

A LABORATORY TECHNIQUE FOR INVESTIGATING THE RELATIONSHIP
BETWEEN GAS TRANSFER AND FLUID TURBULENCE

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ABSTRACT

A technique has been developed to simultaneously measure fluid turbulence and gas exchange rates across an air-water interface. Instantaneous fluid velocity vectors are determined using a streak photography method. From these vectors, turbulent velocities, length scales, dissipation rates, etc. are evaluated. Gas transfer rates are measured concurrently. Experiments have been conducted in the laboratory by generating turbulence in a tank with a vertically oscillating grid whose stroke length, frequency, and distance from the interface are adjustable. Preliminary results using five gases (O_2 , N_2 , CH_4 , CO_2 , and Rn) indicate that the data are consistent with surface renewal and energy dissipation models of gas exchange.

INTRODUCTION

Gas transfer across an air-water interface is presumed to be controlled by molecular and turbulent processes. Consequently, an understanding of the physics of gas transport and the development of predictive models of gas exchange requires knowledge of fundamental relationships between gas exchange and the parameters characteristic of these processes. Considerable research effort has been devoted to studies of the relationship between gas exchange and molecular diffusivity. Unfortunately, the functional dependence of gas exchange rates on molecular diffusivity which different investigations have observed spans the entire range predicted by various theoretical models. The lack of agreement is generally believed to be due to the uncertainty in the measured values of the molecular diffusivities of the gases. Turbulent processes, characterized by eddy motions, transport fluid parcels with differing gas concentrations from one depth to another. Functional relationships between turbulent parameters (e.g. velocity, integral length scale, energy dissipation rate, etc.) and gas transfer have been based upon theoretical principles and empirical data (see Brtko and Kabel, 1978, for a review). However, the lack of concurrent direct measurements of both the requisite turbulent parameters and gas exchange rate has hindered model verification. To circumvent this problem, an experimental apparatus was constructed which enables concurrent measurements of characteristic turbulent parameters and gas exchange rates.

METHODS

Measurement of Turbulence

Turbulent velocities and length scales are determined by streak photography, using an approach similar to one described by Dickey and Mellor (1980). Inert, neutrally buoyant particles of Pliolite VT (Goodyear Chemical Co.) are

added to the water column and illuminated with a high intensity Hg-vapor lamp in a darkened room. Particle diameters of 0.35 mm yield good streak images and are small enough to follow the pertinent scales of motion. Streak photographs are taken with a 35 mm camera equipped with a variable focal length zoom lens. The zoom lens enables the camera to be located at long distances from the plane of illumination which reduces distortion due to refraction. A zoom setting of 105 mm and an image distance of approximately 2 m is used for all experiments. Exposure times are controlled by an opaque rotating wheel with a cutout window, which chops the light beam at a pre-set rate, and are measured with a photodiode and counter-timer. A piece of mylar is placed asymmetrically within the chopping wheel window to create photographic streak images consisting of short and long bright sections, separated by a dim section.

Particle displacement vectors (magnitude and direction) are determined from the lengths of the resulting streak images and the orientation of the short and long sections. Measurements of streak lengths are performed by projecting 35 mm negatives onto a photodigitizing table (~ 60 cm x 40 cm) and digitizing the streaks. The precision of the instrument is 0.1% for lengths of 1 cm or greater. Conversion of the streak images to true distance is accomplished by measuring all streak lengths relative to a set of fiducial points. The photographic distance between fiducial points is calibrated to true distance by photographing a target board of known dimensions which is suspended in the plane of illumination prior to each experimental run. Approximately 20,000 streak images are digitized for each experimental run. Velocities are evaluated by dividing displacement vectors by exposure time.

Computation of the Turbulent Parameters

The photographic section is divided into a computational matrix consisting of 5 horizontal and 18 vertical elements of ~ 9 cm by ~ 2 cm and the streak images falling in each element are used to compute the turbulence parameters for the element. The lateral (x-direction) and vertical (z-direction) mean velocity components are computed by ensemble averaging instantaneous values within each computational matrix element. Fluctuating components are determined using Reynolds decomposition. The three-dimensional turbulent flow field is deduced from the two-dimensional photographs assuming isotropic turbulence in the horizontal plane. Earlier studies by Dickey (1977) and Dickey and Mellor (1980) with a stereoscopic system support this assumption. The horizontally averaged turbulent kinetic energy then may be written as

$$\frac{q^2}{2} = \frac{\overline{u'^2} + \overline{w'^2}}{2} \quad (1)$$

Two point parallel turbulent velocity correlations are computed by a method described by Dickey and Mellor (1980). Briefly, the turbulent velocity vectors for a pair of streaks are resolved onto a line connecting the midpoint positions of each, yielding the parallel velocity components. The product of these two components is computed as a function of the separation distance between the pair. This procedure is repeated for all possible pairs and a normalized correlation function, $f(r)$, is computed. The turbulent integral length scale is computed from

$$L = \int_{r=0}^{\infty} f(r) dr \quad (2)$$

where r is the mean separation distance. Errors in these turbulence parameters are introduced primarily by the number of streaks digitized (i.e., sample size) and are estimated to be $\pm 15\%$ (see Dickey, 1977, for error analysis technique). Values of a turbulent Reynolds number ($Re_L = qL/\nu$) and energy dissipation rate ($\epsilon \propto q^3/L$) are also computed from the turbulence parameters. The latter expression is taken from Mellor (1973).

Determination of Gas Exchange Rate

Gas exchange rates are determined by a disturbed equilibrium method. Tank water concentrations of the gases to be measured are perturbed from equilibrium prior to an experiment and gas transfer coefficients are computed by measuring the rate of return to equilibrium. The time rate of change in the tank water is given by:

$$\frac{dC_w}{dt} = -\frac{K_L}{h} (C_w - C_o) \quad (3)$$

where C_w is the water concentration (mass/volume), C_o is the equilibrium saturation concentration (mass/volume), K_L is the gas transfer coefficient (length/time), h is the water depth, and t is time. Assuming no change in the overlying gas phase through time, the solution to equation (3), with the boundary condition $C_w = C_i$ at $t = 0$, is :

$$\ln \left(\frac{C_w - C_o}{C_i - C_o} \right) = -K_L t/h \quad (4)$$

The gas transfer coefficient is readily computed from the slope of the best-fit line on a semi-log plot of $(C_w - C_o)/(C_i - C_o)$ versus time.

At present, this technique is being used to examine the dependencies of gas exchange on molecular diffusivity and fluid turbulence for the special conditions of internally generated turbulence. Turbulence is generated in a plexiglas tank (62 cm × 62 cm × 76 cm) with a vertically oscillating grid (Fig. 1). The advantages of generating turbulence by this method are that isotropic turbulence can be generated in the horizontal plane and that previous studies on the characterization of fluid turbulence have employed similar arrangements, thereby enabling a comparison with earlier work. The grid is 61 cm square and consists of two planes of stainless steel rods (1.0 cm O. D.) with a mesh size of 5 cm. The position of the grid in the tank, grid oscillation frequency, and oscillation stroke length are all adjustable, which enables the generation of different turbulent flow fields. The interface was intentionally unperturbed (i.e. virtually no surface waves); hence wave, aerosol, and bubble gas transport processes were insignificant. Clearly these effects may be important in natural systems, particularly in high wind conditions, and shall be the focus of future experiments in wind-wave tunnels. Currently, the exchange rates of five gases are measured during each experiment.

Prior to an experimental run, tank water concentrations of O_2 and N_2 are reduced to approximately 50% of saturation by stripping with helium. Concentrations of CO_2 , CH_4 , and Rn are elevated above saturation by bubbling CO_2 and CH_4 gas through the water and by the addition of water high in Rn activity. The water is adjusted to a pH of 3.5 to 4.0 to eliminate the effect of chemical reaction on CO_2 transport. Tank water is stirred after these procedures to insure homogenization. Grid oscillation is then initiated. A typical experimental run lasts 4 to 6 hours. Water samples are drawn every 20 minutes for O_2 , N_2 , CO_2 , and CH_4 and every hour for Rn . Water salinities and temperatures are nearly constant for all runs, ranging from 33°/° to 36°/° and 18°C to 21°C, respectively. Samples are drawn from several depths in the tank during early runs and the dissolved gas concentrations are found to be homogeneous throughout the tank.

Dissolved O_2 , N_2 , CO_2 , and CH_4 are measured by injecting 1 ml water samples into a Swinnerton stripper, connected in series with a dual-column, dual detector gas chromatograph (Carle Inst. Co. Model AGC 311). Oxygen, N_2 , and CH_4 are measured immediately after sampling using a 3/16" × 8' molecular sieve 5A column at 48°C. Carbon dioxide analyses are run on a 1/4" × 6' chromosorb 101 column at 55°C. Water samples for CO_2 analyses are drawn sep-

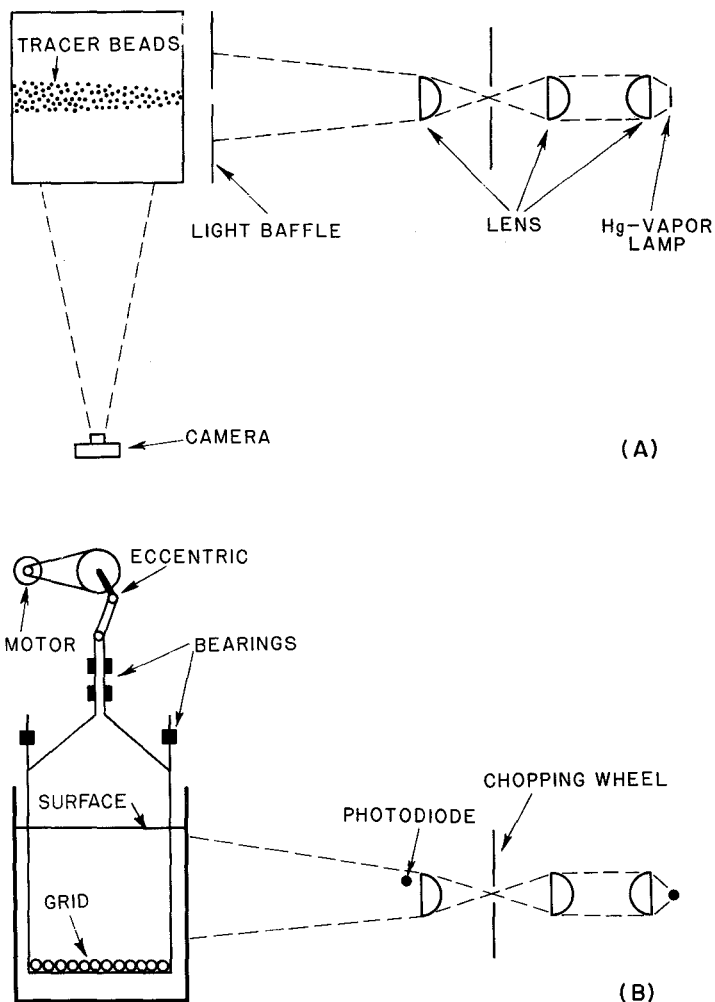


Fig. 1: Schematic diagram of the turbulence tank apparatus used for the gas exchange experiments. A. Top view. B. Side view. Grid not shown in top view. Tracer beads not shown in side view.

arately and stored in glass syringes for 5 to 24 hours prior to analysis. To prevent exchange during storage, syringe tips are stuck into rubber stoppers immersed in water, and the assemblies are stored in a refrigerator. Chromatographic peaks are recorded on a two-pen chart recorder (Houston Inst. Co.) equipped with a disk integrator. For some runs, peak areas are measured on a photodigitizer. Gas concentrations are computed from the area under the chromatographic peaks. Analytical precision of the gas analyses is $\sim 3\%$ as determined by replicate analyses. Dissolved radon concentrations are determined by stripping 25 ml water samples with helium, passing the gases through a drying column (CaSO_4) into an evacuated cell, and alpha counting in scintillation chambers. Water samples are generally stripped within minutes of sampling. Analytical precision for these analyses is $\pm 5\%$.

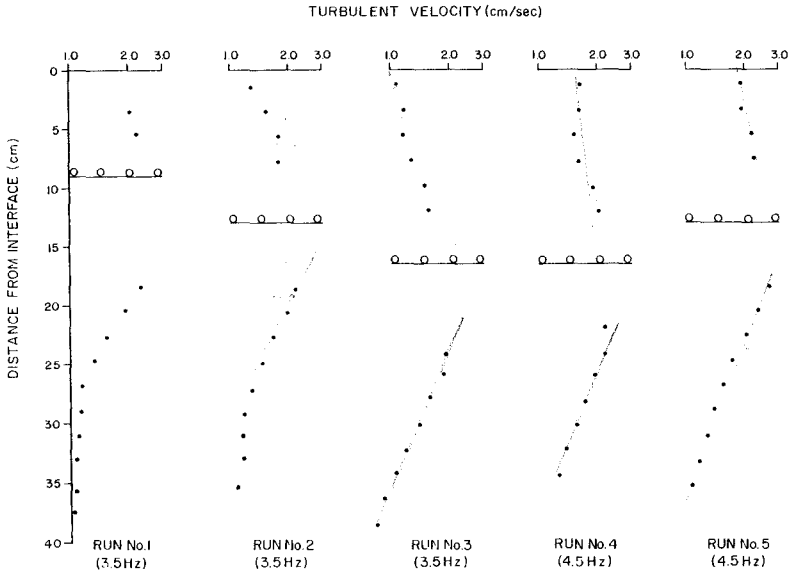


Fig. 2: Vertical profiles of turbulent velocity versus distance from the interface. The grid location is indicated by the lines with circles. The stroke length is 6 cm for all runs and the grid oscillation frequencies are shown in parentheses beneath run numbers.

RESULTS

Fluid Turbulence

Streak photographs have been taken and the fluid turbulence has been characterized at five different grid settings. The conditions were chosen to fall within the range of measured values of gas exchange in natural systems and to insure minimal disturbance of the surface. Profiles of the turbulent velocity (see Eq. 1) are shown in Fig. 2. As expected, turbulent velocity decreases with distance from the grid in all experiments. The profiles may be reasonably fit by simple exponential relationships for distances < 20 cm from the grid, but over the entire water column are better described by a power law function. The range of power laws computed for these experiments below the grid are comparable to values obtained from previous experiments (e.g. Hopfinger and Toly, 1976). The decay of turbulence above the grid is not as rapid as below the grid as illustrated by the slope of the profiles. Additionally, the values for a given distance away from the grid are larger below the grid. The reason for these effects are not obvious, but probably are due to the influence of the interface on the turbulent flow above the grid. The effect of the interface may be to homogenize the energy throughout the upper portion water column, and thus the observed energy and velocity profiles above the grid are more uniform than below.

Profiles of the integral length scale are presented in Fig. 3. Below the grid, the length scale increases linearly with distance. The slope of the

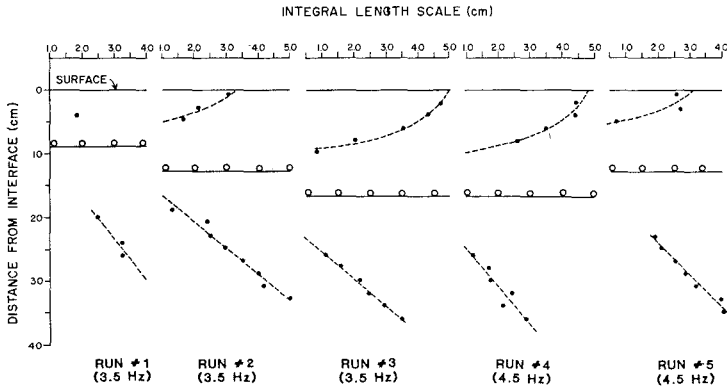


Fig. 3: Vertical profiles of integral length scale versus distance from the interface. The grid location is indicated by the lines with circles.

best-fit line is relatively constant for all runs ranging from .15 to .23. These slopes are close to slopes observed by Thompson and Turner (1975) and Hopfinger and Toly (1976). Above the grid, the dependence appears to deviate from a linear relationship. A less rapid increase near the surface is consistent with the concept of the flattening of eddies near a boundary (e.g. Thomas and Hancock, 1977, and Hunt and Graham, 1978). The vertical fluctuating velocity is approximately one-half the horizontal fluctuating velocity within a distance of the order of the integral length scale away from the surface. This is in general agreement with the theory of Hunt and Graham (1978) and the experiments of McDougall (1979). Turbulent length scale appears to depend only upon distance from the grid, as illustrated by the similar values and profiles for experiments conducted at the same grid position (runs #2 and #5; runs #3 and #4). Stroke length (here 6 cm) is probably also important, however this dependence was not investigated. The similarity of the profiles of q and L obtained from all runs and the agreement of the measured parameters with theoretical principles of turbulence and with earlier studies incorporating similar systems are evidence supporting the validity of this technique for characterizing fluid turbulence.

Dependence of Gas Exchange Rate with Fluid Turbulence

Characterization of the gas exchange rate in terms of the fluid turbulence requires selection of the relevant turbulence parameters. In the preliminary analysis which follows, it is assumed that the eddies controlling gas exchange are those closest to the interface. Furthermore, it is assumed that these eddies are characterized by the turbulent velocity, q , and the integral length scale, L . Estimates of the values of these parameters at the interface are obtained by extrapolating the observed profiles to the interface. This procedure is straightforward for q , since the functional dependence of this parameter with distance from the grid is clear. However, estimation of L is more subjective, because of the uncertainty in the dependence of L with z above the grid. Thus, estimates for L are obtained by drawing a curve through the data based upon a best visual fit (Fig. 3). The values obtained by this approach are within 10% of values obtained from a simple linear fit to the data.

Dimensional analysis of the observed molecular and turbulent parameters indicates that the transfer coefficient may be proportional to $[D_m(q/L)]^{1/2}$ where D_m is the molecular diffusivity of a given gas. This is identical in form to the relationship given by the surface renewal models of gas transfer proposed by Higbie (1935), and later by Danckwerts (1970), where the surface renewal rate is given by $s = q/L$. Fig. 4 shows this relationship for the

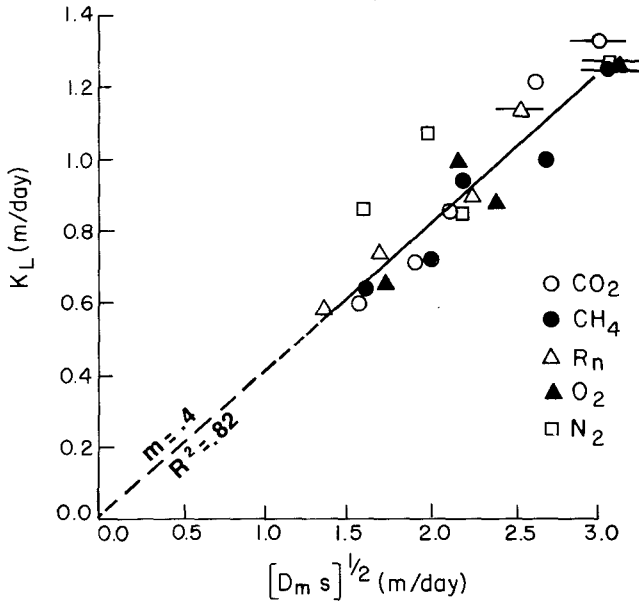


Fig. 4: Relationship between the gas transfer coefficient and the square root of the product of molecular diffusivity and surface renewal rate. The solid line shows the least square fit to the data, (m is the slope, R^2 the correlation coefficient) and the dashed portion is the extrapolation of this line. Horizontal bars are drawn through data points from Run #1 and indicate the range of values for this run.

measured transfer coefficients. Lamont and Scott (1970) suggested that the gas transfer coefficient is proportional to the square root of the molecular diffusivity and to the one-quarter power of turbulent dissipation rate. Data obtained from our experiment are also consistent with this formulation (Fig. 5).

CONCLUSION

The present experimental techniques appear to enable quality measurements of fluid turbulence and gas exchange. Preliminary experiments suggest that the surface renewal and energy dissipation models of the gas exchange rate give reasonable descriptions for a system with internally generated turbulence which has minimal interface deformation. Application of the approach described herein to other systems, such as wind-wave tunnels, should improve our understanding of the relationship between turbulence and gas exchange.

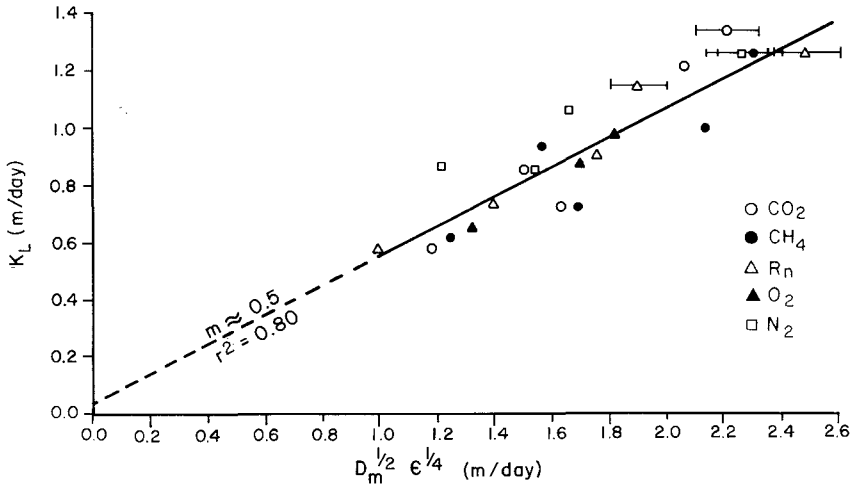


Fig. 5: Relationship between the gas transfer coefficient and the functional form of the energy dissipation model of Lamont and Scott (1970).

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