A FLUORESCENCE TECHNIQUE TO MEASURE CONCENTRATION PROFILES IN THE AQUEOUS MASS BOUNDARY LAYER

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Abstract. A laser-induced fluorescence (LIF) technique has been developed to measure vertical concentration profiles of dissolved gases in the aqueous mass boundary layer at a wavy interface. An optical wave follower is used to track the surface with a CCD camera. Time series of vertical concentration profiles with a temporal and spatial resolution of 2 ms and $30\,\mu m$, respectively have been measured in the circular wind/wave facility at the Institute for Environmental Physics, University of Heidelberg at low and medium wind speeds. From these time series, mean vertical profiles are computed. The mean boundary layer thickness and the transfer velocity are determined. The latter is compared with oxygen transfer velocities obtained by the classical mass balance method. The boundary layer shows substantial variations in thickness. The time series also reveal large eddies sweeping parts of the boundary layer down into the bulk.

1   Introduction

Despite significant experimental and theoretical efforts the mechanisms controlling the transfer processes across a gas-liquid interface are only superficially understood. It is still state-of-the-art to use various mass balance methods to determine mean flux densities across the interface. Unfortunately these techniques do not give much insight into the mechanisms. It is, for example, impossible to distinguish large-scale eddy (surface renewal) models from multi-stage eddy diffusivity models with these techniques even if the Schmidt number dependency is measured by multitracer experiments (Jähne *et al.*, 1989).

Thus there is an urgent need for the development of new measuring techniques that perform measurements within the aqueous mass boundary layer. This paper describes a laser-induced fluorescence (LIF) technique that measures vertical concentration profiles within the aqueous mass boundary layer with very high spatial and temporal resolution. The fundamentals of the technique used here have already been described in earlier papers: Jähne (1991) and Jähne (1993). Here we present the first experimental results.

2   The aqueous mass boundary layer

The transfer of moderately soluble and slowly reacting gases is controlled by a thin aqueous mass boundary layer. This layer is only $20 - 200\,\mu m$ thick, roughly one order of magnitude less than the viscous sublayer. Mass transport

through this layer is described as an interplay between molecular and turbulent processes. Boundary layer models describe the turbulent transport part either by a turbulent diffusion coefficient (K-model) caused by small eddies (see e.g. Coantic, 1986) or by statistical renewals of the surface layer by large eddies (SR-model) (see e.g. Münnich and Flothmann, 1975). Without any assumption about the transport mechanism one can define the transfer velocity, k, and the characteristic vertical length scale (*boundary layer thickness*) z_*:

$$k = \frac{j}{\triangle C}; \quad z_* = \frac{\triangle C}{\frac{\partial C}{\partial z}\big|_{z=0}} = \frac{D\triangle C}{j} = \frac{D}{k} \quad (1)$$

The transfer velocity is given as the ratio of the flux density, j, and the concentration difference between the very surface and some suitable reference depth. At the very water surface Fick's first law is obeyed and transport is caused only by molecular diffusion. Measurements of the mean concentration profile within the aqueous mass boundary layer give a direct measure of the boundary layer thickness and, according to eq. 1, the transfer velocity. In contrast to mass balance based measurements of the transfer velocity, vertical profile measurements can distinguish different conceptual models, since they result in different profiles (Jähne *et al.*, 1989, see also figure 4).

3   Principle of concentration measurements within the aqueous mass boundary layer

High-resolution concentration profile measurements at the water surface require non-contact optical techniques. So far, exclusively laser-induced fluorescence techniques have been used. While Wolff *et al.* (1991) measured oxygen profiles via the quenching of fluorescence by oxygen, the technique used here effectively replaces the flux of the gas across the boundary layer by a flux of a fluorescent pH indicator. This has the advantage of a significantly better signal to noise ratio compared to the oxygen quenching technique.

Using such a system requires that the fluorescent light be directly proportional to the concentration of the tracer transported through the aqueous mass boundary layer. The simplest chemical system that meets this requirement is a buffer solution containing both forms of a pH indicator, indicated here as HR and R$^-$, in equal concentrations. The following equilibrium holds:

$$\frac{[H^+]\,[R^-]}{[HR]} = K_i \quad (2)$$
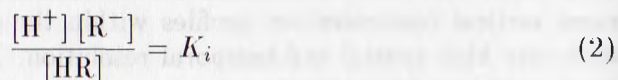
where K_i is the equilibrium constant of the fluorescent indicator. The transfer process is initiated by injecting traces of an alkaline or acid gas, e.g. NH$_3$ or HCl, into the air space of a wind/wave flume. The gas is quickly transported to the air-water interface, where it promptly dissociates. At the very water surface the R$^-$ gets instantaneously protonated into HR. This process constitutes a sink for R$^-$ and a source for HR resulting in a concentration difference across the aqueous mass boundary layer (see figure 1). Using the left hand part of eq. 1
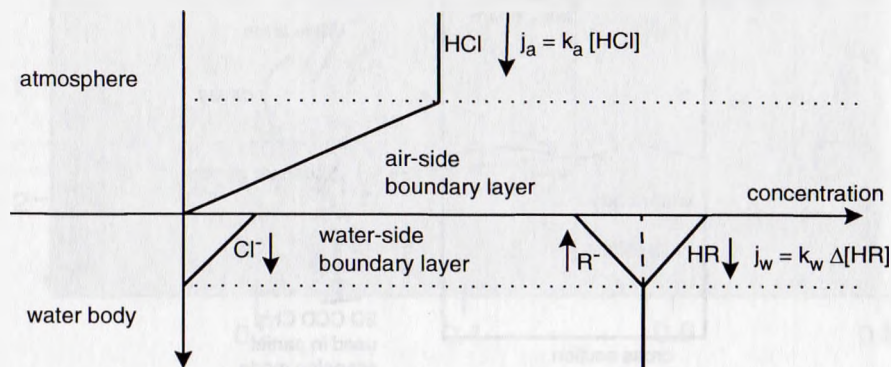
Fig. 1. Schematic representation of the vertical concentration profiles at the air-water interface, when HCl is absorbed by a buffer solution.

the flux density is therefore given by

$$j_w = k_w \, \Delta[\mathrm{HR}] = -k_w \, \Delta[\mathrm{R}^-] = j_a = k_a[\mathrm{HCl}] \tag{3}$$

The H^+ concentration adjusts in such a way that the chemical equilibrium is maintained everywhere, but since HR and R^- are much more abundant than H^+ (at least two orders of magnitude) no significant concentration changes for HR and R^- occur due to this reaction. In conclusion, HR and R^- behave in the bulk like an inert gas tracer except for a different molecular diffusion coefficient. The R^- concentrations are obtained by measuring the intensity of the fluorescent light, which is proportional to the concentration of the fluorescent anion (Münsterer, 1993).

4   Measurements

Measurements were performed in the circular wind/wave facility at Heidelberg University. This facility consists of a 30 cm wide and 70 cm high gas-tight annular channel with an outer diameter of 4 m. Wind is generated by a rotating paddle-ring driven by 24 small DC motors. The channel is filled up to a height of 25 cm; the water and air volumes are 0.88 and 1.6 m^3, respectively.

Fluorescein was added to the deionized water (conductivity $< 1\,\mu\mathrm{S}$) to form a $2 \cdot 10^{-5}$ M solution which was titrated to its buffer point at pH 7 (to obtain equal concentrations of HR and R^-, see eq. 2). At the beginning of each experiment about 2.5 – 3.5 N cm^3 of HCl were injected into the air space resulting in an initial concentration of about 2 ppm. Fluorescence was excited by a 20 mW argon ion laser focussed on the water surface by a 200 mm lens resulting in a diameter of the illuminated spot of about 0.3 mm. An optical wave follower was used in the optical path of the CCD-camera (figure 2) to track the water surface with an accuracy better than 1 mm. More details of the experimental setup
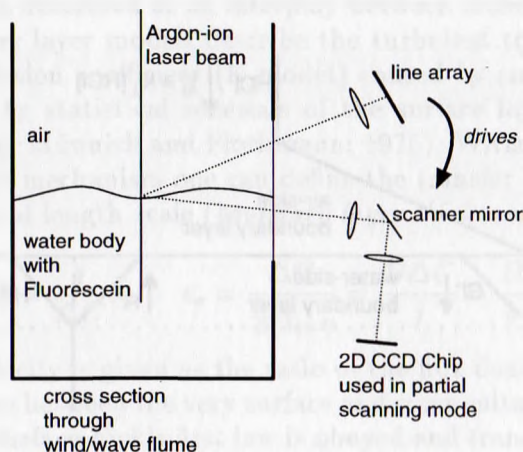
Fig. 2. Sketch of the experimental setup with optical wave follower and imaging CCD-camera.

are described Münsterer (1993). The CCD-camera took images of a 0.3 mm (horizontal) x 6.6 mm (vertical) sector at a rate of 600 frames per second.

These image sectors were averaged over the horizontal width of 0.3 mm in order to integrate the fluorescence intensity over the whole width of the laser beam. The resulting columns were stacked to form so called space-time images. One of those space-time images consists of 8000 single concentration measurements or 13.3 s.

5   Results and Conclusions

Figure 3 shows a 0.8 s long part of a space-time image at 2.4 m/s wind speed. By using digital image processing techniques it is already transferred into a z-coordinate system relative to the moving water surface (Münsterer, 1993). The aqueous boundary layer is visible as a thin dark layer at the top of the image. The boundary layer thickness shows fluctuations in time. Such fluctuations were also reported by Wolff (1991) although not as a time series with comparable time resolution. At about 0.3 s part of the boundary layer is swept into the bulk.

Averaging over such an image results in a mean boundary layer profile. Figure 4a shows such a profile together with the theoretical profiles for the K- and SR-model. The measured profile seems to agree better with the mean concentration profile predicted by the SR-model. The deviation of the measured profile from the predicted linear profile right at the water surface is caused by the still limited resolution of our optical system of about 30 μm.

The experiments were performed together with classical oxygen mass balance measurements. Figure 4b shows a comparison of the results. The mean boundary layer thickness is systematically measured too high by the LIF technique. This deviation is obviously caused by the limited resolution and difficulties in detecting the water surface with image processing techniques. Therefore further improvements in the system's resolution are required.
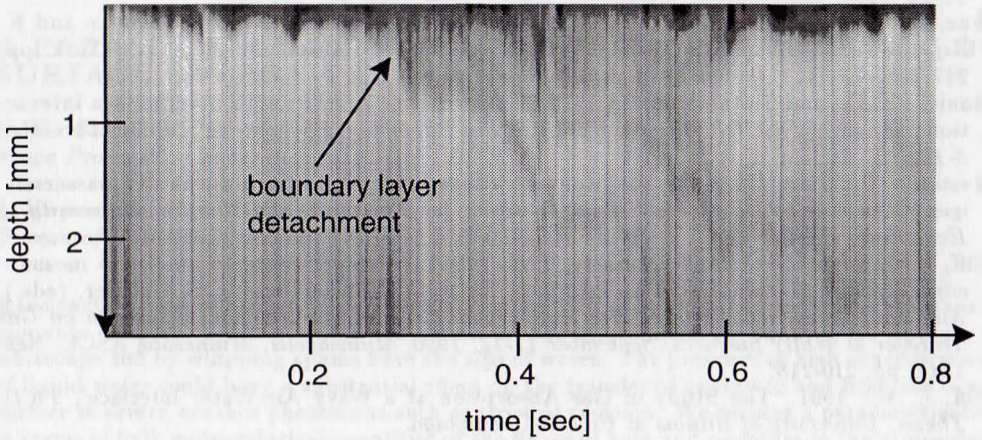
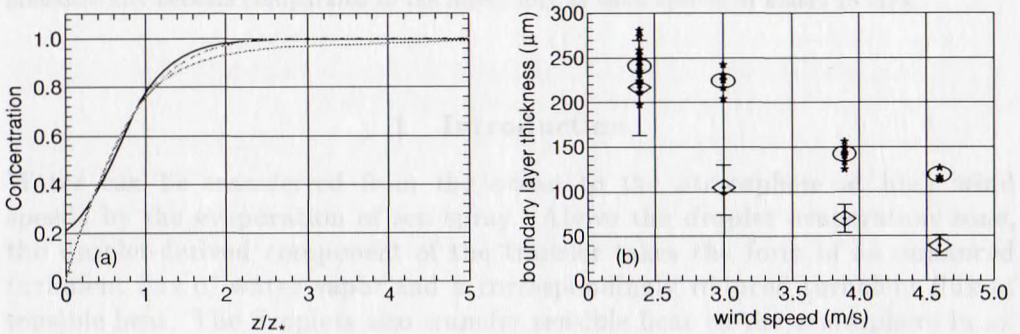Fig. 3.   Space-time image in the frame of reference of the moving water surface.

Fig. 4.   a) Comparison of a measured mean concentration profile (black solid line) at 2.4 m/s with the theoretical predictions of the SR-model (grey dashed line) and the K-model (grey dotted line). b) Measured boundary layer thicknesses for different wind speeds. Stars denote single measurements averaged over 13.3 s, ovals stand for the average over all these single measurements for one wind speed and diamonds show the result of the simultaneous oxygen invasion measurements.

6   Acknowledgements

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