

# EFFECTS OF BREAKING WAVES ON AIR-SEA GAS TRANSFER (LUMINY)

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## 1. INTRODUCTION

Gases such as carbon dioxide, methane and nitrous oxide have been identified as important greenhouse gases. Other gases are important for climate because of their role in cloud formation (e.g., dimethylsulphide or DMS) or in chemical reactions involving ozone (e.g., methyl bromide). The oceans act as a reservoir for such gases, providing both a source and a sink. For poorly soluble gases, the exchange between the ocean and the atmosphere is slow. The rate of exchange of each gas is expressed in an exchange coefficient, the air-sea transfer velocity, which (at least for poorly soluble and unreactive gases) depends on molecular and turbulent transfer in the sea surface micro-layer. The value of air-sea transfer velocities and their dependence on environmental conditions is only known approximately [Liss and Merlivat, 1986; Watson et al., 1991; Wanninkhof, 1992]. Breaking waves are a major but as yet poorly understood factor.

Most theories of the transfer of gas across the marine micro-layer are based on in the description of transport in a turbulent shear layer. Consideration of shear-produced turbulence alone appears mistaken when in most sea conditions wave breaking will greatly influence the character of sub-surface turbulence [Kitaigorodskii, 1984]. In the parameterisation of gas transfer velocities proposed by Liss and Merlivat [1986], a "wave breaking regime" at wind speeds greater than 13 m/s is transposed from wind tunnel results. However, there is no *prima-facie* evidence to suppose that wave breaking will be unimportant at moderate wind speeds (much less than 13 m/s).

Three quite distinct mechanisms of gas transfer are associated with large-scale wave breaking and air entrainment:

- (1) Transfer associated with patches of turbulence in the upper ocean generated by breaking waves [Kitaigorodskii, 1984].
- (2) Transfer mediated by bubbles, where gas is within a bubble during an interval of its exchange between atmosphere and ocean [Merlivat and Memery, 1983].
- (3) Transfer across the sea surface where the micro-layer has been disrupted by bubbles bursting at the sea surface [Monahan and Spillane, 1984].

The principal aim of the LUMINY project is to understand and quantify the effect of breaking waves on gas transfer through the sea surface micro-layer in terms of environmental parameters that are routinely available (e.g., wind, atmospheric stability and sea state) and in terms of satellite measurements (e.g., radar backscatter and microwave brightness temperature). The results will be used to develop parameterisations that can be used to better incorporate the influence of the oceans in global climate models, and to relate satellite observations to gas exchange. Breaking waves have a distinct remote sensing signature from other sea surface roughening and the parameterisation of effects of breaking waves could be combined with remote sensing information for global measurements of air-sea gas exchange.

## 2. APPROACH

The major driving force in the exchange of gases between the water surface and the atmosphere is the difference in concentration (or partial pressure)  $dC_x$  of gas  $x$  between the atmospheric and oceanic compartments, or the deviation of these concentrations from their values at oceanic equilibrium concentrations with the atmosphere. The constant of proportionality, or exchange coefficient  $K_x$ , in these flux calculations is the factor that needs parameterisation:  $F = K_x \cdot dC_x$ . In the field it is usually difficult to measure, control and observe the combination of parameters that influence the mass transfer coefficient  $K_x$  across the water-atmosphere interface. However, in laboratory experiments the governing parameters can be controlled. Thus the individual processes can be simulated in an idealised situation and the effects on the transfer coefficients of parameters like wave height, bubble fluxes, wind velocity and air and water temperature can be determined. The influence of individual parameters or combinations of parameters can be deduced by varying each of these in turn.

A series of experiments, supported by a strong modelling effort, was carried out in the large air-sea interaction simulation tunnel of the Institut de Recherche sur les Phénomènes Hors Equilibre, Laboratoire Interactions Océan-Atmosphère de Luminy (IRPHE-IOA) (Marseille, France) [Bonmarin and Ramamonjiarosa, 1985]. In the tunnel, a quite realistic, mature wave field including breaking waves was generated by a combination of mechanical wave generation and wind stress. Further, whitecaps were simulated with bubbles generated using a submerged grid of aeration devices.

A number of test gases were introduced in the water or in the air and their concentrations were measured to accurately determine the respective effects on gas transfer between air and water: carbon dioxide ( $\text{CO}_2$ ), nitrous oxide ( $\text{N}_2\text{O}$ ), methane ( $\text{CH}_4$ ), dimethyl sulphide (DMS), methyl bromide ( $\text{CH}_3\text{Br}$ ), 4-helium ( $^4\text{He}$ ) and sulphur hexafluoride ( $\text{SF}_6$ ). These gases offer a wide range of solubilities and molecular diffusivities. The dimensionless Henry's Law constants (air/water) vary from 230 for  $\text{SF}_6$  to 0.14  $\text{mol} \cdot \text{dm}^{-3} \cdot \text{atm}^{-1}$  for DMS and the molecular diffusivities from  $6.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for He to  $1.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for DMS.

Modelling is central to developing the chief, final products - an improved parameterisation of air-sea gas transfer velocities, and a practical algorithm - by combining our findings with models of breaking wave frequency, and other gas transfer mechanisms. Models are developed to describe the physics of the observed processes and understand their relevance for climate. Bubble-mediated transfer inferred from the measurements will be compared to estimates from the measured bubble distributions and theoretical transfer coefficients. Also, a semi-empirical model of gas transfer rates is applied to the measured gas transfer velocities with terms describing the theoretical dependence of transfer on the solubility and molecular diffusion constant of the gases in the water, and coefficients determined by fitting the model to the measurements. Modelling is also required to determine the effect of differences between laboratory and field conditions (e.g., the flux and dispersion of small bubbles).

## 3. RESULTS

Two experiments were conducted in the IRPHE-IOA Large Air-Sea Interaction Simulation tunnel. A pilot experiment was carried out during three weeks in September 1996, as a preparation for the Main Experiment from the third week of February until the first week of April, 1997. Different conditions were established in the tunnel as regards reference wind speed, the use of paddle-generated waves and the use of bubbles. Some of the conditions were repeated several times.

### Gas exchange

The gas exchange rates were determined from the variation of the concentrations in the water and in the air using three different methods. An analytical model was developed at TNO that describes the exchange of gas between the water and air sections of the tunnel and the leakage from the air section to the laboratory [Kunz, 1998]. After determination of the tunnel leakage rate with this model, it was applied to  $\text{CO}_2$  data. As shown in Figure 1, the model appears to describe the transfer rates well, even though chemical buffering was not accounted for. The effect of chemical reactions in the water phase on the gas transfer rates, as determined with the analytical model, still need to be determined.

A four-reservoir model was developed that not only takes into account the leakage of the tunnel head space to the laboratory, but also exchange between the laboratory and the atmosphere. In addition, to account for the chemical buffering in the water phase, data on the pH and total inorganic carbon (TIC) are used to determine the  $\text{CO}_2$  exchange coefficients.

Results assembled on  $N_2O$  show that both the paddle wave and the bubbles generated artificially with the aeration devices do enhance the gas transfer velocity over that measured with wind waves alone. The effect of the artificial bubbles is larger than the effect of the paddle wave, leading to the conclusion that wind velocity alone does not well represent the gas exchange process in the wind wave tunnel.

The third effort considers only the concentrations of the gas in the water phase, and its time evolution as determined by the concentrations in the water and in the air. Pairs of invasion experiments with the aeration devices fed sequentially from outside of the laboratory and from the head space were conducted for four different combinations of wind, waves and bubble flow rate. As an example, time series of  $C_a$  and  $C_w$  for He and  $SF_6$  for such a paired experiment, at 2.5 m/s wind speed, are presented in Figure 2. The analysis of such data shows that there is a very striking difference in behaviour between very poorly soluble gases (e.g., sulphur hexafluoride and helium) and more soluble gases (e.g., methyl bromide).

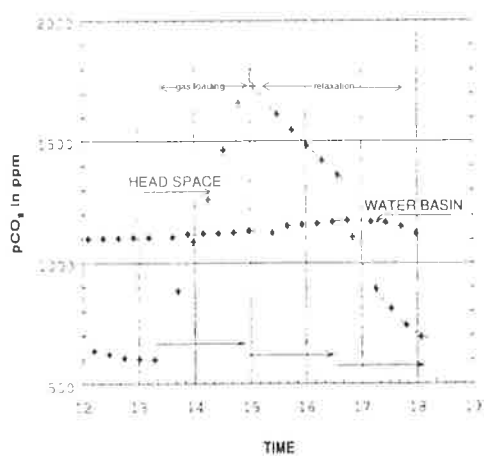


Figure 1: Gas concentrations calculated from the analytical model (solid lines) and measured gas concentrations (symbols) in the head space (+) and in the water (◆). Data of 28 February 1997.

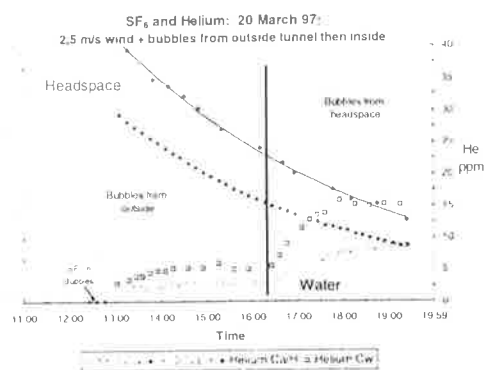


Figure 2. Concentrations of He and  $SF_6$  in water and in air, measured at a wind speed of 2.5 m/s. The lhs panel shows data obtained with bubbles aerated with air from outside the tunnel air space, in the rhs panel the air is aerated from the tunnel head space

## Wave breaking

The effects of bubbles and turbulence will be related to wave breaking properties. A strong effort has been made to characterise wave breaking and wind stress [Caulliez et al., 1998], to determine whitecap coverage, and to study properties of bubbles and bubble plumes. As illustrated in Figure 3, the wave breaking rate appears to be closely related to the friction velocity  $u_*$ , irrespective the wave conditions at the surface. This somewhat surprising result suggests that at high wind speeds in the tunnel the turbulent momentum transfer processes throughout the air surface boundary layer are to a large extent controlled by breaking phenomena at the water surface.

## Bubbles

Bubble size distributions were determined with different optical techniques that were later compared and intercalibrated in a separate laboratory experiment at TNO-FEL. The bubble video imaging system (BVIS) was used, among others, to monitor characteristics of bubble plumes resulting from waves breaking at fetches from 17.5 m to 25 m. Enormous variety was observed from plume to plume in regards to bubble density, plume physical dimensions, the intensity and extent of both structured and unstructured turbulence, and induced fluid flows

leading to diverse evolutionary paths. An example bubble plume is shown in Figure 4, illustrating structured turbulence and the high bubble density within the plume.

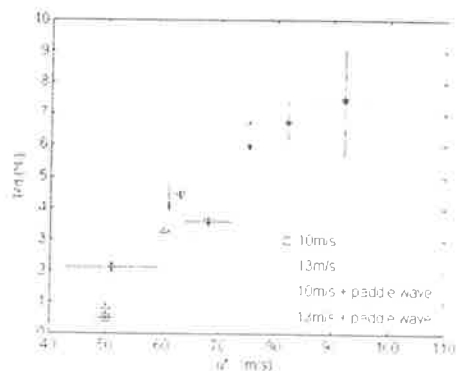


Figure 3. Wave breaking rate  $R_d$  versus friction velocity  $u_*$ , for wind speeds of 10 and 13 m/s with and without mechanical wave generation.

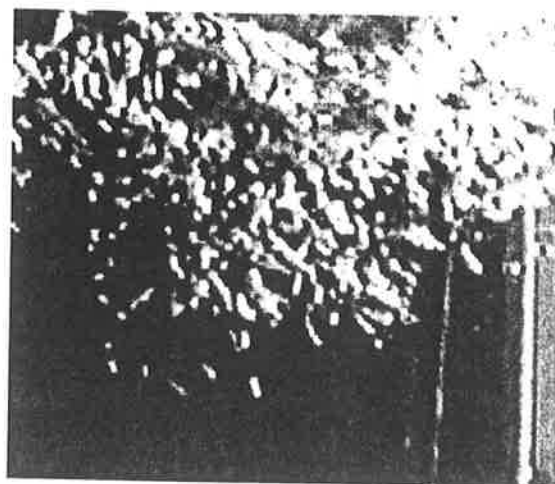


Figure 4. Bubble plume image

#### 4. CONCLUSION

Effects of breaking waves are quantified through laboratory experiments in the IRPHE-IOA Large Air-Sea Interaction Simulation tunnel. The effects of bubbles and shear-generated turbulence on gas exchange are determined from combinations of experiments under controlled conditions. The analysis of the wave data has resulted in a better understanding of the effect of shear on breaking waves. Extensive results are available on transfer rates of climatologically relevant gases, in combination with wave breaking results, friction velocities, bubble size distributions and bubble plume characteristics. Methods have been developed to measure bubble plumes and size distributions, and initial attempts have been made to apply these techniques at sea. Models are being developed to describe the air-sea transfer processes and to eventually develop parameterisations that can be used in climate models and in remote sensing algorithms.

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