute the gas transfer velocity of CO_2, that accounts for the contribution of wind and water current. Based on this relationship, the spatial and temporal variability of the gas transfer velocity in the Scheldt estuary was investigated. Water currents contribute significantly to the gas transfer velocity in the Scheldt, but the spatial and temporal variability (from daily to seasonal scales) is mainly related to wind speed variability.

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Model estimates of air-sea gas exchange under non-stationary high wind conditions

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High winds create explicit non-stationarity in near-surface air and water layers. The numerical non-stationary upper ocean model [*D'Alessio et al., 1998*] is modified by air gas constituents transfer equations included. The modified model is used to simulate transfer processes in cases, when wind velocity increases for several hours from the mean climatic one to a given higher value being in the range circa 10-25 m/s. Source functions, describing gas exchange between bubble population and water environment at high winds, are calculated and included in the gas transfer equations [*Bortkovski, 2002; Bortkovski, 2003*]. The gas transfer by bubbles, generated by breaking wind waves, is considered along with the diffusive transfer through the air-sea interface. The sum of them is treated as the total gas flux.

The instant fluxes of air gas components under high wind conditions are calculated for given wind speed values using the modified model. Influence of the seawater carbonate system on the carbon dioxide transfer at non-stationary conditions is evaluated. Changes of dissolved gases sub-surface concentrations caused by wind speed increase are taken into account. It is found that these wind dependent changes visibly influence on air-sea gas exchange.

Total gas flux dependencies on wind speed for several key ocean locations are obtained. These dependencies are not universal, because the significant part of total gas transfers is conditioned by the upper ocean layer structure, which varies from place to place. Mean gas fluxes are estimated using wind speed probability distributions in the locations discussed. The high wind contribution in mean air-sea gas exchange is estimated. It is found that the contribution is significant for mean CO_2 exchange, and determines the oxygen exchange almost completely.

The obtained estimates of mean fluxes are compared with fluxes calculated by well-known routine procedures. The significant differences are found and explained. The necessity in mean gas exchange calculations to take into account the revealed dependence on wind speed of air-water gas concentration difference is shown.

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Seasonal variability of ocean CO_2 partial pressure and air-sea CO_2 fluxes in the subantarctic zone of the Southern Ocean

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Six CARIOCA lagrangian drifters were deployed in the Subantarctic Zone of the Indian and Pacific Ocean successively in January 2002 and 2003 and in March-April 2004 during the SAGE experiment south of New-Zealand. Hourly ocean CO_2 partial pressure, pCO_2, sea surface temperature, SST, salinity, SSS, fluorescence, surface wind speed, atmospheric pressure and air temperature were recorded during 36 months. Continuous time series of measurements made during all seasons indicate that pCO_2 in sea water is undersaturated with respect to the atmospheric value and consequently the subantartic province of the Southern Ocean acts as a sink for atmospheric CO_2.

A large part of the pCO_2 variability appears at short (day to week) time scale. We analyze the origin of this variability in each biogeochemical province (as defined by [*Longhurst*, 1998]) visited by the buoys, by looking at the measured physical and biological parameters, SST, SSS and fluorescence. The variations of the total carbon content, Ct, are derived from pCO_2 and alkalinity estimated from SSS measurements. Analysis of Ct variations compared to SST-SSS diagrams allows discriminating between variations of pCO2 related to mixing of different water masses and those related to local warming. Satellite measurements of SST and ocean color are used to interpret the observed time and space variability displayed in the Carioca measurements. We will focus on the analysis of the 2 buoys deployed in March April 2004. They are presently drifting in the Pacific sector of the Southern Ocean.

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Seasonal and interannual air-sea CO2 exchange between Tasmania and Antarctica: a high variability

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To reach a more realistic global carbon budget estimate, it is essential to have a better understanding of the seasonal and interannual variations of the oceanic carbon cycle in the Southern Ocean. In this area, the lack of long-term monitoring in situ data leads to large carbon budget uncertainties. Furthermore recent models indicate that the Southern Ocean would be very sensitive to climate change. Since 2002, the distribution of carbon dioxide partial pressure (pCO2) in surface seawater is measured between Hobart (43°S, Tasmania, Australia) and Dumont D'Urville (67°S, Adelie Land, Antarctica) during 8 cruises onboard the S.S. *L'Astrolabe* (MINERVE program) and 1 cruise onboard the R.V. *Marion-Dufresne* (OISO program) in the frame of the long-term observational CARAUS/INSU/IPSL project. Hydrological and biogeochemical parameters (TA, TCO2, nutrients, carbon 13, Chlorophyll, ….) were collected complementary to the pCO2 data.

Data of the carbon dioxide system in the ocean collected in 2002-2004 are used together with those obtained in previous cruises in 1996-1997 in the same area; in mid-summer they present large and contrasting interannual changes in the different zones. In the open zone of the ocean (53°-61°S), we observed a decrease in pCO2 between February 1997 and 2003 mainly governs by the enhancement of the biological activity which could have been favoured by changes in solar radiation, ocean stratification, clouds cover, phytoplankton species and distribution… This interannual decrease, around 70 ppm, is as large as seasonal variation of pCO2. In 2002-2003 the oceanic pCO2 displays a surprisingly high seasonal variability: the open ocean zone is a larger CO2 sink in February than in October. These spatio-temporal variabilities of sources and sinks of CO2 will be presented, and the oceanic and atmospheric forcings associated will be discussed.

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Direct measurement of pH profiles in seawater surface microlayer: ramification to air-sea CO_2 exchange

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We report the first direct measurement of pH profiles in seawater surface microlayer (upper 1 mm) at a depth resolution of 10 μm using pH microelectrodes (tip dia. 5 μm). In offshore seawater, where pCO_2 is lower than lab air, pH increases downward over the microlyer while in coastal seawater, where pCO_2 is high than lab air, pH decreases over the microlyer. The thickness of the microlayer thus determined at laboratory condition is about 100 micrometer and is consistent with other indirect methods.

Calculated CO_2 profiles from this work are non-linear and have a much sharper gradient near the surface. This conclusion contradicts to the linear assumption in the traditional gas exchange model, i.e., the stagnant layer model. Therefore, we suggest that current calculation of air-sea CO_2 fluxes based on CO_2 differences across the air-sea interface may underestimate true CO_2 fluxes.

A diffusion-reaction numerical model is used to interpret the micro-pH profiles. The model involves major acid-base reactions in seawater and the CO_2 hydration reaction. Although the model results simulate well major features of the measured pH profiles, there are consideration differences between them. A significant change in CO_2 diffusion coefficients must be assumed within the surface 60 μm to explain these differences. Several possibilities are explored with the model.

Evidence for an important role of surface water layer processes on air-water gas transfer in the Subtropical Atlantic Ocean.

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Surface water layer characteristics are increasingly recognized as key determinants of air-sea exchanges of materials, such as CO_2 exchange. The CO_2 flux between water and atmosphere is inferred from the pCO_2 air-water gradient, and a gas transfer velocity (k), typically parameterized as a function of wind speed. The lack of a unique relationship between transfer velocity and wind speed suggests that processes other than wind also contribute significantly to regulate gas exchange. A comparison of organic carbon concentrations and CO_2 partial pressure at 5 m depth with those within the top 2 cm of the surface layer of the NE Subtropical Atlantic Ocean provides evidence that (1) organic carbon becomes enriched in the top 2cm layer of the sea surface, with a decline in the gas transfer velocity, standardized for wind conditions, with increasing organic carbon concentrations, and (2) the CO_2 partial pressure is also higher within the top 2cm layer of the sea surface than at 3-5m depth, suggesting an underestimation of the pCO_2 by programs deriving this from water pumped from several meters of depth.

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Model study of the interannual variability of CO_2 air-sea fluxes

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Studying the interannual variability of the air-sea CO_2 fluxes is useful in determining the ocean role in the CO_2 cycle. Such studies also help in assessing Ocean Carbon Cycle Model (OCCM) ability to reproduce transient states. Our work takes place into the frame of the Northern Ocean Exchanges Study (NOCES) project. This project aims at assessing the interannual to decadal variability of the air-sea CO_2 fluxes. Our model is a 3-D Ocean Global Circulation Model (OGCM) coupled to a 3-D OCCM. It is forced by daily atmospheric data from the NCEP reanalysis over the 1948-2002 period. We present a preliminary study of the CO_2 fluxes at the interannual and decadal timescales. The respective roles of physical (temperature, circulation ...) and biological (export production ...) processes are also examined.

Wave Effect on the Gas Transfer at Water Surfaces

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The gas transfer at the water surface is more complicated than the bulk aerodynamic relation for the heat and momentum transfer. For chemical compounds with reaction time scales longer than the surface layer turbulence time scales, the constant flux layer assumption may be invoked. The flux of the gaseous compound (c) is characterized by a deposition velocity, v_d, which is the inverse of the resistances,

$$v_d = < w'c' > /(c - c_s) = 1/(r_a + r_b), \qquad (1)$$

where r_a is the aerodynamic resistance governing turbulent transport of species c; and r_b is the surface resistance, governing the diffusion transport over the laminar sublayer (Geernaert, 1999). Both r_a and r_b depend on the surface roughness length z_0.

Usually, the roughness length z_0 is determined regardless of the ocean waves. To investigate the wave effect on the resistances r_a and r_b, Wavewatch-III implemented to the South China Sea (Chu et al., 2004) is used. The Charnock constant for determining z_0 depends on the significant wave height. The model is integrated with twice daily NCEP reanalyzed winds for the whole year of 2002. Large difference is found in r_a and r_b, which indicates the role of ocean waves on the gas transfer at water surfaces.

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Seasonal variations of VHOC concentrations and fluxes at the ocean -atmosphere interface in a coastal area of the Western English Channel.

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Coastal zones are characterized by high primary productivity and constitute significant sources and sinks of numerous compounds that can influence atmospheric chemistry. Among these compounds, the volatile halogenated organic compounds with both anthropogenic and natural sources are globally emitted by the ocean and are known to influence the atmospheric ozone chemistry. Production of biogenic VHOC by macroalgae has been reported in numerous studies but the seasonal variations of production and fluxes at the ocean - atmosphere interface have been poorly studied. The Western English Channel has one of the most important macroalgal beds in the world ocean and is therefore a key area to study the production and fluxes of the biogenic VHOC by macroalgae.

Seasonal variations of different volatile halogenated organic compounds (iodinated : CH_3I, brominated : $CHBr_3$, $CHBr_2Cl$ and chlorinated : $CHCl_3$) are presented. Measurements have been realized simultaneously in surface water and air at a minimum monthly interval (sampling frequency was increased during periods of important variations in concentrations). Concentrations of VHOC in water and air showed important seasonal variations. The maximums concentrations were observed during spring and summer when the development of the macroalgae was maximal. Minimums concentrations were observed during winter. Concentrations ranged for water between 19.3 and 180.8, 1.2 and 6.8, 1.0 and 6.3, 1.3 and 6.2 $ng.l^{-1}$ for air between 1.8 and 112.5, 18.2 and 102.6, 0 and 11.3, 21.3 and 259.1 pptv respectively for CH_3I, $CHBr_3$, $CHBr_2Cl$ and $CHCl_3$.

VHOC fluxes at the ocean – atmosphere interface have been calculated following the relations of Liss and Merlivat (1986) and Nightingale *et al.* (2000). VHOC fluxes showed as for concentrations important seasonal variations. The Western English Channel coastal zone was a source of CH_3I, $CHBr_3$, $CHBr_2Cl$ for the atmosphere during the major part of the year but was a sink for $CHCl_3$. Finally, a budget of the annual fluxes of these four VHOC taking into account the important seasonal variations is presented.

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Interannual variability of the carbon dioxide system and air-sea CO_2 fluxes in the high latitudes of the North Atlantic Ocean: 1993-2003 (SURATLANT Program)

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The North Atlantic Ocean, north of 50°N, is believed to act as a strong ocean sink for atmospheric carbon dioxide, about -0.3 to –0.4 PgC/yr on average [*Takahashi et al.*, 2002]. In this region it is expected that air-sea CO_2 flux is varying, possibly modulated by large-scale climatic event such as North Atlantic Oscillation (NAO), through thermodynamics, ocean circulation, wind speed and/or biological processes. The evaluation of both interannual variations, decadal trends and rapid (or slow) changes of air-sea CO_2 flux requires repeated in-situ observations at different years and at different seasons as it has been well documented that the ocean carbon cycle experienced strong seasonality in high latitudes of the North Atlantic Ocean. In this study we analyze the variations of sea surface dissolved inorganic carbon (DIC) and total alkalinity (TA) observed along the same track, between Island and the Newfoundland (SURATLANT Program) over the period 1993-2003. We use these ocean properties to evaluate the sea surface ocean fugacity ($f CO_2$) as well as satellite wind-speeds observations to compute the associated air-sea CO_2 fluxes. The analysis is focus on the open ocean region, 53°N-62°N/45°W-20°W. The DIC and TA concentrations appear relatively stable over ten years indicating a complex balance between primary production, vertical mixing and anthropogenic CO_2 increase. On the other hand, we found that seasurface $f CO_2$ has regularly increased from 1993 to 2003, a signal clearly controlled by the warming of sea surface waters, up to 2°C over 10 years. In addition, the oceanic $f CO_2$ increase appears faster than in the atmosphere, resulting in a decrease of the oceanic carbon uptake. As an extreme case, we observed that region was a CO_2 source during all seasons in 2003.

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Carbon dioxide production and oxygen depletion in the upper reach of the Pearl River estuary during a very drought winter

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We examined partial pressure of carbon dioxide ($p\mathrm{CO}_2$), dissolved oxygen (DO), carbonate system and nutrients in the upper reach of the Pearl River estuary during a very drought season in February of 2004. We observed very low DO, down to <0.4-1 mg L^{-1} in the surface water, upstream of the vicinity of the Humen outlet, one of the major water channels into the estuary. The oxygen depleted water body encompasses a surface area of >20 km^2 within a salinity range between 1 and ~5. Accompanied with the low DO were extremely high $p\mathrm{CO}_2$ (up to > 7000 µatm) and nutrients (ammonia > 600 µmol kg^{-1} and nitrate > 200 µmol kg^{-1}). In addition to the aerobic respiration, processes such as nitrification may have substantially contributed to the high $p\mathrm{CO}_2$ (> 7000 µatm) in the water body with a salinity range of 1-4. Denitrification appears closely coupled with nitrification, both of which hold significant impact on the distribution pattern of carbonate system parameters including pH and $p\mathrm{CO}_2$. Oxygen depletion was also observed in this area during our prior cruises in other seasons, signifying an alarming environmental condition in the region. Additional data are being collected from an on-going cruise under similar hydrological condition in order to further evaluate the contributions of nitrification to the production of CO_2.

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Sea surface pCO$_2$ and diurnal mixed-layer dynamics

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Diurnal warm layers are as regular as the rising sun in many ocean regions, particularly those regions where winds are insufficient to vertically mix the accumulated heat. This widespread and infinitely repeating process has a number of important consequences for sea surface $p\text{CO}_2$ and air-sea fluxes. Surface heating alters CO$_2$ fluxes by increasing the $p\text{CO}_2$ at the surface [McNeil and Merlivat, 1996; Ward et al., 2004]. Nocturnal breakdown of the warm layer leads to a strong increase in convective velocities that subsequently increase gas fluxes [McGillis et al., 2004]. Isolation of the warm layer can deplete or accumulate CO$_2$ at the surface and change the sea surface $p\text{CO}_2$ within a short time frame [DeGrandpre et al., 2004]. The mixed-layer also determines the volume over which the loss or gain of CO$_2$ through the air-sea interface is distributed. Prediction of the evolution of sea surface $p\text{CO}_2$ at a given saturation level is therefore strongly dependent upon mixed-layer depth. In this presentation, we focus on depletion of CO$_2$ in the isolated warm layer and the importance of the diurnal mixed layer in ocean CO$_2$ models. We use a mixed-layer model to show that the diurnal air-sea loss of inorganic carbon in eastern equatorial Pacific water reduces the sea surface $p\text{CO}_2$ by 1-2 μatm [DeGrandpre et al., 2004]. The importance of including the diurnal mixed-layer depth in models is evaluated by comparison of model results using mixed-layer depths in the equatorial Pacific Ocean and the Labrador Sea.

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CO_2 variability in the Guadalquivir Estuary (SW Iberian Peninsula).

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To investigate the air-water CO_2 transfer in the Guadalquivir estuary (SW of Iberian Peninsula), it has been done some sampling of the gas gradient in the estuary in summer of 2002 and 2003. It was continuously registered the concentration of the CO_2 on the water and air using an underway CO_2 system as the one designed by Koertzinger et al. (1996). In order to study the tidal variation there were selected 2 sites for 13 hours sampling each one as well as some transect along the estuary.

The values of the alkalinity in the Guadalquivir estuary are extraordinary high reaching values up to 8mM upstream of the estuary. The pCO_2 in the surface water is oversaturated respect to the atmospheric value in all the sampling. The pCO_2 decreased with the salinity until 30-40% in most of the marine station in comparison with the most fluvial ones. The higher value of the flux account was 550 $mmol \cdot m^{-2} \cdot d^{-1}$.

In spite of the substantial uncertainty in the flux computation relationship in estuaries, the role of this system is clearly a source of CO_2 to the atmosphere as well as a source of carbon to the coastal adjacent waters.

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Carbon dioxide dynamics in Antarctic pack ice and related air-ice CO_2 fluxes

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There is increasing evidence that sea ice can exchange directly CO_2 with the atmosphere. These exchanges are driven by the evolution of the partial pressure of CO_2 (pCO_2) within sea ice and controlled by its permeability. Both these CO_2 fluctuations and permeability are linked to peculiar physical and biogeochemical processes such as sea ice temperature and texture, biological activity or precipitation of calcium carbonate minerals ($CaCO_3$). Among them, sea ice temperature was suggested as one of the main physical control of the pCO_2 dynamics and CO_2 transfer. Highest oversaturation of CO_2 (pCO_2 up to 915 ppmV) were encountered in coldest ice and result from winter processes (increased brine salinities, calcium carbonate precipitation, bacterial remineralization). However cold ice is generally not permeable either to gas or water transfer. As the temperature crosses the threshold of about -5°C, sea ice become permeable to gas, and sea ice begins to release CO_2 to the atmosphere (up to 1.9 $mmol.m^{-2}.d^{-1}$). However, at the same time brine convection develops bottom-up in the sea ice cover and by fuelling microalgae primary production in nutrients, triggers strong undersaturation of CO_2 (pCO_2 down to 30 ppmV). Sea ice therefore turns into a CO_2 sink with CO_2 fluxes ranging from 0 to -6 $mmol.m^{-2}.d^{-1}$ depending, among other parameters, on the ice texture. On the whole, spring and summer Antarctic pack ice appears to act as a CO_2 sink which magnitude could be of significant importance in the budgets of air-sea CO_2 fluxes over the Southern Ocean.

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A coupled boundary layer mixing length model for gas transfer at the air-water interface

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Heat and mass fluxes across the air-water interface are generally limited by the resistance to transfer in the thin viscous sub-layers adjacent to the interface. On the other hand most measurements of the temperature or concentrations of the substance being transferred are made well away from the interface – so called “bulk” measurements. The mass transfer rates are usually parameterized in terms of these bulk measurements, so that effective gas transfer models must extend away from the interface in both directions and necessarily be coupled. This paper describes a model of this type based on mixing length theory. It is asymptotic to standard Monin-Obukhov boundary layer models in the fully turbulent atmospheric boundary layer, but the breaking of surface waves of various lengths alters the usual M-O boundary layer structure beneath the interface and explains the sensitivity of transfer rates of various slightly soluble gases to wind speed. Comparisons with laboratory measurements of wind, waves and mass transfer rates are used to test the model.

Measurements of humidity flux in Hurricanes Fabian and Isabel

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In order for present dynamical models to produce realistic hurricanes, they require constaints on the momentum and latent heat fluxes at high winds. As these constraints require a fundamental change in the fluxes from their known behaviour at lower winds (<< 20m/s), the measurement of these fluxes is a primary goal of the CBLAST-hurricane program. For the past 30 years, NOAA-AOC Orion WD-P3 aircraft have played a key role in hurricane research. As part of CBLAST, the turbulent gust probe system installed in the P3 nose as part of TOGA-COARE (1990) was operated, in addition to the NOAA/FRD BAT probe system, to obtain turbulent momentum flux. A fast response humidity package, incorporating a LICOR-7500, was added to obtain latent heat flux. Here we present these measurements of latent heat flux in hurricanes from the 2003 field season.

The Labrador Sea Gas Exchange Study during a Phytoplankton Bloom

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The Labrador Sea can be a significantly high atmospheric CO_2 sink and is one of the areas of North Atlantic Deep Water (NADW) formation. During spring 2004, the Labrador Sea experienced a strong plankton bloom, and is a large sink for atmospheric CO_2. Deep convection during the subsequent winter mixes the CO_2 rich waters throughout the water column. The newly formed NADW is then transported southward towards the Antarctic, with a circulation time scale of approximately 1000 years. Consequently, the air-sea CO_2 exchange characteristics in the Labrador Sea are particularly important because it is one of the few areas of the global ocean that is a long term CO_2 sink. In this presentation, the study will be described which included measured air-sea CO_2 fluxes and the surface physical processes controlling them during the Labrador Sea spring bloom. The experiment was conducted from the air-sea interaction spar (ASIS) buoy. The buoy was instrumented to measure eddy correlation air-sea CO_2 fluxes, CO_2 profiles in the atmospheric boundary layer and water column, along with supporting variables: wind speed, wind stress, atmospheric stability, surface waves, upper ocean turbulence and mixing. Additional instruments deployed on the mooring line to 35-m measured key parameters such as CTD, PAR, DO, fluorescence, particulate organic carbon which governing mixed layer CO_2 dynamics. This activity, part of the International SOLAS program will provide a measure of the variability of air-sea CO_2 fluxes with physical and biological processes.

An Air-Sea Gas Exchange Buoy in the Labrador Sea

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The Labrador Sea is highly significant as one of the areas of North AtlanticDeep Water (NADW) formation. During spring, the Labrador Sea experiences a strong plankton bloom, and is a large sink for CO_2. Deep convection during the subsequent winter mixes the CO_2 rich waters throughout the water column. The newly formed NADW is then transported southward towards the Antarctic, with a circulation time scale of O(1000) years. Consequently the air-sea CO_2 exchange characteristics in the Labrador Sea are of particular interest because it is one of the few areas of the global ocean that is a long term CO_2 sink..

We describe here an experiment which measured the air-sea flux of carbon dioxide and the surface physical processes controlling it during the Labrador Sea spring bloom. The experiment was conducted from an air-sea interaction spar (ASIS) buoy. The buoy was instrumented to measure eddy correlation air-sea CO_2 fluxes, CO_2 profiles in the atmospheric boundary layer and water column, along with supporting variables: wind speed, wind stress, atmospheric stability, surface waves, upper ocean turbulence mixing . Additional instruments deployed on the mooring line to 35m measured key (e.g. CTD, PAR, DO, fluorescence, particulate organic carbon) governing mixed layer CO_2 dynamics. This activity, part of US SOLAS ("Surface Ocean-Lower Atmosphere Study"), will provide a measure of the variability of air-sea CO_2 fluxes with physical and biological processes.

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Biogeochemical 1D ERSEM ecosystem model applied to recent carbon dioxide and nutrient data in the North Sea

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The European Regional Seas Ecosystem Model (ERSEM) coupled to the Princeton Ocean Model (POM) one-dimensional physical model was applied to the first results of the pluridisciplinary data set acquired in the North Sea during four cruises carried out from 2000 to 2001. We introduced a CO_2 submodel in ERSEM and we focused on simulations at a station in the southern North Sea. A basic validation of the simulations is presented which indicates that results are in a good agreement with the field measurements. The model reproduces the vertical structure and the temporal variations of biogeochemical variables, both qualitatively and quantitatively. An inorganic carbon limitation function of phytoplankton growth was also implemented in the model to investigate potential changes of ecosystem structure with predicted future increases of atmospheric CO_2 levels. A sensitivity analysis was carried out suggests that diatoms and large phytoplankton are more sensitive than flagellates and picophytoplankton to predicted future increases of atmospheric CO_2 levels.

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Experiments Investigating Gas Transfer and Momentum Flux across Air-Water Interfaces

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Improved understanding of the physical mechanisms that control air-sea gas transfer will ultimately lead to more accurate models of climate change and global warming. The presence of surfactants on the sea surface influences the free surface behaviour, propagation characteristics of waves and alters the near-surface turbulent length and velocity scales. These effects are thought to inhibit surface renewal and therefore reduce the rate of air-water gas and heat transfer [*Saylor et al. 2000*]. A number of laboratory experiments in wind-wave tanks have shown that the presence of a surfactant results in significant reductions in the air-water gas transfer rate [e.g. *Zappa et al. 2001*].

In this study, we completed a series of experiments in a wind-wave flume at the University of Washington, Seattle. Measurements were made at wind speeds from 4 to 10 m/s with clean and surfactant contaminated water. Digital Particle Image Velocimetry (DPIV) was used to measure the two dimensional turbulent velocity fields beneath the air-water interface. Bulk gas transfer velocities were measured during these experiments for two gases, He and SF_6.

The wind waves were damped in the presence of a surfactant as expected. The DPIV data was used to study the characteristics of the wind drift layer and near-surface turbulence. The mean velocity profiles were observed to be logarithmic and this facilitated accurate calculation of the water-side friction velocities and roughness heights. The ratio of the energy dissipation rate in surfactant contaminated water, to that in clean water decreased from 1.0 to 0.70 as the wind speed increased from 4 to 10 m/s. At low wind speeds a large percentage (60-90%) of the total vertical momentum flux was transferred through the wind drift current and the near-surface turbulence was generated primarily via shear production. At wind speeds greater than 7 m/s a much smaller percentage of the vertical momentum flux was transferred via the wind drift current (i.e. ~20% in clean water and ~35% in the presence of a surfactant) and the production of near-surface turbulence was dominated by microscale wave breaking. Measured bulk gas transfer rates were significantly lower across surfactant contaminated water surfaces compared to clean surfaces at the same wind speed.

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Seasonal Variations in the Concentrations of Three Greenhouse Gases (CH_4, CO_2 and N_2O) in a Shallow Coastal Area Affected by Inputs of Organic Matter and Nutrients

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The concentrations of three greenhouse gases, methane (CH_4), carbon dioxide (CO_2) and nitrous oxide (N_2O), were measured in the surface waters of Rio San Pedro (Bay of Cádiz, NW Spain), in order to characterised the dynamics of these biogases within the system. The study was carried out in a shallow inlet characterised by semidiurnal mesotides which is affected by inputs of large amounts of organic carbon and nutrients coming from the discharges of three aquaculture plants. The study covered all four seasons during 2004, and different tidal conditions.

The concentrations of these gases in samples were determined using a gas chromatograph (Varian 3600) equipped with a flame ionisation detector (FID) for CH_4 and CO_2, and an electron capture detector (ECD) for N2O. Gases were extracted from the water sample using a head space method.

The concentrations of dissolved CH_4, CO_2 and N_2O varied between 11-88 nM, 36-108 mM and 14-50 nM, respectively, showing a great seasonal variability. Surface waters were in all cases oversaturated with respect to the atmosphere, reaching values above 4500 % for CH_4, 1000% for CO2, and 800 % for N_2O. In general, maximum saturation values were found during the summer. Results also showed a variation with respect to tidal conditions, with higher values during low tide, which points out the importance of diagenetic processes in the production of these biogases. Quantification of air-sea fluxes showed mean values of around 50 mmol m-2 d-1 for CH_4, 85 mmol m-2 d-1 for CO_2 and 35 mmol m-2 d-1 for N_2O, indicating that this system is a net source of these gases to the atmosphere.

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Air-sea gas transfer velocity estimates from the Jason-1 and TOPEX altimeters - prospects for a long-term global time series.

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Estimation of global and regional air-sea fluxes of climatically important gases is a key goal of current climate research programs. Gas transfer velocities needed to compute these fluxes can be estimated by combining altimeter-derived mean square slope with an empirical relation between transfer velocity and mean square slope derived from field measurements of gas fluxes and small-scale wave spectra [*Frew et al.*, 2004]. We previously reported initial results from a dual-frequency (Ku and C band) altimeter algorithm [*Glover et al.*, 2002] for estimating the air-sea gas transfer velocity (k) from the mean square slope of short wind waves (40-100 rad/m) and derived a six-year time series of global transfer velocities based on TOPEX observations. Since the launch of the follow-on altimeter Jason-1 in December 2001 and commencement of the TOPEX/Jason-1 Tandem Mission, we have extended this time series, with improvements to the model parameters used in algorithm and using the latest corrected data releases. The prospect of deriving multi-year and interdecadal time series of gas transfer velocity from TOPEX, Jason-1, and follow-on altimeter missions depends on precise intercalibration of the normalized backscatter. During the Tandem Mission collinear phase, both satellites followed identical orbits with a mere 73-second time separation. The resulting collocated, near-coincident normalized radar backscatter (σ_0) data from both altimeters present a unique opportunity to intercalibrate the two instruments, compare derived fields of transfer velocity, and estimate the precision of the algorithm. Initial results suggest that the monthly gas transfer velocity maps generated from the two altimeters are very similar. Comparison of along-track Ku-band and C-band σ_0 during the collinear phase indicates that observed discrepancies are due primarily to small offsets between TOPEX and Jason-1 σ_0. The adjusted Jason-1 σ_0(Ku) and σ_0(C) values yield an average global transfer velocity difference of about + 0.7 cm h^{-1} relative to TOPEX, while the precision estimated from the two observation sets is 5-10% and scales with k.

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Time Series of pCO_2 in the Central California Upwelling System: 1993-2004

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Temporal and spatial variability has made it difficult to characterize the magnitude and trends of air-sea carbon fluxes in coastal upwelling systems. Significant variability of sea surface pCO_2 can be observed on time scales ranging from hours to years and spatial scales as short as one kilometer. Time series results will be presented from a hydrographic line that is perpendicular to the California coast at 36° 48' N. CO_2 measurements have been made along the inner 60 km this line at least monthly from 1993 to the present. These measurements have been complemented by seasonal cruises extending out to 400 km and occasional regional surveys. Results from these transects indicate that most of the variability in sea surface pCO_2 is confined to the inner 100 km. Additional data have been provided from several moorings that have the ability to make hourly measurements of the air-sea difference of pCO_2. One mooring located near the mean center of an upwelling plume has generated continuous pCO_2 data since 1997 with only minor interruptions.

Coastal upwelling is usually most intense in the spring and early summer, leading to extreme variability of sea surface pCO_2. Periods of highest sea surface pCO_2 tend to coincide with the strongest winds during this season leading to large sea to air CO_2 fluxes. These events are frequently followed by relaxations when biological carbon uptake of carbon exceeds the physical supply, thus reversing the flux. Late summer and fall are times of low to moderate upwelling and the mean sea surface pCO_2 tends to be below atmospheric values. In the winter sea surface pCO_2 is frequently close to atmospheric values, however wintertime upwelling events can generate long lasting elevated pCO_2 levels since biological uptake rates are suppressed during this season. On average the yearly sea to air CO_2 flux is on the order of 0.5 M m^{-2}, but the range is from less than –1 M m^{-2} during the 1997 El Niño year to almost 2 M m^{-2} in 1999.

A Laboratory Investigation of the Effect of Rain on CO_2 Gas Exchange

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A preliminary gas-transfer experiment of CO2 invasion from the air into the water body in the presence of rain was carried out using a small water tank (75 cm × 60 cm × 30 cm) placed within a closed Plexiglas chamber of dimensions 100 cm × 70 cm × 130 cm (length × width × height). The tank was filled with fresh water free of surface contamination. Circulation within the chamber and the tank were provided by a small rotary fan and stirrer, respectively. Artificial rain was generated with the help of 160 hypodermic needles that were fixed in a 3 cm triangular grid pattern to a 60 cm × 40 cm plastic tub that was mounted on top of the chamber (i.e., 100-120 cm above the water surface). The rain covered about 32 % of the water surface. At the beginning of each experiment, pure CO_2 was injected into the air volume of the Plexiglas chamber, thus resulting in an initial CO_2 concentration of about 6300 ppm (vol). The partial pressure of CO_2 in the air of the chamber was inferred from CO2 concentration measurements performed using an infrared CO_2 sensor; pH was measured in the water tank from which we derived the relative partial pressures of CO_2 .

Each experiment was carried out in five 60 minute-long consecutive phases: during the first phase, the water body (including the surface) was at rest without any water movement or turbulence present. During the second phase, turbulence in the bulk water was produced by the small mixer so as to mimic wind-induced small-scale turbulence near the surface. During the third phase, rain was generated with a rain rate of 190 mm/h, and during the fourth phase, the rain rate was increased to 280 mm/h, and was turned off during the final phase. During the second lightly stirred phase, the CO_2 levels decreased and increased slightly in the air and water, respectively. In the third rain phase, CO_2 levels decreased and increased substantially in the air and water, respectively. The higher rain rate during the following phase caused a slight decrease and increase of CO_2 in the air and water, respectively. During the last phase, the CO_2 levels remained constant.

The CO_2 transfer velocity for the lightly stirred phase was calculated to be 4.2 cm/h, for the rain phase a value of 28 cm/h was obtained. Our results provide clear evidence that the invasion of CO_2 into water is strongly dependent on the local rain rate and the resulting turbulence in the surface layer. It remains to be seen, through further experiments, whether this holds true for lower, more natural levels of CO_2 in the air and more natural-type rain (realistic raindrop diameters, terminal velocities, and rain rates).

Gas Transfer Velocity as a critical variable in coastal ecosystem metabolism studies

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Net ecosystem production (NEP) estimates were performed in the mixed-layer of the Randers Fjord (Denmark) during two field cruises in April and August 2001 and using two different approaches: (1) dissolved inorganic carbon (DIC) budgets based on the apparent zero end-member (AZE) method and (2) the Response Surface Difference (RSD) based on diel oxygen (O_2) technique. In order to estimate the variation of either DIC or O_2 due to biological processes (gross primary production and community respiration), an assessment of the transfer of CO_2 or O_2 across the air-water interface is critical. These fluxes depend on the air-water gradient, the solubility coefficient and the transfer velocity of the considered gas. While the two first variables can be easily constrained, estimating the gas transfer velocity, which depends on the surface water turbulence, is more problematic and has been, most of the time, parametrized as a function of wind speed. Although this relationship has been shown to be site-specific in estuaries, a generic formulation is often used in open-system methods to estimate NEP. In this study, we computed NEP values using the two approaches cited above and several gas transfer velocity parameterizations among which one was estimated in this estuary during the two cruises based on the floating dome technique. Gas fluxes and consequent NEP results were strongly affected by the choice of the parameterizations, such as antagonist conclusions on the metabolic status (autotrophic or heterotrophic) of the mixed-layer of this fjord. Moreover, we show that the formulation based on the floating dome technique is the only one to provide similar NEP rates using the AZE and RSD approaches. This illustrates that the evaluation of the gas transfer velocity is critical in ecosystem metabolic studies based on open-system methods.

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Influence of oceanic biota on carbon dioxide flux at atmosphere-ocean interface

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In this study, starting with model of Nefedova and Tarko [1995], we investigate the carbon cycle dynamics using mathematical modelling. In our model [Glushkov *et al.*, 2003], the CO_2 global turnover of the ocean (its surface is ice-free) is divided into 28 latitudinal belts with 5° width. The typical vertical ocean stratification includes: a) the upper quasi-uniform (or mixed) layer (UQL), b) the layer of temperature's sudden change (seasonal thermocline), c) the main thermocline, and d) the deep-sea layer (DL). It is supposed that the water between 40 S and 40 N goes slowly up and at the high latitudes goes slowly down; the water movement is from equator to pole in the UQL and has reverse direction in the DL. The vertically uniform atmosphere is divided into same zones as the ocean. The model variables are the molar concentration of non-organic carbon in each ocean block and carbon content as CO_2 in each atmospheric zone. The model time step is one month.

The seasonal dynamics of global carbon cycle is described with system of 112 non-linear common differential equations. The model considers the activity of ocean biota as both the rate of organic substance production in the UQL and the rate of organic substance decay in the UQL, thermocline, and DL. The system of equations is numerically integrated using the four-order Runge-Kutta method with prescribed initial conditions.

Our main results are follows. First, the maximal partial pressure of carbon dioxide dissolved in the UQL is registered at equator whereas the minimal values of this variable are observed at the polar ocean, where, moreover, the strongly pronounced annual variations occur. Other essential distinction of polar ocean consists in the largest differences between the results obtained with and without taking into account the oceanic biota. Next, the tropical ocean is the source of CO_2 for the atmosphere whereas in the polar regions the carbon dioxide flows from the atmosphere into the ocean. At that, owing to the oceanic the carbon dioxide exchange at the atmosphere-ocean interface increase somewhat towards the flux from the atmosphere. Finally, our model estimation of the adaptation time on the human economic activities for global climate system show that if the ocean biota is taken into account, this time may be significantly decreased.

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Seasonal and interannual variability of sea-surface carbon dioxide species at the ESTOC site between 1996 and 2004

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Seasonal patterns in hydrography, partial pressure of CO_2, fCO_2, pH_t, A_T, C_T, nutrients and chlorophyll a were measured in surface waters on monthly cruises at the European Station for Time Series in the Ocean at the Canary Islands, ESTOC, located in the Northeast Atlantic subtropical gyre. With over nine years of oceanographic data starting in 1996, seasonal and interannual trends of CO_2 species and air-sea exchange of CO_2 were determined. Net CO_2 fluxes show this area acts as a minor source of CO_2, with an average outgassing value of 179 mmol CO_2 m^{-2} yr^{-1} controlled by the dominant Trade Winds blowing from May to August. The effect of short-term wind variability on the CO_2 flux has been addressed increasing air-sea fluxes by 63% for 6 hourly sampling frequency. The processes governing the monthly variations of C_T have been determined. From March to October, when C_T decreases, mixing at the base of the mixed layer (11.5 ± 1.5 mmol m^{-3}) is compensated by air-sea exchange, and a net organic production of 25.5 ± 5.7 mmol m^{-3} is estimated. On an annual scale, biological drawdown accounts for the decrease in inorganic carbon from March to October, while mixing processes control the CT increase from October to the end of Autumn. After removing seasonality variability, fCO_{2sw} increases at a rate of 0.99 ± 5.8 uatm yr^{-1} and as a response to the atmospheric trend, inorganic carbon increases at a rate of 0.69 ± 1.9 umol kg-1 yr^{-1}.

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Methane in Lake Baikal

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The first travelers who have visited Baikal in XVII century described gas escapes from the lake bottom. Such escapes have been investigated during XIX and XX centuries. Results obtained during these studies allow to suppose that intensity of gas escapes has significantly decreased during last 50-60 years. This may be due to lowering of a number of catastrophic (9 - 10 points) earthquakes in Baikal region. Systematic investigation of gas escapes from the bottom was recently started after the gas hydrates have been discovered in Baikal bottom sediments.

In 2003 - 2004, ten regions of "shallow-water"(water depth down to 300 m) gas seeps were found, which are characterized by anaerobic conditions at the water-sediment interface. Among them, two types are distinguished: 1. *Solitary seeps* (near the capes Ukhan and Krestovskii, near the bay Proval, near the Posolsk settlement, on the cross-section Peschanaya – Istok); 2. *Group seeps* (two regions characterized by seepage near town of Babushkin, three such regions near Posolskaya bank).

The pattern of vertical methane distribution within the water column was investigated during six 2002 - 2004 expeditions. In the background lake regions, the methane concentration in surface water ranges 100 to 200 nl l^{-1} decreasing to 10 - 30 nl l^{-1} in the deep zone. In the shallow-water regions, characterized by gas escapes from sediments, and in the areas adjacent to the deltas of large tributaries (the Rivers Selenga, Kichera, Upper Angara) as well, the methane concentration was 6000 - 40000 nl l^{-1}, in some cases it reached 150000 nl l^{-1}. In winter, the methane concentration increased under the ice: it was 150 to 300 nl l^{-1} in Southern Lake Baikal. An increase was due to the methane input from the sedimentary sources in some shallow-water areas. The rate of methane growth within the water layer adjacent to the ice is close to the mean intensity of its emission to the atmosphere during the period when there is no ice cover.

In deep-water part of Southern Baikal, there is the mixed water layer of 100 - 200 m thickness. Its existence may be caused by the input of both methane and low-mineralized water resulted from the gas hydrates decomposition within the bottom sediments. In the deep-water zone, highly increased methane concentrations (300 - 14000 nl l^{-1}) were found at solitary sites. Maximal concentrations were registered in the region near mud volcano mTSG in Southern Baikal. In the pelagic part of Lake Baikal, the methane in surface water is characterized by wider range of concentrations both from site to site and from season to season.

Out of the zones of direct sepage influence, the methane flux from lake surface to the atmosphere ranges at different sites from $-280\cdot10^{-6}$ to $+20\cdot10^{-6}$ g m^{-2} day^{-1}; it equals $-20\cdot10^{-6}$ g m^{-2} day^{-1} on average. In Lake Baikal, the methane flux to the atmosphere is substantially less compared to normal shallow lakes and is close to the fluxes typical of the ocean.

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Gas Transfer Velocities in a Tropical Reservoir and its River Downstream: Wind Speed and Rainfall Effect.

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We have measured simultaneously the methane (CH_4) and carbon dioxide (CO_2) surface concentrations and fluxes in the Petit-Saut reservoir (French Guiana) and its tidal river (Sinnamary River) downstream the dam, during two field experiments in wet (May 2003) and dry season (December 2003). Gas fluxes were measured with floating chambers (FC) on the artificial lake and on the river, and with the eddy covariance (EC) technique for CO_2 during a 24h experiment on the lake. For each chamber measurement, wind speed was measured at 1m above the water surface and recalculated at 10 m using the formulation proposed by Amorocho et DeVrie (1980). During the 24h EC experiment the wind speed at 10m (U_{10}) and the rainfall rates were recorded by a meteorological station. For each flux measurement the gas transfer velocity normalized for a Schmidt Number of 600 was computed.

On the lake and excluding all rainy events, we obtained cubic relationships between k_{600} and U_{10} for both gases (k_{600} (CH_4) = 2.02 + $0.03U_{10}^3$ n= 38, FC fluxes and k_{600} (CO_2) = 2.81 + $0.036U_{10}^{2.8}$ n= 127, FC and EC fluxes). The comparison of individual FC and EC k_{600} for CO_2 showed some discrepancies due to differences in measurements durations (FC: 5-10 min versus EC: 30 min) which resulted in different average wind speeds (FC: 0.18 to 7.8 $m.s^{-1}$; EC: 0.18 to 3.87 $m.s^{-1}$). Nevertheless, when comparing FC and EC K_{600} for a given wind speed, both methods gave similar results. At low wind speed ($U_{10} \leq 3$ $m.s^{-1}$), k_{600} (CO_2) was significantly higher than k_{600} (CH_4) suggesting the occurrence of chemical and/or biological enhancement of the CO_2 flux in these acid waters (pH=6) with low buffering capacity (Alkalinity 0.1$meq.kg^{-1}$). k_{600} was also positively related to rainfall rates reaching 29 $cm.h^{-1}$ for a rainfall rate of 42 $mm.h^{-1}$. Using a tropical raindrop size distribution, we obtained a linear relationship between the residual k_{600} and the kinetic energy flux consistent with the formulation of Ho et al. (1997). Concerning the wind effect alone, when comparing our results with literature data [Cole and Caraco, 1998 and references therein; Frost and Upstill-Goddard, 2002; Crucius and Wanninkhof, 2003], no evident statistical differences appear from one lake to another.

In the tidal river downstream the dam, we obtained a linear relationship between k_{600} and U_{10} ($k_{600} = 4.24U_{10} + 5.46$) with no significant difference for the two gases and with higher k_{600} than in the lake due to the turbulence induced by water currents. The slope of this linear relationship fitted well to the formulation as a function of surface area (on a log-log scale) proposed by Borges et al. 2004. This confirms that, in rivers and estuaries, the formulation of k_{600} is site specific, the intercept being related to water current and depth and the slope to fetch limitation (surface area).

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Mechanisms controlling the air-sea exchanges of CO_2 in the eutrophied coastal waters of the Southern Bight of the North sea: a modelling study.

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A description of the carbonate system has been coupled to the MIRO biogeochemical model (Lancelot et al., 2004) to explore the sink or source role of the Belgian coastal waters for atmospheric CO_2. For this application, the model is implemented in a simplified three-box representation of the hydrodynamics of the Eastern Channel and the Southern Bight of the North Sea under the influence of the rivers Seine and Scheldt. Results obtained by running the model over the 1996-1999 period are successfully compared with data recorded over the same period in the central Belgian Coastal Zone (BCZ) at station 330 (51°26.05' N; 002°48.50' E). Budget calculations based on model simulations of carbon uptake and mineralization rates indicate for BCZ a low annual sink of atmospheric CO_2 (-0.17 mol C m^{-2} y^{-1}). On the opposite, surface water pCO_2 in the Western English Channel (WCH) is estimated to be at annual equilibrium with respect to atmospheric CO_2. The seasonal dynamics of CO_2 exchanges at the air-sea interface and their controlling factors are further explored by running model scenarios with separate closure of biological activities and/or river inputs of carbon. The suppression of biological processes reverses direction of the CO_2 flux in BCZ that become, on an annual scale, a significant source for atmospheric CO_2 ($+0.53$ mol C $m^{-2}y^{-1}$). Overall, biological activity has a stronger influence on the modelled seasonal cycle of pCO_2 than temperature. In particular, the spring growth of *Phaeocystis* colonies is associated with an important sink of atmospheric CO_2 that counteracts the temperature-driven increase of pCO_2 at this period of the year. On the other hand, river inputs of organic and inorganic carbon are shown to increase the surface water pCO_2 and hence the emission of CO_2 to the atmosphere.

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Estimation of air-sea gas and heat fluxes from infrared imagery and surface wave measurements.

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Water surface infrared images as well as surface wave slope data were obtained during the GASEX2001 experiment in the South Equatorial Pacific waters and during the laboratory experiment at AEOLOTRON wind wave tank at University of Heidelberg in October 2004. Previous laboratory and field experiments suggest that at low to intermediate wind regimes the surface gas fluxes are better correlated with surface wave slope rather than with wind speed or wind stress [*Frew et al.,* 2004]. Our observations of infrared imagery and wave slope during these experiments also indicate the same trend. Furthermore, they reveal two distinct regimes of heat and gas fluxes. The surface wave slope data show the existence of sporadic steep slope events, whilst the infrared imagery demonstrates intermittent passage of strong temperature fronts with steep gradients in the heat flux estimates. They therefore suggest the coexistence of weak background turbulence and intermittent small scale breaking events. The former yields moderate heat fluxes, while the latter are associated with enhanced subsurface turbulence and much higher heat fluxes. In addition, the infrared imagery analysis reveals potentially significant effects of near surface temperature stratification on the heat and gas flux estimation and highlights ambiguity in the present definition of the “bulk temperature”. Previous interpretations of the infrared images relied on the surface renewal model, in which the water surface is assumed to be occasionally renewed by bursts of turbulent eddies reaching the water surface [*Garbe et al.,* 2004]. A new complementary model based on stationary and spatially periodic turbuent eddies is developed to reinterpret the infrared images. It is also shown that the difference in the surface boundary conditions for heat and gas affects the gas transfer velocity estimates based on the observed heat transfer velocity using the Schmidt number scaling.

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Dissolved Inorganic Carbon dynamics in the northern Bay of Biscay during a Coccolithophore bloom.

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In the framework of the Belgian global change programme, we have developed a project devoted to the study of the inorganic carbon cycle in the Bay of Biscay where coccolithophore blooms occur frequently. The study focuses on processes associated with the oceanic production and dissolution of calcium carbonate and related CO2 fluxes. Real time remote sensing allowed to localize the coccolithophore bloom that the R.V. Belgica visited in June 2004 during a multidisciplinary scientific cruise. We will present vertical profiles of pH, Talk, along with other parameters (salinity, temperature, chlorophyll a and phaeopigments) and 14C incorporation experiments. Inorganic carbon fluxes will be discussed in the photic zone, in correlation with the biological activity of phytoplankton (biological and carbonate pumps).

Rain and wind-induced air-water gas exchange

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The relationship between rain and gas exchange has been determined in a series of laboratory experiment, in both freshwater [*Ho et al*., 1997] and saltwater [*Ho et al*., 2004]. Furthermore, the mechanisms responsible for the gas exchange enhancement have been examined [*Ho et al*., 2000]. However, the interaction between rain and wind, and how they combine to influence air-water gas exchange has not been studied. Results will be presented from a series of experiment conducted in the Windwave-Rain Tank at the University of Delaware's Air-Sea Interaction Laboratory. During the experiments, 2 rain rates and 3 wind speeds were used. The SF_6 evasion method was used to determine the bulk gas transfer velocity, airside profiles of wind, temperature, water vapor and carbon dioxide were used to estimate the momentum, heat, and gas fluxes. Flux-profile relationships [*McGillis et al.,* 2001] for marine atmospheric boundary layers are explored by the comparison between bulk fluxes and atmospheric gradient measurements. In addition to ascertaining the fluxes with and without rain in a wind-wave boundary layer, measurements of airside, waterside, and interfacial physical properties were obtained. These included shear, turbulent kinetic energy dissipation, stability, and wave properties. The augmention in the controls and magnitude of the air-water transfer of momentum, heat, and gas under wind-rain conditions will be discussed. The implications for scaling-up to field measurements will also be addressed.

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Spectral signature of breaking surface waves

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Wave breaking has profound impacts on the upper ocean turbulence properties, the disruption of the surface cool skin, the generation and entrainment of air bubbles into the water column, and the composition of small scale ocean surface roughness [e.g., Thorpe, 1983; Melville, 1984] and various aspects of ocean remote sensing, for example, sea spikes [Frasier et al., 1998] and bubble entrainment [e.g., Ding and Farmer, 1984]. All the factors cited above are known to be important mechanisms modifying the gas transfer across the air-sea interface. The clarification of the spectral properties of surface wave breaking may contribute to a better understanding of the gas transfer process in the ocean [e.g., Monahan, 2002; Asher et al., 2002].

One common assumption about wave breaking is that its spectral properties are expected to be broad band, conjectured upon the observation that breaking events occur far apart in space and time, thus spiky in space/time, broadband in wavenumber/frequency. Field observations on breaking waves are difficult to make and the confirmation or disproval of the basic and widely accepted assumption remains uncertain.

Two decades ago, Phillips [1984,, JPO, 14, 1425-1433 1985] presents a method to derive the dissipation function of the wave action conservation equation from the functional dependence of the dimensionless wave spectrum on the dimensionless wind friction velocity. The approach is most suitable for application in the region of short scale waves where the magnitude of the nonlinear wave-wave interaction term is comparatively smaller than the wind input and breaking dissipation terms. Obtaining reliable measurements of short waves in the ocean is a demanding task, mainly due to the complicated issue of Doppler frequency shift that renders the interpretation of the length scale of the measured encounter frequency spectrum an uncertain task. This problem is significantly mitigated by free-drifting operation that provides measurements in a frame moving with the advecting currents that cause the Doppler frequency shift. The Phillips' method is applied to the spectra of intermediate scale waves (wavelengths between 0.02 and 6 m) measured in the ocean using wave gauges mounted on a free-drifting platform. The results show that the breaking dissipation function displays a quasi-singularity behavior in the neighborhood of meter-long wave components, suggesting that the spectral property of wave breaking is localized in the wavenumber space [Hwang and Wang, 2004]. This is in contrast to the common assumption of broad band property of breaking waves. Further analysis of the field data suggest that the spectral signature of breaking waves reflects the wave breaking probability that decreases exponentially with increasing breaker size [e.g., Frasier et al., 1998]. Weighed by the breaking probability, the resulting breaking dissipation function displays a nonmonotonic behavior, with a maximum located in the neighborhood of meter-long waves based on field data of wind-sea dominant conditions. In the presence of swell, the breaking scale shifts toward smaller breaker sizes and the size range expands, reflecting the interaction of orbital velocity and short waves.

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Air-Sea Gas Transfer; Schmidt Number Dependency and Intermittency.

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It is well known for years that the Schmidt number dependency on the gas transfer velocity changes with the boundary conditions at the sea surface. For a smooth interface, the Schmidt number exponent is about –2/3, for a rough and wavy interface it is about –1/2. This change is theoretically well understood but only confirmed by few experimental data. However, the available experimental data are not accurate enough to learn more about the details and nature of this transition. Is it a rather steep jump or a more continuous transition?

Gas exchange experiments were conducted in the air-sea interaction facility at the Institute for Environmental Physics ("Heidelberg Aeolotron") for precise measurements of the Schmidt number exponent under different boundary conditions. Four gases with a wide range of diffusivities were used: He, H_2, N_20, and dichlorodifluoromethane (F12). New experimental procedures were developed to ensure low systematic errors in the relative difference between the simultaneously measured transfer velocities of the four gases. The Schmidt number exponent is estimated with an accuracy which is at least five times more precise than previous measurements. The results clearly indicate a gradual transition of the Schmidt number exponent from about -0.7 to -0.5.

Additionally, an active thermographic technique was deployed to investigate the heat transfer process across the thermal boundary layer. This technique considers the boundary layer as a black box in linear system theory. The input is a periodically varying heat flux, the output the amplitude and phase shift of the water surface temperature. The measured phase shifts clearly indicate that the transfer process is strongly intermittent.

A novel physically based model of the Schmidt number dependency on the transfer velocity is presented. It takes the measured Schmidt number exponent and the intermittency of air-sea gas transfer into account. Both the Schmidt number exponent and the nondimensional momentum transfer resistance are modeled as a function of the mean square wave slope. Different assumption about the influence of waves on turbulence result in different relations of the transfer velocity as a function of friction velocity, nondimenisonal transfer resistance, and mean square slope of waves. The theoretically derived relationships are compared with the measured data.

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The Heidelberg Aelotron - new perspectives for laboratory investigations of small-scale air-sea interaction.

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A large annular wind/wave facility with quasi unlimited fetch has been built at the Institute for Environmental Physics University of Heidelberg, Germany. The facility is designed to perform detailed studies of small-scale air-sea interaction. It is optimized for imaging short wind waves, accurate measurements of gas transfer velocities and to deploy infrared imaging techniques.

The annular water channel has an outer diameter of 10 m and a width of 0.7 m. It is 2.4 m high and can be filled with water up to a height of 1.2 m, which corresponds to a water volume of approximately 21 m^3. Wind is generated by a rotating paddle wheel up to 15 m/s. The air space is gas tight and the walls are insulated. Experiments can be performed with deionized water, artificial sea water, surfactants, and reactive gases. An air conditioning system controls independently humidity and air temperature. In conjunction with an air flushing system net heat fluxes at the water surface can be adjusted from -500 to 1000 W/m^2. A water current with a speed up to 5 m/s against the wind direction can be generated separately by a set of thrusters.

Air temperature, water temperature, relative humidity, water current and wind speed are continuously monitored. Standard measurements techniques include a color imaging slope gauge (mean square wave slope and wave spectra), an infrared imaging system (heat transfer velocity), and infrared absorption spectroscopy (gas transfer velocities of He, H_2, N_20, and F12).

We plan to focus in the next decade on measurements revealing the mechanism of air-sea gas transfer including the effects of surfactants and waves. The experimental possibilities of the facility are detailed to show the opportunities for international cooperation.

Dynamically Consistent Computation of Exchange Processes at the Air-SeaInterface

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A dynamically consistent framework for modelling atmosphere-ocean exchange processes must take account of surface waves and other movements of the air-water interface, either explicitly or implicitly. In order to calculate the effect of waves, it is necessary to employ a consistent formulation of the balance of energy, mass and momentum, within the airflow, wave field, and water column, taking into account the Earth's rotation for periods of time greater than a few hours. It is also advisable to use a coordinate system which can represent vertical variations at scales much smaller than the wave height, for example, a surface-following coordinate system. We may account for the waves explicitly by employing a numerical spectral wave model, and applying a suitable theory of wave---mean flow interaction. A closed system of equations may be obtained to second order in wave slope by applying wave action conservation equations in the propagation of the spectral wave components. A coupled model system may also take account of the effect of turbulence and depth-varying currents on wave propagation and dissipation, the presence of surface films and sea ice, and the generation of Langmuir circulations. An outline is given of how this formulation may be applied to the atmosphere--ocean exchange of gas species and particulate material.

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A Laboratory Study of Infrared Techniques to Measure Heat Flux

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Air-sea fluxes can be expressed in transfer laws with the general form that the flux is equal to a driving potential divided by a resistance, which is typically represented by its inverse in the form of a transfer rate. For the net heat flux, $Q_{\mathrm{NET}} = \rho c_p k_{\mathrm{H}} \Delta T$, where the bulk-skin water temperature difference, ΔT, is the driving potential, the heat transfer velocity, k_{H}, is the transfer rate, and ρ and c_p are the density and specific heat capacity of water, respectively. Surface renewal theory predicts that k_{H} and the gas transfer velocity, k_{G}, will scale between each other with the square root of the ratio of their diffusivities. This scaling has motivated the use of infrared (IR) techniques to measure heat flux as a means of investigating air-water gas transfer.

Over the past 7 years, our laboratory and field investigations have shown consistently that k_{H} from the active controlled flux technique (ACFT) and k_{G} measured using deliberate tracer gases do not scale as predicted [*Asher et al.*, 2004; *Atmane et al.*, 2004; *Zappa et al.*, 2004]. During the FAIRS and GasEx01 cruises, the net heat flux measured directly, Q_{MEAS}, was compared to Q_{CFT}, the net heat flux calculated using k_{H} from ACFT and ΔT measured using a radiometer and a thermistor. These two measures of heat flux were found to be linearly related but the average $Q_{\mathrm{MEAS}}/Q_{\mathrm{CFT}}$ was approximately 7. In contrast, *Garbe et al* [2004] and *Schimpf et al.* [2004] have reported good agreement between Q_{NET} measured directly and inferred from IR techniques. The main differences between our approach and theirs is that they use passive IR techniques to measure k_{H} and ΔT.

Here we report on a recent laboratory experiment to investigate the validity of the Driving Potential-Resistance relation for Q_{NET}, with emphasis on interpretation of ΔT. The experiment took place in the NASA Air-Sea Interaction Research Facility in Wallops Island, VA. Measurements included k_{H} from ACFT, k_{G} using deliberate tracer gases, T_{skin} from a radiometer, near-surface T profiles using a fast-response thermistor, and Q_{NET} using the gradient technique. We compare the net heat flux based on direct measurement of ΔT with that based on ΔT derived from IR imagery.

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Interpretation of the effect from the CO_2 buffer system on the air-sea exchange coefficient

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Estimation of CO_2-fluxes across the air-sea interface is associated with many sources of uncertainties. Here we investigate one of these, namely the chemistry in the water phase. The flux is usually estimated from the concentration difference in CO_2 across the air-sea interface by equations of the form:

$$F = K\Delta pCO_2 \qquad (1)$$

where ΔpCO_2 is the concentration difference across the interface and K is a transfer velocity, being function of several parameters, notably the wind speed or the surface stress.

Several forms of K have been suggested in the literature, but chemistry in the water column is normally not taken into account in the evaluation of the K, and has therefore often been regarded as a factor, which can explain some of the uncertainties between the differences measurements and models. Here we show that the effects of chemistry much to our surprise justify the use of (1).

The basic assumption behind the use of (1) is that the concentrations in the air and the water are homogeneous and stationary in the two fluids with the only concentration gradient to be right at the interface.

We have studied the effects of the vertical concentration gradient in the water induced by the flux across the interface, including both the chemistry and the diffusion processes. The methodology has been to solve the flux budget for the chemical reaction equations.

It is shown that the effects of water chemistry on the Air-sea exchange coefficient are negligible.

The skin-layer still contains the largest resistance and therefore controls the flux. The reason why the effect is small is mainly because of the size of the carbonate buffer and the speed of the chemical reactions involved. The theoretical result also shows that measurement of the near-surface CO_2 gradients in water are practical impossible as the layer where the gradients occur and the equilibrium is reached is within the first meter. The occurrence of waves makes such measurements nearly impossible.

Oceanic air-water exchange of persistent organic pollutants and aerosol organic carbon at a global scale.

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The estimation of the global oceanic air-water exchange of organic carbon is important to understand its fate, sink and implications for ocean biogeochemistry. On the other hand, persistent organic pollutants (POPs) are not only a stressor for aquatic ecosystems but their study provides clues on the cycling of organic carbon. In the present study we develop and apply a methodology to estimate the diffusive air-water exchange fluxes of POPs over the Atlantic Ocean. Furthermore, inferences of the dominant atmospheric depositional process are also obtained. The methodology is based on atmospheric field measurements of PCBs and PCDD/Fs during north-south Atlantic Ocean transects, satellite retrieved parameters (SST, wind speed, rain, aerosol size distributions,...) and novel parameterizations of size-dependent dry deposition velocities, air-water exchange and wet deposition. Those parameterizations account for the enhancement of diffusive gaseous air-water exchange due to the turbulence generated by rain and the adsorption of organics on the rain drops. Finally, after validating the estimations with measurements for individual organic compounds, the methodology is used to estimate the global atmosphere ocean exchange of organic carbon.

Influence of sub-daily processes on the air-sea flux of CO_2.

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The air-sea flux of CO2 is driven by the difference between the partial pressures of CO2 in the ocean and atmosphere and scaled by the gas transfer velocity. The gas transfer velocity is dependent on wind speed and sea surface temperature (SST) while the partial pressures of CO2 depend upon air pressure, humidity, SST, sea surface salinity, solar radiation, chemical and biological interactions and turbulent mixing through the water column. Many of these variables change on a diurnal time scale and many of them are highly correlated. These short time scale variations and covariations are ignored when monthly averages are used to estimate CO2 flux leading to large errors in flux [eg: *Wanninkhof et al., 2002*]). Here we present a thorough analysis of the effects of sub-daily processes on air-sea CO2 flux using a 1-d bio-geochemical ocean turbulence model consisting of a general ocean turbulence model (GOTM) coupled with the Hadley Centre ocean carbon cycle (HadOCC) model. The model is forced with high frequency meteorological data from a number of locations with diverse meteorological/oceanic conditions to demonstrate regional differences in flux errors due to temporal averaging.

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The biogeochemical cycling of methane in a shallow coastal inlet at the onset and end of seasonal upwelling (Ria de Vigo, NW Spain)

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The Ria de Vigo is one of four submarine incised valleys (Rias Baixas) on the Spanish Atlantic Coast subject to seasonal upwelling. Geophysical data have shown evidence of shallow gas accumulation in sediments (accoustic turbidity) and gas escape (pockmarks), with CH_4 shown to be a major component of this gas. Here we present data from two field campaigns at the onset (April 2003) and end (September 2004) of seasonal upwelling investigating the biogeochemical cycling of CH_4 in the Ria de Vigo. Typical estuarine 2-layer stratification of the water column was observed in April indicating up- or out-welling conditions, with a mixed water column in September. We found CH_4 supersaturation with respect to atmospheric levels in surface waters during both field campaigns. CH_4 concentrations up to180 nmol L^{-1}in September were approximately a factor of 2 higher than in April. This was attributed to enhanced methanogenesis in surficial sediments, which utilised exported carbon from the overlying water column after the summer productivity maximum. Sediment core profiles of porewater CH_4 and $\delta^{13}CH_4$ as well as microbial incubations indicated microbial methanogenesis in deeper sediments and methane oxidation near the sediment water interface. CH_4 sources to the Ria de Vigo water column were dominated by sedimentary inputs, while riverine inputs and water column methanogenesis contributed a small fraction of the source total. A preliminary mass balance budget for the biogeochemical cycling and sea-air flux calculations of CH_4 in the Ria de Vigo are presented. Although the Rias Baixas have been shown to be a net sink for atmospheric CO_2 over an annual cycle, our data suggest that much of the exported carbon may return to the atmosphere as CH_4.

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On the marine atmospheric boundary layer at very strong winds

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Dynamics of the Marine Atmospheric Boundary Layer (MABL) at strong winds is considered. Motivation of this study is the field and laboratory findings on the effect of suppression of surface drag and the saturation of the surface roughness at very strong and hurricane winds. In the present study the main attention is paid on the effect of sea droplets on atmospheric turbulence through the buoyancy forces (the spray contribution to net evaporation is ignored). Production of the spray droplets at the sea surface is described in terms of the spray generation function (SGF). Model calculations done for the empirically derived estimates of the SGF. It is shown that if SGF is used as the surface boundary condition (as an upward flux of droplets from unit surface), then the effect of spray on MABL is negligible at any strong wind speeds. An alternative approach is proposed. It based on a modified droplets conservation equation accounting for the different spray generation mechanisms. The bubble generated droplets produced by the upward droplets flux at the surface. On the other hand, generation of the spume droplets are accounted for through a volume source describing their production by wind tearing of wave crests. It is shown that spume droplets play a crucial role. At strong winds (> 30 m/s) spume droplets suppress the turbulence in the near surface layer, that results in suppression of the surface drag and acceleration of the airflow. The comparison of model prediction with available field and laboratory observation is discussed.

Parameterization of the CO_2 air-sea transfer velocity using an inorganic carbon mass balance approach and a micro-meteorological method: two studies from the Baltic Sea

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In order to improve our understanding of the transfer velocity - wind speed relationship, we studied the CO_2 air-sea exchange using an inorganic carbon mass balance approach for the Gotland Sea (Baltic Sea) surface water. During winter 1999/2000 the Gotland Sea showed high CO_2 partial pressures and a clear mixing depth that facilitated the calculation of the CO_2 evasion flux by measuring the loss of inorganic carbon in the surface water. Moreover, low biological activity and reduced lateral water transport during winter only had a small impact on the carbon budget. The results of the study show that the widely used parameterizations for k(u) considerable underestimate the CO_2 air-sea exchange fluxes. Based on measurements of the CO_2 partial pressure difference between the air and sea, and high resolution wind speed (u) data, it was shown that both $k=(0.45\pm0.10)\bullet(Sc/660)^{-0.5}\bullet u^2$ and $k=(0.037\pm0.008)\bullet(Sc/660)^{-0.5}\bullet u^3$ yielded reasonable fits to our flux data. To resolve the issue as to whether a cubic or a quadratic parameterization better represents the mechanism of gas exchange across the air-sea interface a field study was started in 2003. High resolution micrometeorological flux measurements of CO_2 using an open-path infrared gas analyzer and a fast response sonic anemometer in combination with seawater CO_2 partial pressure measurements by a sensor (type SAMI-CO_2) were made at a platform in the central Arkona Sea (Baltic Sea). Preliminary results of this study don't seem to better constrain the k(u) parameterization. The high transfer resistance in the water phase only led to very small CO_2 sea surface fluxes. Under these conditions the assumption of constant flux between the sensors at 6 m height and the sea surface seems questionable and may be the main reason for the observed scatter of the k(u).

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Modelling of whitecap coverage in coastal environment

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Whitecap is a major process affecting aerosol and gas fluxes at the air-sea interface. The whitecap fraction, commonly denoted W, is the ratio between the area of the sea surface covered by whitecaps to the total sea surface area. In coastal zones, the whitecap coverage differs from open ocean conditions due, e.g., wave-current interactions, bottom influence, the geometry of the coastline, as well as the variability in space and time of both the wind speed and the wind direction. This work concerns the modelling of the whitecap fraction in coastal zone using in situ measurements of W and of coincident wave and wind parameters. The results are based on an extensive series of data obtained in Mediterranean coastal sites. First, wave analysis allows determination of specific relationships between non-dimensional parameters including wind speed, fetch, wave significant height and spectral peak frequency. Then we study the sensitivity of W on wind and waves. We show that the whitecap coverage depends on the wind parameters (such as wind speed and friction velocity) but also on coupled meteo-oceanic parameters (such as wave age and dimensionless energy). Useful relationships between W and these wind-wave parameters are obtained. Finally, these relationships were implemented in a coastal wave numerical model to predict the spatial variations of the whitecap coverage. Some experimental events were successfully modelled using a spatially and temporally homogeneous wind input.

Bubble Plume Bubbles from Wind-Steepened Wave Breaking

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Breaking-wave bubbles are important to many geophysical processes; however, most bubble measurements are of the steady-state background population rather than the formation population, i.e., bubbles in the bubble plumes. Measurements of bubbles inside bubble plumes from wind-stress breaking waves were made during the LUMINY experiment using a non-invasive, video bubble measurement system. The bubble-plume bubble-population is much greater than in the background population, and the distribution is much shallower. Thus, compared to the background population, bubble plumes are enriched in large bubbles.

Bubble plumes showed significant variability in dynamics, bubble distributions, and physical extents. To preserve this diversity, a classification scheme was developed and time-resolved, bubble size-distributions were calculated for each plume class. Comparison of the bubble distributions suggested the most important distinction was between bubble plumes termed «dense» and «diffuse». These distinctions were based on the optical ability to obscure the background and related to the relative importance of large ($r > 1000$ μm) bubbles, where r is radius. At injection, diffuse plumes were weakly size dependant to $r \sim 1000$ μm, decreasing steeply for larger bubbles. Dense plumes were multimodal with a steeply decreasing small bubble population and a second peak at $r \sim 1700$ to 2000 μm, decreasing steeply for larger bubbles. Dense plumes were significantly enhanced in large bubbles compared with diffuse plumes. Surprisingly, void fractions of diffuse plumes were greater at maximum penetration than void fractions of dense plumes. Finally, the injection and rise phases were approximately equal in time.

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Bubble Plumes, Bubbles, and Wave Characteristics from Wind-Steepened, Breaking Waves

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Breaking wave-generated bubbles are important to many geophysical processes of direct impact on climate, in particular air-sea gas exchange. It is well established that the air-sea exchange rates of most greenhouse gases significantly increases at high wind speeds, when breaking waves and bubble plumes disrupt the sea surface. This increase is closely related to the bubble distribution [*Schudlich and Emerson*, 1996]. However, few studies have related the formation bubble distribution and bubble-plume characteristics with wave evolution and development. To fill this gap, as part of the LUMINY experiment, breaking waves, breaking-wave generated bubbles, and bubble plume characteristics were measured simultaneously in the large IRPHE wind-wave facility for conditions of wind-forced wave breaking. It was observed that bubble plumes exhibited a wide range of bubble distributions, physical extents, and dynamics. A classification scheme was developed from measurements of ~3500 bubble plumes. Bubble plumes were segregated into major, minor, or micro classes depending upon physical plume dimensions. Plumes also were segregated into diffuse or dense classes based upon their ability to obscure the background optically. The plume formation rate, *P*, as well as the wave and wave breaking characteristics were determined for different experiments and over a range of fetches, *F* – i.e., wave development.

The wave-breaking rate was found non-homogeneous along the test section of the wind-wave tank. This fetch evolution was strongly correlated with the RMS wave height. Thus, maximum wave breaking was observed at *F* of the largest RMS wave height. Although the plume formation rate, *P*, also followed wave development, *P* for major dense bubble plumes (the largest in terms of size and number of bubbles) was at a maximum just downstream of the *F* of peak wave-breaking, while *P* for micro and minor plumes peaked both slightly upstream of this *F* and also further downstream, in the region of wave-field regeneration after breaking. The ratio of dense to diffuse plumes also followed the trend with *F* in wave development.

Using the formation or injection, bubble-population, size distribution, and *P* for each plume class, the global, injection bubble-plume size-distribution, $\Psi_i(r)$, was calculated, where r is the bubble radius. Ψ_i decreased as $r^{-1.2}$ for $r < 1700$ μm and $r^{-3.9}$ for larger r, with the volume injection rate divided approximately equally between bubbles smaller and larger than $r \sim 1700$ μm. Using plume volumes at the maximum penetration depth for each class, a bubble concentration distribution was calculated which showed that plume bubble concentrations are greater than the background population by one to several orders of magnitude depending upon r.

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Modeling the turbulence generated by microscale breaking waves

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The turbulence generated by microscale breaking waves beneath the air-water interface is simulated numerically. The goal of this study is to improve our understanding of the physical processes governing the transfer of gases across the ocean surface. The model predictions will ultimately be used to aid the development of a new parameterization of air-sea gas transfer that accounts for microscale wave breaking. Our specific objective is to quantitatively assess the hypothesis that microscale wave breaking is an important factor in the global air-sea flux of carbon dioxide. Microscale breaking waves are small scale breaking waves for which surface tension is sufficiently strong to prevent air entrainment. They are about 10 to 50 cm in length and a few centimeters in height. In the ocean microscale breaking waves occur much more frequently than white caps. Laboratory investigations have shown that at wind speeds from 4 to 10 $m \cdot s^{-1}$ microscale wave breaking is the dominant physical mechanism that controls the rate of heat, momentum and gas transfer across the air-water interface [*Zappa et al.* 2001, *Siddiqui et al.* 2004].

Wave breaking provides a mechanism for the injection of both kinetic energy and momentum from air to water. A one dimensional 2.5 level turbulence closure scheme is used to model the enhanced near surface turbulence produced by microscale breaking waves. The model was originally developed to simulate the turbulence generated by large scale breaking waves [*Craig and Banner,* 1994]. We have modified this model so that it accurately simulates the near-surface turbulence beneath microscale breaking waves. The effect of the viscous sublayer was incorporated in the model by modifying the turbulent length scale close to the air-sea interface. Model predictions of the mean horizontal velocity and vertical profiles of the rate of dissipation of turbulent kinetic energy are compared with the results of an earlier laboratory experiment performed in a wind wave tank [*Elkamash and Loewen,* 2004]. The effect of microscale wave breaking is simulated in the model by a turbulent kinetic energy flux at the upper boundary that is equal to $\alpha\, u_*^3$, where u_* is the friction velocity in the water and α is the 'wave energy factor'. *Craig and Banner* [1994] found that α is of the order of 100 for large scale breaking waves. Beneath microscale breaking waves we found that α is approximately 10, an order of magnitude smaller than the value for large scale breaking waves. The vertical distribution of turbulent kinetic energy beneath the water surface is also investigated. `Detailed comparisons with the laboratory measurements demonstrated that the model is able to provide accurate predictions of the near-surface turbulent structure beneath microscale breaking waves.

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Measurements of the air-water CO_2 flux using atmospheric profiles

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Studies deploying atmospheric flux-profile techniques in laboratory wind-wave tanks have been performed to demonstrate and verify the use turbulent transport models in the air to accurately determine the air-water gas exchange. Air-water gas transfer velocities have been estimated using the CO_2 atmospheric flux-profile technique in laboratory wind-wave tanks both at the NASA Wallops Flight Facility, USA and Kyoto University, Japan. Gas fluxes using the flux-profile and the waterside mass balance technique have been reconciled. Air-water fluxes H_2O and momentum were also measured simultaneously a linear wind-wave tank. The waterside mass balances used the evasion of SF_6. The CO_2, H_2O, and momentum fluxes were calculated using the atmospheric flux-profile technique over a wind speed range of 1 to 14 m s^{-1}. The CO_2 and H_2O atmospheric profile model uses airside turbulent diffusivities derived from momentum fluxes. These studies demonstrate that the quantification of air-water CO_2 fluxes using the atmospheric flux-profile technique can be implemented in the laboratory. Effects of surfactants, wind speed, and wind stress on air-water transfer are also explored using the profile flux technique. Validation of the air-water CO_2 gas exchange in laboratory wind-wave tanks provides evidence and support that this technique may be used in field studies. Air-water gas fluxes using the dome technique will also be discussed.

Air-Sea Fluxes of O_2 and N_2 Observed During Hurricane Frances

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As part of a larger program designed to measure mass, heat and momentum fluxes during hurricanes, two neutrally buoyant Lagrangian floats, each equipped with dissolved gas sensors, were air deployed into the path of Hurricane Frances (September 2004) in the NW Atlantic. Each float was equipped with a CTD, a dissolved O_2 sensor, and a recently developed fast-response gas tension device which measured total dissolved air pressure. Dissolved N_2 levels were calculated using gas tension, O_2, water temperature and salinity. The floats were pre-programmed to take profile measurements before and after the passage of the hurricane to a depth of 200 m. The floats adjusted their buoyancy to be neutral within the mixed layer during the passage of the hurricane. Vertical currents and turbulence cycled the floats up and down through the mixed layer ~ 100 times. The mixed layer deepened from ~ 30 m before the hurricane to ~ 90 m after the hurricane passed. The observed changes in mixed layer O_2 and N_2 levels during the storm allow budget derived air-sea gas flux estimates to be made after account is taken of entrainment processes. Independent estimates of air-sea gas fluxes are derived from the co-variance between the dissolved gas measurements and float velocity. Measured air-sea gas fluxes will be compared with fluxes predicted using various air-sea gas exchange models and meteorological information. We will investigate wind speed dependence of the air-sea gas transfer rate, or 'piston velocity', derived from our measurements and make comparisons with standard parameterizations. Implications for carbon fluxes will be discussed.

Fluxes of N_2, O_2 and CO_2 in Nearshore Waters off Martha's Vineyard

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We present results of a study that assessed the use of accurate, continuous, hourly time series measurements of dissolved CO_2, O_2 and N_2 to study fluxes and transformations of these gases in the complex and dynamic nearshore environment. The measurements were made at 5 m depth over 10 days in June 2002 near Martha's Vineyard, MA (41° 19.722' N and 70° 33.096' W) in water of 13 m depth. Supporting measurements include water temperature, salinity, fluorescence and local meteorological conditions. We analyzed the data by partitioning it into discrete, short duration, events that were characterized by representative meteorological and oceanographic conditions. Three events comprising approximately 30 % of the total data set were chosen for detailed analysis: two 'Wind Events' ($5 < U_{10} < 11$ m/s), and one 'Calm Period' ($U_{10} < 5$ m/s). Heat and salt fluxes were used to identify data which were suitable for interpretation using a 1-D budget. During the 'Wind Events' budgets of the biologically inactive N_2 provided estimates of air-sea gas transfer rates. These estimates were then scaled, using appropriate air-sea gas exchange models, and used to calculate air-sea fluxes of CO_2 and O_2. Budgets of O_2 during the stratified 'Calm Period' provided estimates of biologically controlled carbon fluxes. We found the air-sea carbon flux during the 'Wind Events' to be 9 to 34 % of the biological fluxes observed during the 'Calm Period'. A second estimate of air-sea O_2 flux was derived from the non-biologically controlled O_2 variability, based on Redfield ratios and knowledge that air-sea gas exchange will equilibrate O_2 faster than CO_2. Our observations provide quantitative estimates of air-sea gas exchange velocities in the complex near-shore zone, elucidate the role of bio-physical interactions in controlling air-sea CO_2 and O_2, and demonstrate the feasibility of several new methods to measure air-sea gas fluxes. Although this study was conducted in nearshore waters, the methods are appropriate to continental shelf waters and the open ocean.

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Diurnal variations of air-sea flux of CO_2, ocean CO_2 partial pressure, SST and mixed layer depth along drifter trajectories in the North-Eastern Atlantic

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During the POMME experiment (North East Atlantic, February to September 2001), four CARIOCA drifters were launched in the area 20W-15W, 39N-45N in order to collect data at air-sea surface and compute CO_2 flux .In this presentation, we will focus on the analysis of the mechanisms responsible for the short term variability of pCO2 at the sea surface and the CO2 flux at the air water interface during winter months, February and March.

On the water side, hourly measurements of pCO2, sea surface temperature (SST) salinity and fluorescence are made by CARIOCA buoys on samples pumped at a depth of 2 meters. Wind speed is measured at an height of 2 meters in the atmosphere.The value of the dissolved inorganic carbon, DIC,is computed from the distribution of pCO2 and salinity, knowing the relationship which links alkalinity and salinity in the studied area. In some situations ,a regular diurnal cycle of pCO2, SST and DIC is observed.The minimum of SST around sunrise coincides with the maximum of pCO2 and DIC while the maximum of SSTwhich occurs in the middle of the afternoon, around sunrise plus 9 hours is accompanied by a minimum of pCO2 and DIC. The thermodynamical effect due to the influence of SST would have induced a pCO2 change in an opposite direction. Mixing due to either nocturnal convection or wind action and biological processes are the likely candidates to interpret the observations

An estimate of the diurnal cycle of mixed layer depth and SST along the CARIOCA drifter trajectories has been computed by using a one dimensional model forced with hourly heat, salt and wind fluxes. Radiative fluxes (solar and infrared) are derived from satellite. Turbulent fluxes are calculated with bulk formulae from ECMWF air temperature, humidity, wind, precipitation and pressure fields and interpolated along the buoy trajectories (Caniaux et al., 2004)., Initialization of the model is provided by selecting the appropriate nearest CTD cast launched during one of the four mesoscale hydrological surveys performed during the experiment. Mixed layer depths were computed with Thomson and Fine's algorithm

Circumstances are identified when a good retrieval of both daily cycles of SST and SSS computed by the model compared to buoys' data .This indicates that the 1D modeling hypothesis is valid. In winter large diurnal MLD cycles (30m to 120m) occur during weak wind/large solar radiation periods, even by strong nocturnal convection .Stratification occurs at the beginning of March, coincident with SST increase.The daily cycle of mixed layer depth and DIC are tightly linked, the maximum depletion of DIC occurring when the mixed layer depth is the shallower. An estimate of the net community metabolism, NCM is computed under the studied winter conditions. The value of pCO2 at the sea surface is always smaller than its value in the atmosphere. Processes which control the daily variability of pCO2 at the sea surface induce a variability of at most 20% of the gradient of pCO2 between atmosphere and water and consequently on the flux exchanged at the interface. However,the variability of the wind speed remains, the main controlling factor even at short time scale

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Interannual variability of Air-Sea CO2 fluxes in the Southern Indian Ocean: comparing observations, atmospheric inversions and ocean models.

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Observing and understanding the temporal variations of air-sea CO_2 gas exchange is crucial to obtaining a better estimate of the global carbon budget, as well as to mimic complex processes and to the validation of coupled climate models. The Southern Hemisphere, especially south of 50°S, is still sufficiently undersampled that it is not clear if it acts as a source or sink of atmospheric CO_2 on seasonal, interannual or decadal timescale. However, one of the conclusions of the Ocean Carbon Model Intercomparison Project (OCMIP) was that this region serves as a sink of a significant fraction of the anthropogenic CO_2 that is taken up by the ocean. Thus intensive monitoring of this region is an important priority of the measurement community, and the monitorinig needs to be performed in close collaboration with both process-oriented and large-scale models in order to better understand the processes that control air-sea fluxes of CO_2. Here we present an analysis of both measurements and models in order to identify the internal processes and external forcings that controls on variability in sea surface CO_2 concentration and the associated variability in air-sea fluxes in the Southern Ocean. We consider timescales ranging from seasonal, interannual to decadal. We compare and discuss regional estimates deduced from direct observations conducted during the period 1998-2004 in the South Indian Ocean (OISO and MINERVE cruises), indirect methods based on atmospheric data recorded during 1980-2002 (Atmospheric Inverse Model, LMDZ). In addition, we consider output from a Biogeochemical model (PISCES) which has been run online in a global ocean circulation model (ORCA2) over the period 1948-2003, with NCEP reanalysis forcing.

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Sea-ice carbon biogeochemistry: Relationship to atmospheric CO2 fluxes.

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Recent observations of significant carbon dioxide fluxes above first year sea ice [*Pakapkyriakou* et al., 2004; *Semelitov* et al., 2004] have generated fundamental questions about the mechanisms that could possibly be supporting these fluxes, which can be quite large at times. Based on the limited information currently available about carbon transport and storage in sea ice, biological activity, inorganic carbonate geochemistry, and brine and gas permeability, as well as snow cover, may all be contributing to the observed CO_2 fluxes. While unable to definitively answer the question of what mechanism(s) are responsible, recent results from a 6-month ice time series from the coastal Arctic Ocean have refined our understanding of the processes occurring in sea ice that control carbon cycling and established what future work is needed to fully comprehend the role of sea ice in the global carbon cycle.

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Future anthropogenic emissions and climate change impact on the carbon cycle; a study with the LOVECLIM model.

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The climate feedbacks caused by increased atmospheric CO_2 levels have the potential to significantly affect the uptake of carbon by the ocean. Radiative warming, enhanced stratification and circulation changes are among the factors having a significant impact on the ocean carbon cycle either directly (solubility pump) or indirectly (biological pump).

In order to address the carbon cycle response to climate change we use a global model of the Earth system (LOVECLIM). This model is made up of a comprehensive model of the oceanic carbon cycle (LOCH), a coarse-resolution three-dimensional atmosphere-sea-ice-ocean model (ECBILT-CLIO) and a dynamical model of the continental biosphere (VECODE).

We investigate the magnitude and sign of the feedbacks over the period 1750-2300 for various CO_2 emission scenarios.

The main effect of climate change is to reduce the global ocean carbon uptake when compared to experiences with similar levels of atmospheric CO_2 but in which the climate does not evolve. This reduction is mostly due to the increase in sea surface temperature and CO_2 concentrations, which respectively lead to a lower solubility and a larger buffer factor. At the regional scale however some processes may temporarily result in an enhanced uptake with increasing sea-surface temperatures (e.g. sea-ice cover change).

Feedbacks from the biological pump, slightly positive globally, are more complex to analyze. The role of export production, shell building, organic matter remineralization depth are closely examined and their contributions to changes in the oceanic carbon cycle evaluated. In addition a series of tests of the air-sea CO_2 fluxes sensitivity to the biological model parameterization (growth rate, remineralization length scale, rain ratio…) are performed.

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The effect of surfactant concentration on the properties of the aqueous boundary layer beneath wind waves

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We report here on an experimental investigation of the properties the aqueous boundary layer formed beneath a wind-driven water surface influenced by varying concentrations of surfactant. The presence of surfactants damps short surface waves producing a smoother water surface. Viscous dissipation of wave energy in a thin layer just beneath the water surface is responsible for the majority of the damping [*Milgram 1998*]. Research has shown that the presence of surfactants reduces the gas and heat transfer rate across the air-sea interface [*Bock et al. 1999; Saylor et al., 2000*]. Recent laboratory experiments by *Elkamash and Loewen* [2004] compared the properties of the aqueous boundary layer or wind drift layer formed beneath clean wind-driven water surfaces and a water surface contaminated by 1.0 p.p.m. of the soluble surfactant Triton X-100. They found that as expected the wind waves were damped producing lower air-side friction velocities and smaller-shorter waves. However, water-side friction velocities were found to increase by ~15% in the presence of the surfactant. The aqueous boundary layers were in the transition regime between the hydrodynamically smooth and rough regimes for all conditions. The behavior of the wind drift layer at other surfactant concentrations remains to be investigated.

We conducted a series of controlled experiments in a wind-wave flume at the Air-Sea Interaction Research Facility at NASA Goddard Space Flight Center-Wallops Flight Facility [WFF] at Wallops Island, Virginia, USA. The concentration of the surfactant (Triton X-100) was varied from 0.1-5.0 p.p.m. at a wind speed of 7.2 $m \cdot s^{-1}$ and a fetch 4.8 m. Digital Particle Image Velocimetry (DPIV) was used to measure turbulent velocity fields in the water. This data provides estimates of the friction velocity and roughness height in the aqueous boundary layer as well as the rate of dissipation of turbulent kinetic energy. Wave profile data was obtained using a synchronized and collocated digital video camera identical in format to the DPIV camera. This data provides the properties of the wave field such as wave height, slope and spectral characteristics can be computed. Estimates of the air-water heat and momentum fluxes were also measured using the Controlled Flux Technique and gradient methods. Also of interest in this study is the fraction of the total vertical momentum flux that goes into the wind drift layer and its influence on gas and heat transfer rates.

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Sea ice and brine formation in Storfjorden: implications for the Arctic winter time air-sea CO_2 flux

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We investigated the air-sea CO_2 flux associated with the formation of Brine-enriched Shelf Water (BSW) in Storfjorden, a water mass formed by sea ice formation and brine rejection during winter. We used inorganic carbon and auxiliary hydrographic data collected in Aug 2001 and Apr 2002. After accounting for the effects of biological and other processes, we found that the formation of BSW is accompanied by an uptake of atmospheric CO_2. This uptake accounted for a carbon enrichment of 17 ± 4 µmol kg^{-1} in the BSW. About 2/3 of the uptake occurred during winter in a coastal polynya. A winter time CO_2 flux of 65 ± 40 gC m^{-2} was computed for the polynya. The flux was about 13 times lower (≈ 5 gC m^{-2}) for the non-polynya regions of Storfjorden.

The computed areal fluxes were extrapolated to polynyas (and leads) and seasonally ice covered regions in the Arctic. Based on this extrapolation, Arctic coastal polynyas were found to account for a winter time CO_2 uptake of $(2.3 \pm 1.4)\times10^{12}$ gC yr^{-1}. The carbon taken up in coastal polynyas is most likely transported into the deep ocean through brine-driven deep water formation. For polynyas in the central Arctic and for seasonally ice covered regions, a seaward winter time air-sea CO_2 flux of $(43 \pm 22)\times10^{12}$ gC yr^{-1} was computed. Further, it was found that this flux can increase to $(124 \pm 55)\times10^{12}$ gC yr^{-1} around year 2100, if the extent of seasonal ice increases by 43 % (as modeled in *Johannessen et al.,* 2002) and central Arctic polynyas become 10 times larger than present. However, the importance of the computed flux with respect to sequestration of atmospheric CO_2 is not clear, due to limited knowledge on the depth penetration of the brine water associated with the formation of new ice in central Arctic polynyas and seasonally ice covered regions.

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What can global simulations of transient tracers tell us about quadratic vs. cubic formulations for air-sea CO_2 exchange?

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Using recent laboratory and field measurements, it has been proposed that there is a cubic relationship between wind speed and air-sea CO_2 exchange. With this cubic formulation as well as the former quadratic formulation, we have made simulations for bomb radiocarbon and anthropogenic CO_2 in OPA/ORCA, a global ocean general circulation model. We rely on this model because its simulated CFC-11, which exhibits little sensitivity to the gas exchange formulation, generally agrees with the data. Thus we have some confidence in its simulated surface and subsurface circulation fields. Previous work suggests that when the gas transfer coefficient from the quadratic formulation is doubled everywhere in a model, bomb $\Delta^{14}C$ uptake nearly doubles yet anthropogenic CO_2 uptake increases by only 10%. With a similar approach, we are investigating how a change in the spatiotemporal structure of the gas transfer coefficient, from a quadratic to a cubic formulation, affects ocean model uptake of bomb $\Delta^{14}C$ and anthropogenic CO_2. Moreover, we are studying if one of these formulations produces more realistic global distributions of these tracers.

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Temporal variability of atmospheric CO_2 in the Bay of Biscay

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The objective of the project "ECO" is to investigate the anthropogenic CO_2 uptake capability off the Galician coast and Bay of Biscay on a seasonal time scale. Subpolar Eastern North Atlantic waters are formed in the Bay of Biscay and consequently the area plays an important role in the carbon flux to the ocean interior [*Follows et al., 1996*]. To carry out this project, an unattended pCO_2 measuring system, coined "GASPAR" has been installed on board of the RO-RO *L'Audace*, that usually covers the route Vigo (Spain) - St. Nazaire (France) with a frequency of 12 times per month. Continuous measurements of pCO_2 in air and seawater, temperature, salinity, oxygen, fluorescence and speed and direction of wind were recorded during 2003-2004.

The atmospheric pCO_2 measurements carried out on board can be easily contaminated by the own vesel emisions because of that pCO_2 atmospheric measurements from fixed meteorological stations are usually considered to estimate the ocean atmosphere fluxes. We have filtered the atmospheric pCO_2 taking into account the local wind, removing the data under the influence of the vessel emissions and applying also the quality control of atmospheric samples followed *Komhyr (1985)*.

We have estimated the seasonal cycle for the filtered molar fraction of CO_2 in the inner part of Bay of Biscay and we have obtained an annual amplitude of 11 umol/mol and an annual increasing of 2 umol/mol. The temporal evolution of the filtered molar fraction of CO_2 in the inner part of the Bay of Biscay shows a similar trend to the time serie data of two fixes meteorological stations, one in Azores (Portugal) and the other in Mace Head (Irland). Using this approach for atmospheric pCO_2 we avoid the under/overestimate of air-sea CO2 fluxes that can represent even a 50% of error over short time periods. For longer time scales, the use of atmospheric pCO_2 seasonal mean value from fixed stations has no significant effect on the final net magnitude of the air–sea flux, with a difference around 1% for the entire year.

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Surface CO_2 measurements in the English Channel with VOS

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Ships of opportunity were used to investigate ocean-atmosphere CO_2 fluxes in the Biscay Bay. In several times due logistical issues, some of the ship transits between Spain and France were extending further north, up to the English Channel. This way, in the inner zone of English Channel were performed continuous measurements of pCO_2 in air and seawater, temperature, salinity, oxygen and fluorescence during Spring 2003 (20 transects) and Autumn 2003 (2 transects) and 2004 (3 transects).

During Spring the surface waters of the Channel were strongly undersaturated, with a minimum of 260 µatm. The data were divided in two periods according to phytoplankton activity: the peak stage (March-April) and late stage (May-June). The relationship between the chlorophyll (Chla (mg/m^3)) and fCO_2 obtained in the bloom showed a high correlation coefficient ($fCO_2 = 380 - 33.3 * Chla$ $(r^2=0.83)$). With zero chlorophyll level, fCO_2 reachs a close value to atmospheric equilibrium (time data serie of meteorological station of Mace Head (Irland) estimated 378 ppm of atmospheric pCO_2 in this period). The regression corresponding to the late stage yielded a significative correlation coefficient though less important than in bloom period ($fCO_2 = 328 - 8.2 * chla$ $(r^2 = 0.13)$).

During the autumn transects whole Channel was oversaturated in CO_2. The sea surface temperature (SST (ºC)) was the main factor controlling fCO_2 in September 2003, month of the maximum fCO2 average according to Borges et al. (2003), 470 µatm ($fCO_2 = 139 + 16 * SST$ $(r^2 = 0.40)$) and in November 2004 ($fCO_2 = 294 + 7 *SST$ $(r^2 = 0.39)$). This relationship is consistent with the hypothesis suggested by Frankignoulle et al. (1996) that associates the autumn oversaturation with the entrance of warmer water from the North Atlantic.

Air-sea fluxes obtained for the four studied periods were -9.3, -9.5, 11.2 and 2.5 $mmol \cdot m^{-2} \cdot day^{-1}$, respectively, that seems to confirm that English Channel is a continental shelf region with a high variation of surface CO_2 level and without a significant uptake of atmospheric CO_2 on an annual scale.

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Role of air-sea exchanges in the atmospheric budget of oxygenated volatile organic compounds: Model evaluation based on the MANCHOT campaign

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The role of the air sea-exchange process in the atmospheric budget of a selection of Volatile Organic Compounds (VOC) has been studied with a new mechanistic parameterisation, applied in the coupled chemistry-climate model ECHAM5/MESSy [*Joeckel*, 2004].

Focus of the study has been the global acetone budget. A total net global acetone deposition to the oceans of ~10Tg/yr has been inferred based on a top-down budget analysis, in agreement with a previous study with a focus on the Pacific Ocean [*Singh*, 2003]. Even though on a global scale the ocean is a net sink of atmospheric acetone, our model simulations indicate that regionally the ocean can be a source, mainly in the Southern Hemisphere. Our preliminary approach has been tested against measurements within the MANCHOT ship campaign (**M**easurements of **A**ntropogenic and **N**atural **C**ompounds in the southern **H**emispheric **O**ceanic **T**roposphere), which took place in December 2004 over the Indian Ocean.

During MANCHOT simultaneous measurements of the concentration of different organic tracers in the air and in the water have been performed using a PTR-MS (**P**roton **T**ransfer **R**eaction-**M**ass **S**pectrometer) and a GC-MS (**G**as **C**hromatography-**M**ass **S**pectrometer). The measurements, used to evaluate our calculated VOC exchange fluxes, also provide information about the variability of the oceanic VOC concentrations and their correlation with other biogeochemical properties, e.g., chlorophyll or DMS concentrations. Such relationships may be used to develop a more advanced representation of oceanic VOC concentrations in chemistry-climate models, and consequently improve the simulations of VOC air-sea exchanges.

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Dissolved CH_4 and N_2O concentrations during a full tidal Cycle at Wright Myo Mangroves, Andaman Islands, India

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Dissolved CH_4 and N_2O concentrations and nutrients were measured in water collected at a fixed site in a pristine mangrove creek located at Wright Myo, Andaman Isles, over a full tidal cycle during the intermonsoon period (January 2004) and during the wet season (July 2004). In January measured dissolved CH_4 ranged from 282-704 nmol l (11989-27071 % saturation) and N_2O concentrations from 6.0-13.2 nmol l (102- 208 % saturation). Similar ranges in dissolved concentrations were observed in July, dissolved CH_4 concentrations ranged from 324-625 nmol l^{-1} (14422-27608 % saturation) and dissolved N_2O 6.60-10.5 nmol l-1 (127– 168 % saturation). These data demonstrated the creek behaved as an annual atmospheric source for both trace gases. Analysis of these data revealed a laterally sigmoidal trend in temporal distribution of dissolved gas concentrations suggesting a superimposed tidal signal controlled their flux. However the results could not be explained simply in terms of estuarine dilution. A similar trend was seen in the nutrient data. This suggested that fluxes of trace gases and nutrients in mangroves may be a function primarily of tidally controlled hydrostatic pressure with greater concentrations observed at tidal minima and vice versa.

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A Sensitivity Analysis of Gas Exchange Measurements for a Large River Carbon Isotope Mass Balance

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Determining how much terrestrial organic carbon is processed during riverine transport to the coastal ocean is an integral component of the global carbon cycle. Over the past 2 years we have been collecting samples in order to produce a mass balance for bulk carbon and carbon isotopes (^{13}C and ^{14}C) in a 100km stretch of the tidal freshwater Hudson River. In addition to determining how much organic carbon is being processed in the Hudson we are hoping to use the isotopes to ascertain the sources and ages of carbon fueling system respiration by performing an inorganic carbon isotope mass balance. An important part of this endeavor involves quantifying rates of CO_2 air-water gas exchange, which we have been measuring directly using the gradient flux technique in addition to previous studies that have used a purposeful gas addition and the floating dome. The purpose of this talk is to determine how sensitive the DIC and DIC isotope mass balances are to our gas exchange corrections.

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Estimation of transfer velocity using triple oxygen isotopes

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The accurate estimation of transfer of trace gases across air-water interface is required to understand ocean-atmosphere coupling in biogeochemical cycling of material on the earth system. A variety of different parameterizations were proposed to calculate transfer velocity (k). Several empirical equations were developed for k as a function of wind speed using linear, quadratic and cubic relationships. The use of these parameterizations led to k values that may differ by more than a factor of 2. Nevertheless, these estimates have large uncertainties (~30%) resulting in large errors in the flux estimates. We estimated k by a novel method using triple oxygen isotopes. Due to different fractionation mechanisms in the stratosphere (mass-independent) and mass dependent by all processes on the earth surface, such as photosynthesis, respiration, air-sea exchange etc., $\delta^{17}O$-$\delta^{18}O$ relationship of atmospheric O_2 is different from that of mass dependent relationship. This difference is called as $^{17}\Delta$ anomaly. The $^{17}\Delta$ anomaly of dissolved oxygen in the mixed layer is controlled by gross oxygen production (GOP) and influx of O_2 from atmosphere. The former increases the anomaly whereas the latter decreases. Thus, if GOP is known, it is possible to estimate transfer velocity of oxygen using average mixed layer $^{17}\Delta$ anomaly of dissolved oxygen.

We estimated transfer velocity of oxygen in the Sagami Bay, central Japan, using $^{17}\Delta$ anomaly measured in the upper 40m during spring and summer seasons, at 2 hour interval for two days during each season, and GOP was measured using a Fast Repetition Rate Fluorometer (FRRF). The mixed layer $^{17}\Delta$ anomaly was corrected to remove influence of vertical and horizontal advections. The transfer velocity derived by $\Delta^{17}O$ anomaly is grossly consistent with *Wanninkhof* [1992] model. However, anomaly based transfer velocity is higher at lower wind speeds and vice versa that could possibly due to the mixed layer anomaly is an averaged signal over the residence time of oxygen (~one week in case of Sagami Bay); therefore transfer velocity is also a weekly average whereas Wanninkhof model derives instantaneous transfer velocity. This study suggests that weekly to monthly (based on the residence time of dissolved oxygen in the mixed layer) averaged transfer velocity, with reduced errors, can be derived using $\Delta^{17}O$ anomaly and GOP obtained by FRRF in the mixed layer of the oceans.

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CO_2 air-sea exchange and NEP in the Scheldt plume (Belgian coast) over 4 years

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CO_2 partial pressure (pCO_2) of surface seawater along the Belgian coast (from the Scheldt mouth to offshore waters) is measured continuously since September 2000 from an autonomous system deployed on board of the *R.V. Belgica*. In parallel, 30 campaigns were carried on in that area to measure total alkalinity, dissolved oxygen, chlorophyll-a and nutrients (nitrate and nitrite, silicate and phosphate) from January 2001 to October 2004.

We propose then to show the seasonal and annual variability of the CO_2 air-sea fluxes in the Scheldt plume for 4 years (2001-2004) using the different K-Wind speed relationships. To establish, compare and validate a one box LOICZ budget between dissolved inorganic carbon, phosphorus and nitrogen. Finally, to determine the Net Ecosystem Production and calcification with seasonal and annual variability for the outer Scheldt.

Peculiarities in the CO_2 gas exchange during intense nitrogen fixation in the Baltic Sea

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A fully automated system for the determination of the surface water pCO_2 was installed on the cargo ship FINNPARTNER which commutes regularly between the Bight of Mecklenburg in the southwest and the Gulf of Finland in the northeast of the Baltic Sea. Data for more than 150 transects were obtained between June 2003 and October 2004. The seasonal pCO_2 cycle was clearly controlled by biological production and mineralization/deep mixing. Regions with a stable spring/summer thermal stratification were characterized by a pCO_2 minimum in April/May that was due to the spring bloom. A second minimum was observed in July, when the pCO_2 in some regions decreased to levels of 50 – 60 µatm. These extremely low pCO_2 were a consequence of biological production fuelled by nitrogen fixation which is favoured in the Baltic Proper by the low NO_3/PO_4 ratios (approximately 7 - 10) in the winter surface water. The effect of nitrogen fixation on the pCO_2 decrease was enhanced by high C/P ratios (up to 400) in the particulate organic matter and by an increase of approximately 20 % in the dissolved organic carbon. Taking into account these biochemical peculiarities, carbon mass balance calculations which included the CO_2 air/sea exchange were performed for the summer period. The results indicated that the CO_2 gas exchange was overestimated when using current functions for the dependency of the gas exchange transfer velocity on wind speed. We suspect that the formation of surface films impeded the gas exchange and that this effect is not sufficiently taken into account in presently available parameterizations of the transfer velocity.

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Air-Sea Ice-Water CO_2 Balance: the Arctic Ocean

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Climatic changes in the Northern Hemisphere have led to remarkable environmental changes in the Arctic Ocean, including significant shrinking of sea-ice cover in summer, increased time between sea-ice break-up and freeze-up, and Arctic surface water freshening and warming associated with melting sea-ice, thawing permafrost, and increased runoff. These changes are commonly attributed to the greenhouse effect resulting from increased carbon dioxide (CO_2) concentration. The greenhouse effect should be most pronounced in the Arctic where the largest air CO_2 concentrations and winter-summer variations in the world for a clean background environment were detected (www.noaa.gov). Some increased seasonal variation may be a consequence of increasing summer CO_2 assimilation by plants in response to higher temperature and longer growing season . The Arctic Ocean's role in determining regional CO_2 balance has been ignored [Feely et al., 2001], because continuous sea-ice cover is considered to impede gaseous exchange with the atmosphere so efficiently that no global climate models include CO_2 exchange over sea-ice.. However, measurements by Gosink and Kelley in the 1960-70s [Gosink et al., 1976] and our data [Semiletov et al., 2004] showed one year sea-ice was highly permeable to CO_2 at temperatures above –15°C through numerous tiny channels. Mechanism involved in this process has been roughly discussed. In this paper we show that sea-ice melt ponds and open brine channels form an important spring/summer air CO_2 sink that also must be included in any Arctic regional CO_2 budget; both the direction and amount of CO_2 transfer between air and sea during open water season may be different from transfer during freezing and thawing, or during winter when CO_2 accumulates beneath Arctic sea-ice.

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The Air-Water CH_4 Gradient in the Siberian Arctic Seas

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A remarkable coherence seen between measurements of late Quaternary atmospheric methane (CH_4) changes and temperature variations recorded in ice cores suggests that *CH_4 played a significant role in climate change* [IPCC, 2001]. Polar ice cores and marine sediments documents set of interglacial and interstadial episodes marked by dramatic warmings that occurred in just a few decades [IPCC, 2001]. Each of these rapid warmings was closely linked to to a rapid increase in atmospheric CH_4. However, the cause of these rapid warmings have largely remained a mystery. The largest potential sources of CH_4 emission to the atmosphere is natural gas hydrates [Makagon, 1982; MacDonald, 1990]; the *shelf and continental slope reservo*ir is estimated to be roughly 6×10^{18} g (or *6,000,000 Tg*), and the on-shore permafrost reservoir is about 16×10^{18} to 32×10^{18} g. Doubling of the atmospheric methane from present conditions requires release of less than 0.03% of the permafrost hydrate reservoir. Therefore *conversion of a small part of the carbon buried in permafrost might cause a large change in the growth of atmospheric CH_4*. Estimates of the potential gas fluxes to the atmosphere and the timing of these gas fluxes require detailed information on the dynamics of thawing sub sea permafrost and gas hydrate decomposition [Semiletov et al, 2004]. Here we present new CH_4 data obtained over the shallowest and broadest Arctic East Siberian shelf which may indicate that processes of permafrost warming and release of CH_4 from destabilized methane hydrates may already be in progress. Russian literature data are reviewed also to make a full picture for the air-sea CH_4 gradient in the Siberian Arctic seas

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Global Climate Change and Gas Transfer at Water Surfaces in Indian Ocean Region: A study on dynamics of rate of air-sea CO_2 exchange: identification of major dimensions

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The task of calculating The global climate change has caused a serious concern in air sea CO_2 exchange phenomenon and also gas transfer at sea water surfaces besides the significance of anthropogenic pressures and green house emissions at its varying rate. The flux of carbon dioxide (CO_2) between the atmosphere and the ocean has often been considered as two separate problems: to measure or predict the difference in CO_2 concentration across the air-sea interface, which is the thermodynamic driving force for the flux. It is also essential to investigate the rate of exchange, as transfer velocity is a function primarily of wind speed and temperature, but is also influenced by many other minor processes. One of these processes, the enhancement of the exchange rate of CO_2 due to its chemical reaction with water.

A brief overview signified the importance of the global carbon cycle and its role in controlling the climate, the reason behind the intense research effort, which has been directed at this topic for the last 40 years. The present study attempts to explain the gas transfer at water surfaces in Indian ocean with reference to its marine biogeochemistry in order to predict the regional variation as attributed by Indian ocean to global air-sea CO_2 flux, and mention the physical and biological processes which control the thermodynamic parameter, the partial pressure of CO_2 in the surface ocean The study also emphasized the need to consider the effect of intercorrelation between processes in order to make a reasonable estimate of the finely balanced net global air-sea CO_2 flux. The study with its secondary data and data available from review of literature probed into the identification of major determinants that document evidences for gas transfer at water surfaces including its essential parameters that explain the relationship between global climate change and air-sea ocean interaction.

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Seasonal and annual variability of pCO_2 in the North Pacific Ocean Using Satellite Data

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A statistical model of pCO_2 in the sea surface water was proposed based on the extensive field measurements of surface-water pCO_2 in the North Pacific from 1995 to 2001. The model parameters are associated with sea surface temperatiure (SST) and the location information (latitude/longitude) . The monthly distribution of pCO2 in the sea surface water in 1995 was obtained with the spatial resolution of 2^o*2^o. The result was compared with the Takahashi's dataset [*Takahashi,* 2002] and we found the trend of these two results is coincident. But the difference was also found, especially in the eastern portion of the equatorial Pacific which can be considerd as the influence of upwelling in this area. We also analysed the temperature effect and physical & biological effect (such as the change of the mixed layer, upwelling deep-sea water, and biological bloom) on the sea surface-water pCO_2 , and found that the variability of pCO_2 is mainly controlled by physical factors and biological effects in the North Pacific. Finally, the air-sea flux of CO_2 was estamited with the (wind speed)^2 and (wind speed)^3 dependence of the CO_2 gas transfer velocity [*Wanninkhof,* 1992, 1999] based on the satellite data of SST and wind speed, and the flux is also increased if the cubic dependence is used, so the sensitivity to wind-speed variability should be noticed in the future.

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Effluxes of N_2O and N_2 and Nitrogen Cycling in River and Estuarine Sediments of Bothnian Bay (Northern Baltic Sea).

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Baltic Sea is a very special marine ecosystem, as the largest brackish water body in the world. Anthropogenic activity has increased the input of nitrogen to rivers and the Baltic Sea provBaltic Sea is a very special marine ecosystem, as the largest brackish water body in the world. Anthropogenic activity has increased the input of nitrogen to the rivers and the Baltic Sea provoking eutrophication. In river and estuarine sediments, microbial processes e.g. nitrification and denitrification can play an important role in reducing the anthropogenic nitrate load by transforming nitrate to nitrogenous gases N_2O and N_2. From these gases N_2O is an affective greenhouse gas and N_2 is harmless in the atmosphere.

The nitrate reduction and nitrogen cycle was studied with a continuous water flow laboratory microcosm with application of nitrogen stabile isotopes (^{15}N) under different environmental conditions. Samples were collected from an estuary of the River Temmesjoki and from various sites in different rivers entering the Bothnian Bay. The results show that at natural NO_3^- concentrations denitrification removed up to 10% of added nitrate. N_2O/N_2 remained always below 1%. Surprisingly, other processes, reduction of nitrate to ammonium (DNRA) and immobilization to the microbial biomass were found to be prevailing under some specific conditions. The impact of these processes is redundant in concern of reducing the anthropogenic nitrogen load to the Baltic Sea in a long period of time.

Modeling surface renewals

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Soloviev and Schluessel (1994) developed a renewal model for parameterizing the temperature difference across the cool skin and interfacial gas transfer velocity. The more readily available cool skin data were used for an adjustment of the gas transfer parameterization. Extensions of the renewal model included the effects of solar radiation (Soloviev and Schluessel, 1996) and rainfall (Schluessel et al., 1997). In this work, the renewal model has further been extended to include the current velocity difference across the viscous sublayer. The renewal model has also been upgraded to account for the stage of surface wave development. The empirical coefficients that enter the renewal model have been specified more accurately using new field and laboratory data on the cool skin. The coefficient linking the cool skin and gas transfer parameterizations has been determined from the Garbe et al. (2001) probability distribution function for renewal events. At light winds, the renewal model with refined coefficients predicts larger temperature differences across the cool skin and smaller gas transfer velocities compared to the original model of Soloviev and Schluessel (1994). Finally, the renewal model is compared with the gas transfer data collected during the *GasEx-98* and *GasEx-01* field campaigns (Hare et al, 2004) and with laboratory results on wind drift coefficient obtained by Zhang and Cox (2004).

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Estimation of near-surface turbulence and CO_2 transfer velocity from satellite data

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The interfacial gas transfer velocity can be linked to the dissipation of turbulent kinetic energy (TKE) *[Kitaigorodskii and Donelan, 1984]* and its patchiness *[Woolf, 1995]* in the near-surface layer of the ocean. In this work, we explore the possibility of estimating the parameters of near-surface turbulence and the air-sea gas transfer velocity from satellite data. A model of near-surface turbulence provides estimates of the dissipation rate of TKE from wind-wave conditions and air-sea heat/buoyancy flux. The model has been validated with the extended near-surface turbulence data set obtained during the TOGA Coupled Ocean-Atmosphere Response Experiment by Soloviev and Lukas (2003). Preliminary tests have also been done in the RSMAS Air-Sea Interaction Saltwater Tank Facility (ASIST). The model uses the TOPEX POSEIDON wind speed and significant wave height data as input to produce a global distribution of the near-surface turbulence dissipation rate and interfacial component of the CO_2 transfer velocity. An advancement of remote sensing algorithm is possible with the incorporation of directional wind/wave data being available from QUIKSCAT and a now-cast wave model. The satellite data on brightness temperature (SSMI and SAR imagery) provides fractional whitecap coverage, which can be combined with parameterization for the bubble-mediated component of the air-sea gas flux. Due to the high solubility of CO_2, bubble mediated transfer velocity is presumed important only at relatively high wind speeds, which reduce potential errors associated with uncertainties in bubble parameterizations.

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Fluxes of water vapour and CO$_2$ using the dissipation technique

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It is difficult to obtain good data sets of fluxes using the direct covariance technique and other conventional meteorological data in the marine atmosphere since these methods are sensitive to the motion on a ship and flow distortion caused by the large structure of a ship or a marine platform. The measurements are additionally challenging due to the very small fluxes occurring over the marine surface. The inertial-dissipation method is a good alternative to the covariance technique because it relies on measurements at high frequencies, which are not affected by platform motions. Furthermore the method is believed to be less sensitive to flow distortion caused by the ship. The method is best documented for momentum, but has also recently been tested for temperature, humidity and CO$_2$ [*Fairall, et al*, 1990, *Edson et al*, 1991, *Larsen et al*, 2001].

Here we present fluxes of CO$_2$ and water vapour estimated by the dissipation technique and other micro meteorological techniques. The measurements used are obtained from a forest site in Denmark, a coastal site in Sweden, a platform in the North Sea and a ship in the Greenland Sea. The fluxes were measured by three instruments: a Licor, an Ophir and an infrared sensor developed by KNMI (the IFM sensor), using the inertial dissipation method, the covariance and the relaxed eddy accumulation technique. The inertial dissipation method was carried out using the dissipation functions (eq.1 and eq.2).

$$u_* = \left(\frac{f S_u(f)}{\alpha}\right)^{1/2} \left(\frac{2\pi}{\bar{u}} \frac{\kappa z}{\phi_\varepsilon} f\right)^{1/3} \qquad 1)$$

where u_* is the friction velocity, α the Kolmogorov constant (α=0.52), u is the mean wind speed, κ the von Karman constant (κ=0.4), z is the measurement height, ϕ_ε is the stability function and S_u is the spectral value. The spectral value is obtained from the power spectrum of the horizontal wind velocity.

$$\left|\overline{w\gamma'}\right| = \left(\frac{\alpha}{\beta} \frac{\phi_\varepsilon}{\phi_{N_\gamma}} \frac{f S_\gamma(f)}{f S_u(f)}\right)^{1/2} u_*^2 \qquad 2)$$

where γ is the scalar and in both (1) and (2) f is the frequency [Hz] and it is understood that the equations apply to the inertial subrange where the spectra vary as $f^{-5/3}$.

The data analysis shows that water vapour and CO$_2$ fluxes obtained by using the inertial dissipation method compares well to fluxes obtained from other data analysis methods. Problems with the very small CO$_2$ fluxes, close to zero, are not captured when the dissipation method is applied, due to noise limitations. The same noise limitations means that the inertial subrange of the CO$_2$ spectra have to be estimated at frequencies somewhat lower than the assured inertial subrange, leading to the need of a spectral correction.

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Experimental investigation of turbulent boundary layer beneath a wind-driven water surface

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Quantitative properties of turbulent boundary layer beneath a wind-driven water surface are investigated by means of laboratory experiments, which are carried out using a wind-wave tank, 17m long, 0.6m wide and 0.8m deep. Instantaneous streamwise, transverse and vertical velocities in the water are measured at a fetch of 10.75m by using a three-component acoustic Doppler velocimeter, and they are obtained at reference wind speeds of 5.0, 7.5 and 10m/s. Wind speeds and surface displacements are also measured using a Pitot-static tube and capacitance-type wave gauges, respectively.

Power spectra of the velocity fluctuations show that a spectral region in proportion to –5/3 power of the frequency f forms over a frequency range lower than the peak frequency due to dominant waves f_p. Also, the turbulence in ranges $f < 0.1$Hz and $f > f_p$ is found to be anisotropic. It is seen from cospectra of the streamwise and vertical velocity fluctuations that in the region of low wind speeds, most of the Reynolds stress is contained in a lower frequency range than f_p, and that the Reynolds stress around f_p becomes large with increasing the wind speed and is decreased exponentially with increasing the water depth.

Turbulent velocity fluctuations at lower frequencies than f_p are separated from wave-induced velocity fluctuations on the basis of simple cutoff filters. Vertical profiles of the turbulent intensities, the Reynolds stress, the turbulent energy and the turbulent energy flux are obtained from the turbulent fluctuations. These profiles nondimensionalized with the friction velocity and the roughness length on the waterside become independent of the wind speed, i.e., they can be expressed universally. On the other hand, the vertical profiles obtained from the wave-induced fluctuations can be described on the basis of the small-amplitude wave theory.

Taylor's hypothesis enables us to transform frequency spectra of turbulence into wavenumber spectra. The dissipation rate of the turbulent energy is determined by applying a semi-empirical universal spectrum function to the wavenumber spectra. Vertical profiles of the dissipation rate can be expressed universally by using the friction velocity and the roughness length as well as the other turbulent characteristic quantities. The values of the dissipation rate close to the water surface are increased by about ten times those based on the wall-layer scaling. The present data support that the vertical profiles of the dissipation rate agree approximately with a previous empirical relation, which was obtained from field observation data [*Terray et al.*, 1996].

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Variations of whitecap properties with meteorological and wave-field conditions

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Whitecaps play an important role in gas transfer processes across the air-sea interface because of the entrainment of bubbles and the breaking of the interface. Whitecap coverage becomes an effective parameter for estimating the gas transfer velocity and the drag coefficient on the sea surface. The purpose of this study is to investigate how whitecap properties such as whitecap coverage and bubbly layer depth vary depending on meteorological and wave-field conditions on the basis of field observations. The observations were conducted from 11 November to 9 December 2003 and from 13 February to 5 March 2004, at the storm surge observation tower of the Shirahama oceanographic observatory of Kyoto University, which is located in the west region of Tanabe Bay, Wakayama, Japan and 2 km off the nearest coast.

Images of whitecaps were taken every 7 hours in the daytime using a 3CCD digital video camera fixed at 14 m elevation, and they were stored automatically in a hard disk video recorder at a time interval of 1 s. Wind speeds at 23 m were measured using an ultrasonic anemometer at a sampling rate of 10 Hz. An acoustic Doppler current profiler (WAVEADCP) was set on the sea bed at a distance 20 m apart from the tower. Statistical wave characteristics such as the significant wave height, spectral peak period of waves and directional wave spectrum were obtained from the WAVEADCP data. The determination of whitecap coverage was made by means of a digital image processing. The depth of bubbly layer generated by whitecaps was estimated from vertical distributions of echo intensities measured by WAVEADCP.

The present results show that the 1/3 power of whitecap coverage increases linearly with increasing the friction velocity and it is influenced by the near-water air stability. On the basis of the deflection angle between propagating directions of wind waves and swell, wave-field conditions are classified into four cases [*Donelan et al.*, 1997]. Whitecaps are produced most activity under the condition of pure windsea and they tend to be suppressed by the presence of swell. It is difficult to find a certain relation between whitecap coverage and the deflection angle. Explanations about the relationship between the depth of bubbly layer and wave characteristics will be given at the colloquium.

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Estimating air-sea gas exchange using bomb ^{14}C: Revisited

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Wind-speed dependent bulk formulations of gas transfer velocity have traditionally been scaled to the oceanic inventory of bomb ^{14}C (Wanninkhof 1992, Wanninkhof and McGillis 1999). The recent advances in our ability to estimate both the first two moments of global wind-speeds and the inventories of bomb ^{14}C inventories call for a reanalysis of this anchor point as well as an exploration of its implications on oceanic carbon uptake. We present a reanalysis of ^{14}C flux estimates which proceeds from global to regional scales using both the traditional global inventory approach directly from data as well as inverse calculations of oceanic transport which permit us to resolve atmosphere-ocean ^{14}C flux in 10 regions. Using a best fit, in a least squares sense, between 8,000 measurement-based estimates of bomb ^{14}C in the upper 1500 m of the water column and three different configurations of a GCM we see a discrepancy between our inventory and the Broecker et al. (1985 and 1995) bomb ^{14}C inventories used by Wanninkhof (1992) and Wanninkhof and McGillis (1999). Our preliminary results suggest that the average global piston velocity may be over estimated by as much as 25%. However, large discrepancies between data and model-based inversions in surface waters of the high latitudes will need to be further investigated. A regional analysis shows that while total world ocean inventories are similar, there is a large model dependent variation in the location of the bomb ^{14}C surface fluxes. In particular, average surface fluxes of bomb ^{14}C from 1954-1994 are extremely dependent on the model parameterizations picked in the Southern Ocean.

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Heat fluxes across the water surface and the variability of the surface skin temperature: results from a wave tank experiment.

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The ocean skin, the sub-millimeter thick topmost layer of the ocean, constitutes the thermal boundary between the bulk of the ocean and the overlying air. The skin is nearly always cooler than the bulk of the ocean due to heat losses by sensible and latent heat fluxes as well as outgoing longwave radiation. The thin skin layer is often ruptured by breaking waves, boundary layer turbulence, rainfall, and other disturbances but re-establishes itself within seconds. The mechanism of the skin layer formation and maintenance is not yet fully understood. Several theoretical models have been proposed, but there is a lack of experimental data that could differentiate between the models. Since the exchange processes between the air and the ocean, such as heat and gas transfer, occur through this interface, understanding of the properties of the skin layer is crucial for the understanding of the microphysics of air-sea exchanges.

This study investigates the relationship between the heat fluxes across the water surface and the variability of the surface skin temperature (SST). The investigation is based on an experiment conducted in the Air-Sea Interactions Saltwater Tank (ASIST) at the Rosenstiel School of Marine and Atmospheric Science in Miami. Infrared imagery of the water surface was used to study the spatial variability of the surface skin temperature on scales from 0.1 to 30 cm for a range of wind speeds and air-sea temperature differences that produced different heat flux and stability conditions. The measurements covered bulk air-sea temperature differences from -15K to +15K and wind speeds from 0 to 10 m/s. Infrared images of the water surface in the wave tank were taken with an FLIR Systems High Performance Thermal Imaging System SC 3000. The SC 3000 measures in the spectral range of 8 to 9 microns and delivers thermal imagery with a relative accuracy of 0.02K. A full set of turbulence measurements were taken during the experiment to estimate the heat and momentum fluxes across the sea-air interface. Additionally, a suite of other instruments was employed during the experiment to measure parameters that influence the thermal skin layer. These instruments included micro-thermometers measuring temperature profiles through the uppermost tens of centimeters of the water layer and through the surface, hot-film velocimetry to determine the flow fields below the interface, and an accurate infrared spectra-radiometer to measure the skin temperature.

Earlier work (Szczodrak et al. EGU 2004, presentation) showed that the shape of the SST probability distribution function depends strongly on the sign of the air-sea temperature difference and the wind speed. Here we are investigating the shape of the SST probability distribution function in terms of heat fluxes across the skin layer.

A companion presentation (Donelan) shows modeling results.

Enhanced open ocean storage of CO_2 from shelf sea pumping

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Seasonal field observations show that the North Sea, a northern European shelf sea, is highly efficient in pumping CO_2 from the atmosphere to the North Atlantic Ocean. The bottom topography controlled stratification separates production and respiration processes in the North Sea, causing a CO_2 increase in the subsurface layer, which is ultimately exported to the North Atlantic Ocean. The carbon budget of the North Sea is dominated by the exchange with the North Atlantic Ocean, while the net carbon flows are dominated by the carbon inputs from rivers, the Baltic Sea and the atmosphere. The North Sea acts as a sink for organic carbon and thus can be characterised as a heterotrophic system. Globally extrapolated, the net uptake of CO_2 by coastal and marginal seas would be approximately 20% of the world ocean's uptake of anthropogenic CO_2 thus enhancing significantly the open ocean CO_2 storage.

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Seasonal variation of Chlorofluorocarbons saturation in the water of mixed layer in the western North Pacific

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Chlorofluorocarbons (CFCs, CFC-11, CFC-12 and CFC-113) in the surface layer water and marine air were determined in the western North Pacific. By calculating the surface water equilibrium partial pressures of CFCs with respect to the sir, we found CFCs in the surface water were over-saturated (□6.7% for CFC-11, □3.9% for CFC-12 and □4.0% for CFC-113) in the subarctic region in spring and summer. On the other hand, analysis of CFCs data in seawater revealed CFCs in the North Pacific Central Mode Water (NPCMW) were significantly under-saturated respect to the air, suggesting CFCs in the mixed layer in winter has already been under-saturated, because the mode water is considered not greatly influenced by mixing with ambient water after the formation [*Tokieda et al.* 2004]. A result from a simple one-dimensional entrainment model shows the seasonal variation of CFCs saturation in the mixed layer water.

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Effects of bottom shear stress and biological activity on CO_2 flux between air and coastal water

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Wind speed has been regarded as a major factor controlling CO_2 flux between air and water. Some studies, on the other hand, indicated that water current in shallow estuaries or surface micro-layer planktonic activity induces larger CO_2 flux compared with that in the open ocean [*O'Connor and Dobbins* 1956, *Upstill-Goddard et al,* 2003]. However, quantitative analysis of these effects has not been made. In this study, we measured CO_2 flux and transfer velocity in a coral reef and in an estuary using chamber method, and compared the results with vertical turbulence energy (VTE) measured by Acoustic Doppler Velocimeter and with the rate of dissolved oxygen (DO) changes.

The relation between CO_2 transfer velocity and VTE was measured on a coral reef flat and in a river in Isigaki Island, the Ryukyus. Linear correlation was observed between measured transfer velocity and VTE (R=0.99 n=8). Transfer velocity and VTE measured in the coral reef was larger than those in the river. This result is attributable to the difference of sea-floor roughness, and is consistent with a previous study in which increase in CO_2 transfer velocity was explained from the advected shear stress in surface layer generated from the friction between water current and sea-floor [*O'Connor and Dobbins* 1956].

Surface-layer biological effect was examined in a eutrophic lake, Nakaumi, Shimane. Positive correlation was observed between CO_2 flux and rate of DO changes during daytime (R=0.97 n=5). We speculate that this is due to photosynthetic consumption of CO_2 in surface micro-layer, which made the CO_2 concentration gradients larger and therefore enhanced CO_2 flux. But correlation was not observed at night time (R=0.21 n=7). Further study is required for the different relationship during daytime and nighttime.

The average of transfer velocity measured in this study was 7.2 times larger than that calculated from a wind-depending formula (9.2 times for bottom shear stress, 2.9 times for biological activity). Thus coastal CO_2 flux is strongly affected by bottom shear stress or biological activity than wind speed and these parameters should be incorporated into an appropriate formulation calculating coastal CO_2 flux.

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Relationship between free-surface turbulence and air-water gas transfer

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The relationship between the gas transfer velocity and characteristic quantities of free-surface turbulence is investigated experimentally in grid-generated turbulent flows. The horizontal velocity fields at the water surface are visualized using a tracer-particle technique and measured using a particle image velocimetry (PIV). Statistical quantities such as the turbulent energy k_s, the dissipation rate ε_s, the Taylor micro lengthscale λ and the root-mean-square of the surface divergence β_{rms} are obtained from the PIV measurements. The gas transfer velocity for oxygen (O_2) k_L is also obtained through aeration experiments. Furthermore, the process of gas transfer by surface-renewal eddies at the water surface is visualized by using a laser-induced fluorescence technique (LIF), where the carbon dioxide (CO_2) is used as a tracer gas.

The relation between the surface divergence and the statistical quantities can be derived from the definition of the Taylor microscale, i.e.,

$$\beta_{rms}^2 \sim \overline{\left(\partial u'/\partial x\right)^2} \sim \overline{u'^2}/\lambda^2 \sim k_s/\lambda^2 , \qquad (1)$$

where u' is the turbulent velocity fluctuation. The validity of this relation is confirmed by experimental results in this study. Thus, the surface divergence should be expressed in terms of the Taylor microscale. The present results show that the gas transfer velocity k_L is proportional to 1/2 power of β_{rms}, which agrees with previous experimental results for grid-generated turbulence [*McKenna and McGillis*, 2003 and other studies]. Taking into account (1) and the relation $\varepsilon_s = 10\nu_w k_s/\lambda^2$, which is established for homogeneous turbulence and supported by our data, we can inevitably obtain $k_L Sc^{1/2}/k_s^{1/2} \propto Re^{-1/4}$ from $k_L \propto \beta_{rms}^{1/2}$, where ν_w is the kinematic viscosity of water and Re a turbulent Reynolds number defined as $k_s^2/(\varepsilon_s \nu_w)$. This dimensionless expression is found to a certain kind of small-eddy model. In general, the small-eddy model is obtained by assuming that dissipative scale eddies with the Kolmogorov velocity and length control the gas transfer process, while in the above argument on the surface divergence, the Taylor microscale is the scale of turbulent eddies connected with the gas transfer at the water surface. We cannot determine the scale of turbulent eddies from only the Reynolds number dependence of the transfer velocity. In this study, it is seen from the visualization results by LIF that turbulent eddies corresponding to the Taylor microscale stretch and break the CO_2 concentration boundary layer actively. On the basis of both results of PIV and LIF measurements, it is concluded that the Taylor microscale becomes a significant eddy scale for the gas transfer processes at the air-water interface.

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Comparing parameterizations of gas transfer velocity and their effect on the global marine CO_2 budget

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One of the dominant sources of uncertainty in the calculation of air-sea flux of carbon dioxide originates from the various parameterizations of the gas transfer velocity *k* that are in use. Whilst it is undisputed that most of these parameterizations have shortcomings, neglecting processes which influence air-sea gas exchange and do not scale with wind speed alone, there is no general agreement about which parameterizations are most accurate.

The existing parameterizations are based on various non-linear forms of wind speed or friction velocity, on sea surface roughness and, to a lesser extent, on temperature and salinity. Most of these parameters can be retrieved from remote sensing data providing global coverage on daily to monthly intervals. However, the global budgets of carbon dioxide that can be calculated with the help of these data differ substantially in value and meaning depending on the choice of data and equation for the gas transfer velocity. In this work we compare several *k*-parameterizations, employing different types of satellite data in order to obtain a measurement of uncertainty in gas exchange calculations evaluated at both regional and global scales.

We show results based on classic *k*-parameterizations by [*Liss and Merlivat*, 1986], [*Wanninkhof*, 1992] and [*Wanninkhof and McGillis*, 1999] which are all primarily based on wind speed. These are then compared with results based on two newer parameterizations. The first one by [*Woolf*, in press] relates the gas transfer velocity to friction velocity and significant wave height. The second parameterization by [*Glover et al.*, 2002] uses sea surface roughness obtained by an altimeter operating at dual frequency to calculate the gas transfer velocity. Both of these approaches have an advantage over the classic wind-speed based parameterizations; they rely on parameters which should be more directly linked to gas exchange than wind speed, since they have the potential to incorporate effects of natural surface films, boundary layer instability and wave fetch on air-sea gas exchange.

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Quantitative Visualization of CO_2 Gas Transfer at a Turbulent Free Surface.

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Using a laser induced fluorescence (LIF) technique with a pH-sensitive fluorescent dye we directly visualize the water-side physics of CO2 transfer across a free surface. Coupling this technique with particle image velocimetry (PIV), we investigate the contributions of turbulent transport to the gas transfer process in a free surface facility with bottom-generated turbulence. The subsurface turbulence is created by a novel method using an actively driven synthetic jet array, which provides less mean flow than a comparable grid-stirred tank. Results show that the dominant surface structures for gas transfer are concentrated downwellings, rather than the upwellings modeled in surface-renewal theories. Several statistics of near surface eddy-concentration correlations are computed to help guide refined theories. The technique, facility, and results will be discussed for roughly equal amounts of time.

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Air-Sea CO_2 Fluxes in the Caribbean Sea

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A major goal of international ocean carbon research is to determine regional fluxes on seasonal timescales to assess the magnitude and changes in atmospheric CO_2 uptake by the ocean. This effort requires sustained observations of surface pCO_2 as well as a means to interpolate the observations in time and space. A pilot study was initiated in the Caribbean Sea to investigate an approach to reach this goal. From a combination of weekly shipboard measurements of surface water pCO_2 and remotely sensed parameters, weekly flux maps have been created for the Caribbean Sea for the past three years. The pCO_2 measurements were performed on the cruise ship Explorer of the Seas operated by the Royal Caribbean Cruise lines who have installed an oceanographic laboratory on this ship.

For each year a correlation between pCO2 and SST is established using temperature data from the thermosalinograph located near the seawater intake on the ship. This relationship is then combined with the regional 1 by 1 ° weekly temperature data assimilated using *in situ* observations and AVHRR temperature data [*Reynolds, 2002*] to create weekly pCO_2 fields. These pCO_2 fields are combined with wind speeds from the SeaWinds sensor on QuikSCAT to estimate the weekly regional fluxes. The data from 2002 and procedures are detailed in Olsen et al. [2004]. Here we augment these results with observations from 2003 and 2004 and discuss the differences between the years. The algorithms between pCO_2 and SST are very similar for the 3 years and regional pCO_2 fields showed little difference except for local anomalies caused by episodic changes such as passage of hurricanes. Fluxes show greater interannual variability due to changes in wind speeds.

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ASIP: Air-Sea Interaction Profiler

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In order to enhance our understanding of the factors controlling the air–sea fluxes of heat and gas, it is necessary to make a suite of contemporaneous measurements at the ocean surface from a single platform. The Air–Sea Interaction Profiler (ASIP) is an autonomous profiling instrument whose objective is to zero in on the close interplay of physical, chemical, and biological processes at the ocean surface and their respective roles in air-sea exchange. Although the primary focus of the instrument is within the upper 10 m of the ocean, it can profile to a maximum depth of 100 m to include mixed layer measurements. Autonomous profiling is accomplished with a dual counter-rotating thruster, which will submerge ASIP to its programmed depth. At this point the thruster will switch off, and the positively buoyant instrument will ascend to the surface, acquiring data along the way. The sensors on ASIP include: shear (x2) to estimate rates of dissipation; temperature (x2) for microstructure and stratification; conductivity (x2) for microstructure and density; oxygen for chemical gradients in the water; fluorescence/transmissivity for chlorophyll and water clarity; video microscope for high-resolution images of biological species and bubbles. Other measurements are pressure, rate and acceleration, and heading. ASIP also contains an iridium/GPS antenna, which allows real-time reporting of its position between profiles. Power is provided with 6 lithium-ion batteries which can supply up to 1000 Whr during a single deployment. The measurements from ASIP are well suited to enhancing research on air-sea interfacial and near surface processes.

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Parameterizations of bubble-mediated gas transfer; fundamental principles and a laboratory test

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Gas transfer mediated by bubbles is characterized by an altered dependence on the molecular properties of the dissolved gas compared to direct transfer across the main air-water interface. These characteristics can potentially be used to infer the relative importance of bubble-mediated transfer. The dependence of bubble-mediated gas transfer on the solubility and molecular diffusion coefficient of the dissolved gas is derived from first principles. For an unknown bubble population, it is not possible to predict the exact dependence but useful characteristics can be inferred. For gas exchange between a concentrated near-surface bubble plume and a water volume, three asymptotes can be identified. A semi-empirical parameterization of bubble-mediated gas transfer is devised on the basis of these asymptotes.

It is possible to take measurements of the gas transfer coefficients of a number of gases of known solubility and diffusivity and invert the data to produce a partition of direct and bubble-mediated data on the basis of an assumed model of the dependence of bubble-mediated transfer and of direct transfer on these molecular properties [*Asher et al.,* 1996]. It is generally difficult to independently validate the results of this "properties method", since in most experimental settings there is no alternative partition method. Another method of separating direct and bubble-mediated transfer is available in laboratory experiments that use artificial aeration, by manipulating the composition of gases supplied to the aeration devices. This latter method requires no assumptions about the dependence of either transfer route on molecular properties of the gas, but only assumes that net transfer across any air-water interface will be simply proportional to the partial pressure difference of that gas across the interface. This "partial pressure method" - which was first used in a small annular wind-wave tank [*McGillis et al.,* 1995] - is adapted to a large wind-wave tank. Experiments are conducted in which the source of the input to the aeration devices is switched from within the headspace above the tank to outside air. This switch should make no difference to transfer across the main air-water interface; therefore, the perturbation to the time series of dissolved gases at this point indicates a role for bubble-mediated exchange. Transfer coefficients for both direct and bubble-mediated transfer are inferred. These results are compared with results based on the "properties method". The success of inversion by the properties method depends on both the model chosen and the availability of accurate data for gases with a range of molecular properties. In some cases, small errors in individual gases can produce large errors in the implied partition by the properties method. It is particularly difficult to separate transfer mediated by very large bubbles from direct transfer unless data for a sufficiently soluble gas is available. In general, some caution must be applied to partitions based on inversions based on dependence on molecular properties.

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Scaling Gas Transfer with Turbulent Dissipation for a Range of Environmental Processes

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For sparingly soluble gases, theory predicts that the gas transfer velocity, *k*, is controlled by turbulence in the surface aqueous boundary layer, which dictates the rate at which gases can be brought into contact with the surface to exchange with the atmosphere. Since gas transfer has been shown to scale with wind-generated turbulence in many field and laboratory wind-wave experiments, wind-based relationships to model *k* are typically used for gas exchange estimates from the open oceans to estuaries and rivers despite the acknowledged role of physical processes not related to wind (e.g., tidal currents, rain, stratification, surfactants, and water depth). In an effort to explicitly relate turbulence near the surface aqueous boundary layer to gas exchange, models have been developed for *k* based on the turbulent kinetic energy dissipation rate, ε. A fundamental relationship shows *k* scales with $(\varepsilon\nu)^{1/4} Sc^{-n}$, where the Schmidt number, *Sc*, is defined as the ratio of the kinematic viscosity of water, ν, to mass diffusivity. The Schmidt number exponent *n* is believed to vary between ⅔ and ½ depending on the surface boundary conditions. This expression for *k* based on ε is consistent with mass diffusion across a layer of the thickness of the *Batchelor* [1959] scale [*Melville*, 1996], and has been derived by *Lamont and Scott* [1970] using surface-renewal theory [*Danckwerts*, 1951] and also has been derived by *Kitaigorodskii* [1984] in the context of modeling the influence of patches of enhanced turbulence by breaking

Here, measurements will be presented on the turbulent dissipation rate using acoustic techniques and gas transfer velocity using micrometeorological and active controlled flux techniques in the coastal ocean, a macro-tidal river estuary with wind and tidal forcing, a large tidal freshwater river, a model ocean, and wind-wave tanks. The results clearly show that gas transfer under wind, waves, currents, rain, and surfactants indeed scales with the hypothesized model based on the turbulent dissipation rate over a wide range of environmental systems with different types of environmental forcing and processes. The effects of bubbles are considered for the case at high winds in the coastal ocean when the gas exchange was enhanced relative to the model based on turbulence.

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Fluxes of DMS and CO_2 over Antarctic pack ice

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Sea ice formation characterizes the polar regions, ranging in extent from 17.5 × 106 to 28.5 × 106 km2. At its maximum, sea ice covers 13% of the Earth's surface, thus being one of the largest biomes on Earth. Sea ice research over the past decades has resulted in our understanding of many of the physical processes that transform surface waters into a matrix of ice and liquid, and the role this has on large scale processes, such as ocean circulation and air-ocean exchange. Beneath the snow and between floes lie unique habitats that appear to be highly productive during spring and summer and are thought to make a major contribution to global sulfur and carbon cycling. Little is known about physical processes specific to the pack ice environment and its role in gas exchange with the atmosphere. We will present results of the recent Ice station Polarstern (ISPOL) cruise conducted from November 2004 to January 2005. The objective of our study was to quantify the exchange of DMS and CO2 over pack ice in relation to snow and lead water characteristics.

Fluxes of DMS and CO2 were measured by micrometeorological techniques and showed an increase from late spring to early summer. Sea water was supersaturated with CO2 resulting in an efflux towards the atmosphere. In contrast, air in the snow that covers pack ice was undersaturated with respect to the atmosphere, leading to a net deposition of CO_2.

Extremely low concentrations of DMS were found in lead waters surrounding floes. However, a detailed study of near-surface water showed a strong increase of DMS towards the surface, with values at the surface over a magnitude higher than in deeper water. Such stratification was also found in salinity and results indicate an increase of biological activity towards the top layers of the water column.

Air in snow contained 5 ppb to 60 ppb DMS but becomes completely depleted of DMS as snow properties change. In spite of high concentrations of DMS with respect to the overlying air (with DMS concentrations typically in the ppt range), only a very small flux is apparent from snow-covered areas.

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The partial pressure of carbon dioxide and air-sea fluxes in the northern South China Sea: seasonal variation and its possible controls

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Ocean margins play an important role in the global oceanic carbon cycling. Despite of many efforts devoted into the field through major international programs such as JGOFS, the air-sea fluxes associated with ocean margins remain largely uncertain (Fasham et al., 2001). Some researchers argued that mean net CO_2 absorption of the world shelf waters might be on the order of 0.4-1.0 Gt C per year (Tsunogai *et al.*, 1999; Thomas et al., 2004). However, it is important to realize that most of the studied shelves are located at middle-latitude, where biological processes play a significant role in uptaking the atmospheric CO_2. In order to examine the potential difference between different latitudinal regions, air-sea CO_2 flux studies associated with the tropic and subtropical shelf waters are required to be strengthened in order to better constrain the source/sink terms of margins at a global scale (Cai & Dai, 2004).

The South China Sea (SCS) is the world largest tropic and subtropical marginal sea. It is also a typical oligotrophic marginal sea with low biological productivity. Since 2000, we have conducted 7 cruises in the region, which include 5 shelf surveys and 2 basin surveys. The five shelf surveys covered 4 seasons. Nearshore $p\mathrm{CO}_2$ showed a very dynamic pattern due to the influence of river plumes and upwelling. For the offshore region, $p\mathrm{CO}_2$ ranged between 320 and 450 µatm and varied within a narrower range. During most surveys other than Oct 2003 and Feb 2004, the offshore surface $p\mathrm{CO}_2$ values were higher than atmospheric $p\mathrm{CO}_2$. A compilation of all of the $p\mathrm{CO}_2$-based CO_2 sea-air flux estimations in the South China Sea, including an earlier survey along the eastern boundary of the SCS during the summertime by Rehder & Suess (2001) suggest that on an annual base, the outer shelf of the northern South China Sea overall acts as a moderate or weak source of atmospheric CO_2 with uncertainty associated with the potential annual variability. Most field $p\mathrm{CO}_2$ data of ours at the same show that distributions and seasonal variation of the SCS surface $p\mathrm{CO}_2$ were mainly influenced by the variation of SST (Zhai et al., 2005). This study thus reveals that low latitude ocean margins may indeed behave differently as compared to mid-latitude and eutrophic shelves.

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Air-Sea surface CO_2 gas transfer velocity: A Review

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With the development of the measurement technology and the increase of the field experiments, it is known that the air-sea surface CO_2 gas thansfer velocity could be parameterized by wind speed. Based on the comparation of the different models of CO_2 gas transfer velocity, the Tans-90 [*Tans*, 1990] gives the highest value and the LM-86[*Liss*, 1986] the lowest value. At high wind speed the presence of bubble increase the gas transfer, the whitecap coverage has the important effect on the transfer velocity. Monahan [*Monahan*, 1986] gave the cubic relationship between the windspeed and the whitecap coverage, which is coincident with the Win-99 [*Winninkhof*, 1999]. At low to moderate wind speed, the surface roughness seems to be a good parameter because of the surface film. The whitecap coverage influences the brightness temperature of radiometer and the sea surface roughness can be obtained by scatterometer and altimeter. Remote sensing is a good data source to study the variability of the transfer velocity with high spatial and temporal resolution. By using the Win-92 and Win-99 model and the Quikscat wind speed, we analyse and discuss the annual variablity of the gas transfer.

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