International Symposium on Gas Transfer at Water Surfaces

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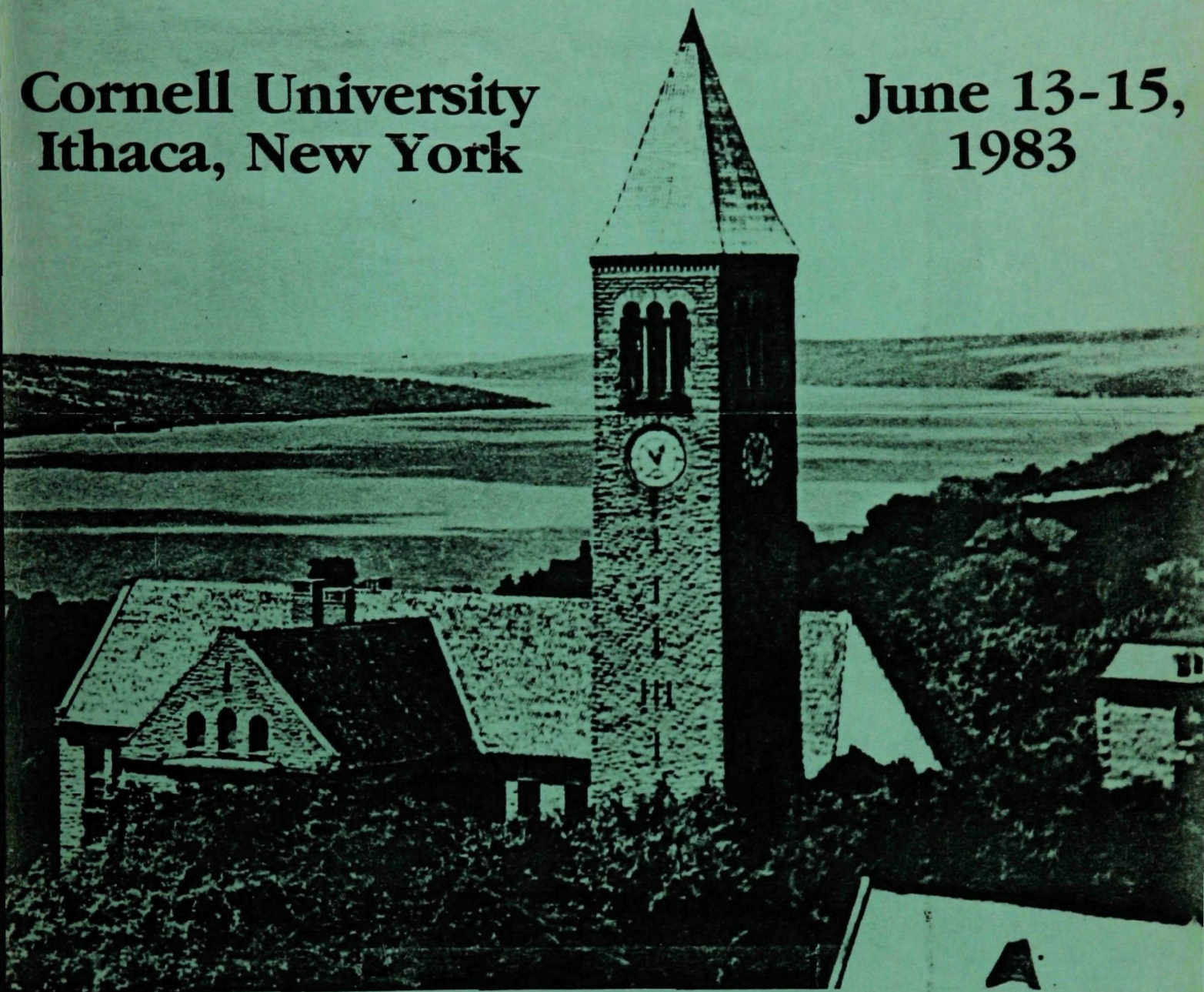
International Symposium on
GAS TRANSFER AT WATER SURFACES

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Editors' Notes: 1) Abstracts are arranged in alphabetical order by
name of first author.
2) This constitutes the first part of the Symposium
Proceedings. The second part will consist of
completed manuscripts that will be referred prior
to publication by D. Reidel Publishing Company.

THE IMPACT OF SURFACE ACTIVE AGENTS ON MASS TRANSFER

By

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The method in which surface active organic compounds interfere with mass transfer across the gas-liquid interface has long been a concern of practitioners in waste treatment. The phenomena causes a significant decrease in transfer efficiency in many systems and therefore. negatively influences the economics of waste treatment. Engineers have, over the last several decades, directed many efforts to understanding this phenomena. To-date, very little progress has been made in presenting a satisfactory explanation of system behavior.

The coefficient alpha, α, has been employed to define the relative transfer efficiency in water containing impurities as opposed to the transfer rate in pure water. Alpha have been shown to vary from waste to waste and even with different aeration devices in the same waste. Values of alpha from 0.35 to 1.6 have been reported by various investigators. Alpha has been observed to change during treatment and generally tends to rise as treatment reactions remove organics from solution.

In order to better understand the phenomena, it is necessary to examine the nature of the mass transfer coefficient K_1a. K_1a is equal to the liquid film coefficient K_1 multiplied by the area, $\not{A}$ through which transfer occurs divided by the tank volume. The liquid film

coefficient and the surface area available for transfer are directly effected by the presence of surface active agents. The paper explores in detail the effect of this relationship.

The liquid film coefficient K_1 has been expressed in a variety of manners by different investigators. The principal phenomena which influence the coefficient appear to be the diffusivity of the solution and the thickness of the film at the liquid-gas boundary. The film thickness is, of course, significantly affected by the accumulation of molecules at the surface. This phenomena being directly related to their surface activity. The diffusive properties of the solution may also be affected by the presence of organic materials. Surface tension is one method of estimating the relative build up of materials in the surface layer. Investigations show, that the rate at which material accumulates in the surface and their tendency to be surface active rather than be dispursed in the system is a function of the nature of the material. The manner in which surfaces tension is measured must reflect this dynamic relationship to accurately relate to the system.

The presence of surface active agents in a system also affect the relative area available for transfer. This is accomplished in a bubble system by decreasing the average size of the bubble that will be produced at a given air flow under fixed conditions of pressure. In an aeration system where surface aeration is the principle mechanism, it can also be shown that the actual surface configuration is altered by the the presence of surface active materials. The degree to which a given surface active material will affect the surface configuration of

an aeration system is a function of the aeration device and the particular surface active material. Furthermore, it can be demonstrated that the same surface active material under different turbulence conditions will have a significantly different effect on the surface generated.

Combining the two part impact of surface active materials, it is possible to describe in a general fashion the forces controlling alpha in a dynamic situation. This behavior model is useful in estimating the type of aeration system which will be least impacted by various materials. The model does not totally define the phenomena but does provide a significant additional insight into this complex surface reaction.

DETERMINATION OF NITROGEN AND OXYGEN MASS TRANSFER BY GAS CHROMATO-GRAPHIC TECHNIQUES

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The purpose of this study was to determine the reason for preferential nitrogen absorption during aeration, and to determine what was needed to prevent excessive nitrogen supersaturation.

This problem was first approached by a theoretical analysis which suggested that preferential nitrogen absorption results primarily from the lower nitrogen solubility in water as compared to oxygen, and that it is aggravated by the use of small air-water ratios.

The remainder of the study was devoted to experimentally testing this hypothesis and consisted of two phases: i) development of a rapid assay method for simultaneous determination of dissolved nitrogen and oxygen, and ii) a study of aeration with mixed gases in a U-tube.

Preferential nitrogen absorption is prevented by employing high air-water ratios and low pressures during aeration. The experiments performed in this research do much to clarify the situation investigated and show that the U-tube aeration of clear liquids can be explained both qualitatively and quantitatvely on the basis of available transport theory.

An accurate in situ gas chromatographic technique was developed for simultaneous determination of dissolved gases in water. Samples were prepared by exposing known volumes of helium carrier gas to the water under analysis across a non-selective Silastic membrane in tubular form. The membrane diffusion cell was incorporated into the sampling circuit of either a Carle 8515 or a Carle 2153 gas chromatograph.

Response of the system to dissolved gas partial pressure is linear and interference between the gases is negligible. The standard deviation of individual measurements from the expected value is about 0.5 percent for both nitrogen and oxygen.

The average liquid phase mass transfer coefficients for oxygen and nitrogen are not significantly different. A 15 meter long U-tube served as the experimental mass transfer device allowing photographic techniques in the evaluation of gas-liquid two phase flow.

Experimental mass transfer efficiencies were in good agreement with predictions based on observed flow patterns and the surface stretch mass transfer model of Angelo and Lightfoot (1968).

VELOCITY FIELD BELOW SURFACE GRAVITY WAVES

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Waves are an expression of surface energy and provide information concerning surface layer dynamics. Although in the upper mixed layer of the ocean turbulence can be generated by many mechanisms, breaking surface wave is one of the dominant mechanisms. Because the turbulent energy is a controlling factor in the determination of mixed layer depth, drift current, surface wave damping, etc., it has become a central subject of investigation in the study of ocean surface layer dynamics. The purpose of this study is to measure the velocity field beneath surface waves and define the statistical properties of the flow field as a means to understand the surface layer turbulent structure.

Experiments are conducted at the NASA Wallops Island Wind Wave Research Facility. The wind wave tank (Figure 1) has a test section 20 m in length and a cross section 1 m in width by 1.25 m in depth. Its operational water depth is 0.75 m with the remainder for airflow. The wind is generated by a suction fan and recirculating ducts. The tank is also equipped with a hydraulic powered, servo-controlled paddle wave maker. During these experiments, both paddle and wind generated waves are studied.

The water surface elevation is measured by capacitance probes which provide a linear response with surface elevation changes. The water velocity field is measured by a two channel backscatter laser Doppler anemometer system. A 4-watt argon laser provides adequate signal to noise ratio and allows separate light frequencies to be employed for the vertical and horizontal (long channel) velocity measurements. Because the wave flow field has reversing velocities, Bragg cells are employed to remove flow direction ambiguities. The tank water is seeded with 2-micron silicon-carbine particles and typical data rates are 200-800 samples/sec.

Wind wave velocity fields are complex systems that can be represented as the sum of a mean drift current, wave orbital components and turbulence. The turbulence component can be produced by the vertical shear of the mean current, and surface wave breaking. To quantify these various mechanisms, two experiment series are being conducted in which (a) sinusoidal or random waves with a fixed frequency distribution but varying amplitude are generated, and (b) fixed amplitude random waves with increasing wind stress. Because a velocity measurement as a function of time includes all the various components which can not be individually measured, their quantification depends upon numerical data reduction techniques. The mean velocity is defined as the record time average. We employ wave theory and surface elevation data to decouple the wave component from the velocity spectra such that the residual spectra are employed as estimates of the turbulence spectra. Cross spectra will be employed to examine the phase relationship between the horizontal and vertical velocities. Preliminary data from the paddle wave and the wind wave study which show general trends which we intend to examine further are included here.

The paddle wave study is designed to investigate wave velocity fields in which horizontal mean currents are minimized as a turbulence generating mechanism. A series of random wvae experiments with increasing amplitude (Figure 2) has been conducted. Figures 3 and 4 show that while the mean horizontal and vertical velocities are small, the surface waves exert a stress which decays with depth and also increases as the wave slope increases. Figure 5 displays a typical comparison of a measured horizontal spectrum and velocity spectra computed from the surface elevation spectrum and wave theory. Three frequency ranges can be identified in Figure 5: (1) low frequency tail, (2) wave dominated region, and (3) high frequency tail. Review of velocity spectra data show that the low frequency tail grows in amplitude as the wave slope increases and it decays slowly with depth. The wave dominated region decays exponentially with depth and "reddens" with depth as shorter wavelengths decay more rapidly than the longer wavelengths. Figure 6 shows a typical pro-file of turbulence spectra. The vertical scale on these turbulence spectra suggest that the velocity power spectrum prediction must be accurate to the order of 0.1% if it is provide turbulence estimates with the precision observed in the low and high frequency tails. The high frequency tails typically decay with frequency at about -5/3 rate. Integrals of the turbulence spectra have been employed to derive turbulence energy decay profiles as shown in Figure 7. Regression analysis of these profiles indicate that both power law and exponential decay models fit the data well and more data would be necessary to determine which one of these models provides a better estimate. Vertical integration of the turbulence energy profiles provides an estimate of the total turbulence energy which has been compared (Figure 8) to a wave turbu-lence model derived from a earlier model proposed by Longuet-Higgins (1969).

This graph shows that the turbulence energy increases with wave steepness but the total level is greater than predicted. This difference may be due to inaccuracies in turbulence energy levels in the wave dominated region of the turbulence spectra and further work is being conducted to validate the data. Figure 9 displays a typical velocity probability density distribution. These distributions are very close to normal with neither high skewness or kurtosis.

The work done to date on the random paddle plus wind stress is very limited, however, a few trends have been observed but not fully quantified. We have seen that at maximum paddle drive with no wind, surface wave breaking is not very active. To achieve rolling and spilling waves, wind stress plays a crucial part. Although this may seem to be an obvious statement, its importance lies in the fact that it suggests that accurate models of wave generated turbulence will probably require more than one independent variable and two likely choices are wave slope and the ratio of wind shear velocity to say wave phase speed or maximum orbital velocity.

Longuet-Higgins, M. S., 1969: "On Wave Breaking and the Equilibrium Spectrum of Wind-Generated Waves," Proc. Roy. Soc., A310, 151-159.

The role of bubbles for gas transfer from water to air at higher windspeeds. Experiments in the wind wave facility in Hamburg.

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Abstract

Measurements of the evasion rate of CO_2 and O_2 from fresh water into the air which have been performed in the wind wave facility in Hamburg show an increased slope of the k vs. $\bar{u}$-curve at wind speeds above 11-13 m/s (fig.1). In order to test the hypothesis that this effect is caused by the additional transport of those gases to the air-water interface by means of air bubbles resulting from breaking waves, the bubble spectrum has been investigated as a function of fetch (fig.2), windspeed (fig.3) and depth (fig.4). A photographic method was used to analyse the bubble distribution.

Bubbles are observed for wind speeds as low as 7 m/s. The bubble density $N(r)$ as a function of radius r is very similar to those that have been observed by Kolovayev and Johnson and Cooke in experiments in the open sea, $N(r) \sim r^{-3-4}$. With no wind-induced turbulence being present, the rise velocity of the bubbles corresponded to Stokes' law. Turbulence increased both the mean and the variance of the rise time distribution.

For a quantitative mass balance the following assumptions were made:
- Uptake of gas from supersaturated water only during rise time of bubble.
- Transfer resistance to the bubbles describable with the film model. No influence of bubble motion upon film thickness.
- All gases behaving ideally. No enhancement of the transfer rate of any gas component due to the presence of others.

- Only bubbles with radii $20\,\mu < r < 2000\,\mu$ relevant for gas transport.

Agreement between calculated and observed enhancements of gas exchange of CO_2 and O_2 from fresh water supersaturated with both gases, as a function of windspeed, is rather good (fig.5). The fact that this enhancement is more pronounced for O_2 than for CO_2 is a consequence of the differences in solubility (Merlivat and Memery 1982). On the basis of the laboratory results, some comments are given concerning the possible role of air bubbles in the gas transfer to and from the open ocean.

Figures

1) Mass exchange coefficient k for the evasion of O_2 (o) and CO_2 (• and +) as a function of windspeed in the Hamburg wind wave facility.

2) Fetch dependence of number of bubbles per liter with diameter d = 300 μ at a depth of 20 cm. Parameter: windspeed.

3) Depth dependence of number of bubbles per liter with diameter d = 300 μ as a function of windspeed. Fetch: 11.5 m. Parameter: depth range.

4) Number of bubbles per liter as a function of bubble diameter (10^{-6} m) at a fetch of 11.5 m. Parameters: windspeed and depth.

5) Calculated enhancement of mass transfer coefficient k for O_2 (+) and CO_2 (•) at higher windspeeds.

ABSTRACT

GAS EXCHANGE MEASUREMENTS IN NATURAL SYSTEMS

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Our direct knowledge of the rates of gas exchange in lakes and the ocean is based almost entirely on measurements of the isotopes ^{14}C, ^{222}Rn, and ^{3}He. The distribution of natural radiocarbon has yielded the average rate of CO_2 exchange for the ocean and for several closed basin lakes. That of bomb produced radiocarbon has been used in the same systems. The ^{222}Rn to ^{226}Ra ratio in open ocean surface water has been used to give local short term gas exchange rates. This method generally cannot be used in lakes, rivers, estuaries or shelf areas because of the input of radon from sediments. A few attempts have been made to use the excess ^{3}He produced by the decay of bomb produced tritium in lakes to give gas transfer rates. The uncertainty in the molecular diffusivity of helium and in the diffusivity dependence of the rate of gas transfer holds back the application of this method. A few attempts have been made to enrich the surface waters of small lakes with ^{226}Ra and ^{3}H in order to allow the use of the ^{222}Rn and ^{3}He methods.

While these studies give broadly concordant results, many questions remain unanswered. The wind velocity dependence of gas exchange rate has yet to be established in field studies. The dependence of gas exchange rate on molecular diffusivity also remains in limbo. Finally, the degree of enhancement of CO_2 exchange through chemical reactions has been only partially explored.

These remaining uncertainties have relevance to some of the key applications of our knowledge regarding gas exchange rates to environmental problems. For example, as our knowledge of the gain or loss of CO_2 from lake surfaces depends on He or Rn based gas exchange rates, the degree of enhancement of CO_2 relative to these gases must be understood. Another example is the uptake of fossil fuel CO_2 by the sea. Improvements of the current 1-D models of the ocean require a knowledge of the regional and seasonal dependence of CO_2 exchange rates. Here the wind velocity dependence becomes important. These and other examples will be discussed.

Turbulence Measurements Near the Free Surface
in Stirred Grid Experiments

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The transfer of different gases across the surface of environmental water bodies is of great ecological improtance. For example, the transfer of oxygen (reaeration) in rivers, lakes or reservoirs determines their biological activity and allowable rates of waste disposal, the volatilization and transfer of toxics (PCB's, freons) is a critical pathway for the management of these pollutants, and finally, several climate factors (carbon-dioxide, nitrous oxide) are controlled by gas transfer across the ocean surface.

It is generally recognized that interfacial gas transfer is governed by an interaction of physico-chemical molecular phenomena and of larger scale hydrodynamic processes, mostly the near-surface turbulance. There are numerous models in the literature that attempt to describe this interaction, however, always in a highly idealized fashion. These conceptual models range from film models, (Lewis and Whitman, 1924), film renewal models (Danckwerts, 1951), with numerous schematizations of the turbulent flow structure (Dobbins, 1956; Fortescue and Pearson, 1967; Lamont and Scott, 1970; Theofanus, Houze and Brumfield, 1976), stagnation flow models (Chan and Scriven, 1970) and variable eddy diffusivity based models (King, 1966). However, to date none of these model conceptualizations has been verified by direct detailed measurements of the near-surface turbulence structure and the associated turbulent gas fluxes. One reason for this omission lies in the inadequacy of past turbulent experimental techniques in measuring sufficiently small scales. Another reason is the inherent difficulty of measuring close to a deformable and fluctuating gas-liquid interface.

Experiments have been conducted in a 50cm X 50cm X 40cm deep mixing tank that is stirred by an oscillating grid (13mm bars at 64mm canters; 36% solidity). A special cable controlled system was developed to isolate the tank from any vibrations caused by the grid motion and, thus, minimizing water surface ripples. Variable grid stirring intensities (stroke amplitude from 13mm to 152mm; stroke frequency from .5 Hz to 4 Hz and variable grid covers (distance between stroke top and surface from 4cm to 20cm) were investigated. Turbulence measurements are made with a hot-film probe in a split-film arrangement that

is mounted on a rotating arm. This allows measurement of one horizontal and the vertical turbulence components. The probe speed is adjusted so as to meet the Taylor frozen-turbulence condition. The probe dimension (0.2mm) and sampling rate are sufficient to measure close to the Kolmogorov length scale for the given turbulence conditions. The concurrent gas transfer (using oxygen by starting with an initially deaerated water sample) is determined by periodic bulk oxygen measurements using an electronic sensor or the Winkler titration method.

Results of the turbulence measurements reveal the vertical distribution of several turbulence properties for the finite space between the grid and the free surface. In the bulk, the outer vertical and horizontal velocity scales decay as $1/z$, where z is the distance from the virtual origin near the center of the grid stroke. This agrees well with the formula of Hopfinger and Toly (1976) (see Fig. 1). Anisotropy is nearly constant with depth in this region, the vertical velocity scale about 30 percent greater than the horizontal scale. However, the velocity scales deviate from the bulk relationship in a boundary layer comprising a depth of about two integral length scales below the surface. Within this region, the intensity of vertical velocity fluctuations decays rapidly toward the surface at all length scales as shown by the power spectra in Fig. 2. The Kolmogorov -5/3 power law holds for scales smaller than twice the distance from the surface. The horizontal velocity scales in this region, however, are nearly constant at all scales sufficiently below the outer scale (Fig. 1), which increases toward the surface. The integral length scale is proportional to z in the bulk, agreeing with the results of Thompson and Turner (1975). The vertical distributions of dissipation rate and Kolmogorov length scale can also be inferred from the turbulence measurements. The results were further analysed in two major respects:
 1) Derived properties (e.g. eddy diffusivities) are compared to theoretical values and earlier data (Dickinson and Long, 1978; Thompson and Turner, 1975; Hopfinger and Toly, 1976) from deep stirred grid experiments in which the surface constraint did not exist. 2) Certain dominant flow structures near the surface can be inferred from the data. These inferred structures can be compared to the assumed schematizations of the different models discussed further above. This model validation (or rejection) is further aided by direct sensitivity analysis of the observed gas transfer rates as a function of different model parameters.

INTERFACIAL MOTIONS OBSERVED DURING EXPERIMENTS

ON AIR-WATER GAS TRANSFER

by

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A number of recent observations have shown that the rate of gas transfer accross an air-water interface may be significantly affected by the interface motions. A better determination of these motions is then needed to understand the detailed mechanism of the gas exchange.

This work first reports on experimental results about the water surface wave statistical properties, especially for waves in the capillarity gravity range. Then, preliminary results on the motion of the underlying water flow are reported. These results were obtained during experiments in the I.M.S.T. wind-water tanks, by using a number of quite sophisticated devices such as precise capacitance wave gauges, a laser wave slope-meter and a laser Doppler velocimeter.

Various observational conditions were considered. Three types of wave fields were then found to be typical :

a/ random capillarity gravity waves in absence of gravity wave ;

b/ random capillarity gravity waves over random dominant gravity waves ;

c/ random capillarity gravity waves and gravity waves superposed to a deterministic   long gravity wave generated by a wavemaker.

It was found that depending upon the conditions, the statistical properties of the wave fields may largely differ from each other. In particular, the space-time structure and the dispersion relation of the capillarity-gravity wave field are strongly influenced by the presence of the random dominant gravity wave and the swell. This suggests the existence of strong interactions among the various fields. On the other hand, the results often depart quite largely from the prediction of the classical potential theory for water waves. Their analysis would in fact take into account the presence of a strong shear layer in the top millimeter of the water flow. This suggests that the waves are generated by an instability mechanism involving the coupled air and water shear layers adjacent to the interface. They would then contribute more efficiently to the mass transport accross the interface in a way which is shortly discussed.

APPLICATIONS OF MOLECULAR DYNAMICS TO VOLATILIZATION STUDIES

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The primary purpose of the present research is to develop a firm basis of physical chemistry toward the understanding of the interphase movement of pollutants both in the context of the natural environment and in the unit operation of water treatment by diffused aeration.

In considering the movement of an anthropogenic pollutant between the aqueous and atmospheric phases, recourse has been made to a treatment in which the pollutant is taken to be a gas and various models of gaseous diffusion are applied (eg Mackay & Yuen, 1981; Chiou et.al., 1980; Smith,et.al., 1980). Previous work by one of the authors (Chrostowski,et.al.,1982) in the study of mass transfer in the removal of pollutants from water by diffused aeration has indicated that the gaseous models may be divided into three general components from a physicochemical standpoint: thermodynamic/equilibrium, kinetic mass transfer, and system controlled mass transfer. In the current research, concepts from physical chemistry such as scaled particle theory and the solubility parameter are applied to a better understanding of the three physicochemical components of volatilization. Topics considered include structure-activity relationships to solubility and volatility, mass transfer dynamics, matrix effects such as salting in/ out and surface action, and the role of temperature.

For example, the literature has indicated an ambiguous role for temperature in the volatilization process (Mackay & Leinonen,1975; Kavanaugh & Trussell,1980) with different investigators varying as to whether temperature is directly or inversely related to the rate constant for volatilization. Experimentally, it was determined that the relationship was one of direct proportionality in a dynamic diffused aeration system. The etiology of this was investigated mathematically via a flow scheme similar to that in Figure 1. It was determined that temperature contributed to volatilization primarily through the kinetic mass transfer parameter rather than through a

shift in equilibrium or an effect on the system. This type of infor-
mation will aid future investigators in understanding which properties
of a pollutant-water system, whether chemical or hydraulic, will
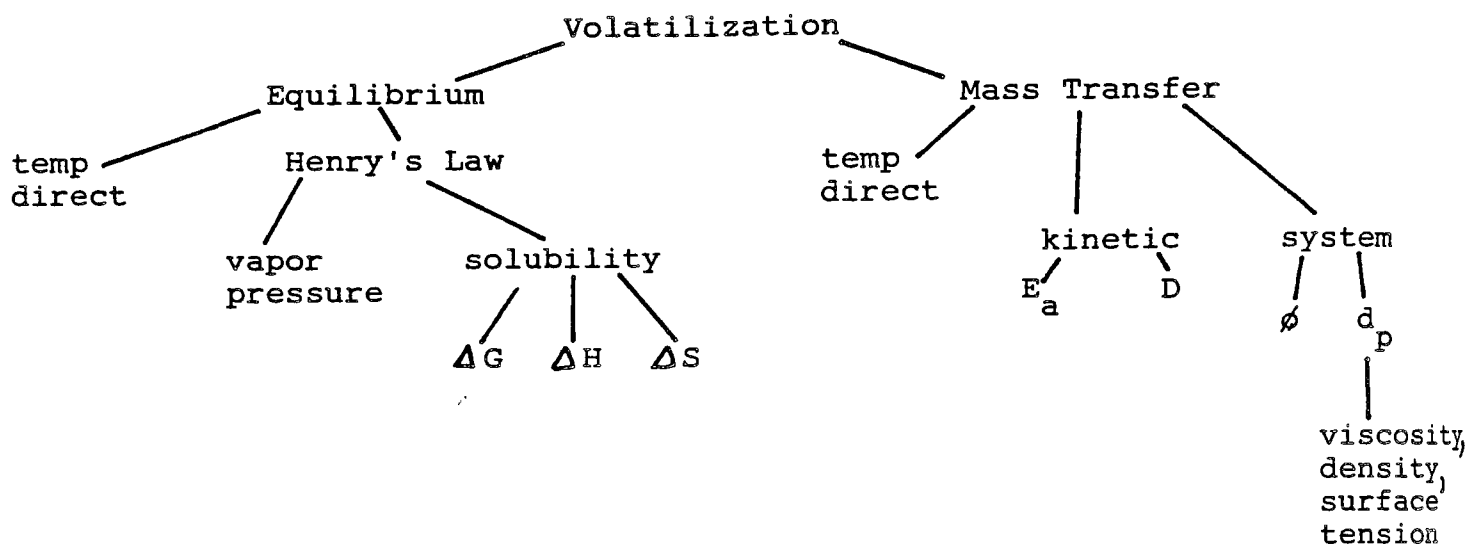ultimately determine the outcome of a volatilization situation.

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Figure 1-- Scheme for Analyzing Volatilization Components
(Δ G = free energy, Δ H = enthalpy, Δ S = entropy,

E_a = activation energy, D = diffusivity, $\emptyset$ = gas holdup,

d_p = bubble diameter)

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

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A technique has been developed to simultaneously measure fluid turbulence and the exchange rate of gases across the air-water interface of a tank under controlled laboratory conditions. Turbulence is generated with a vertically oscillating grid whose stroke length, frequency, and distance from the interface may be varied. Instantaneous fluid velocity vectors are determined using a streak photography method. Tracks of neutrally buoyant particles are recorded photographically, digitized, and the displacement is determined. Exposure times are controlled by a light chopping wheel and measured with a photo-diode and timer system. Ensemble average turbulent velocities and turbulent integral length scales are then computed as functions of distance from the grid.

The gas transfer rates of five gases (O_2, N_2, CH_4, CO_2, and Rn) are measured concurrently with the turbulence measurements described above. Before each run, tank water concentrations of O_2 and N_2 are reduced to about 50% of saturation by stripping the tank water using helium. Concentrations of CO_2, CH_4, and Rn are elevated above saturation by bubbling CO_2 and CH_4 through the water and by adding water with high Rn activity. The water is stirred to insure homogeneous conditions before initiation of the experiment. Small samples of water are taken at various time intervals to determine the rate of change in gas concentrations. The mass transfer coefficient for each gas is computed from this data, assuming the rate of exchange is proportional to the deviation from atmospheric equilibrium. Experiments have been conducted utilizing three different locations of the grid and two oscillation frequencies. The turbulent velocity decreased nearly exponentially with distance from the grid while the turbulent integral length scale increased

linearly with distance from the grid. The mass transfer coefficients appear to be proportional to the square root of the molecular diffusivities and to the square root of the ratio of the turbulent velocity to the turbulent integral length scale. This is in accordance with the surface renewal concept of gas exchange.

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Dichlorodifluoromethane (Freon-12) as a Tracer for Nitrous Oxide Release from a Polluted River

A Freon-12 tracer technique has been developed to measure gas exchange coefficients for nitrous oxide in a reach of the Assabet River receiving the effluent of the Westborough,Mass. sewage treatment plant. Stirred-tank experiments were performed to measure the relative exchange coefficients of nitrous oxide and Freon-12. Nitrous oxide is produced during chlorination of sewage and by microbial metabolism and is highly oversaturated in rivers receiving treated sewage effluents. Release of N_2O to the atmosphere can contribute to significant destruction of stratospheric ozone and to "greenhouse" warming. Magnitudes of the nitrous oxide exchange coefficient have been determined with greater precision than is possible through use of predictive equations. Preliminary results also suggest a strong wind effect not accounted for by predictions based on depth and velocity. The Freon-12 tracer technique facilitates the determination of the respective biogeochemical roles of sediment and water column with respect to N_2O production. The required sampling for this tracer technique is logistically simple and the sample analysis is rapid.

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TURBULENCE STRUCTURE
OF WAVY STRATIFIED AIR-WATER FLOW

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This work deals with experimental studies of near hrozontal stratified gas-liquid flows. Experimental results on the local turbulent structure presented here concern two phase flow modelization in pipes and the prediction of interfacial exchanges in environmental air-water flows.

Indeed, two sorts of flow conditions were studied: one flow is an internal fully developped stratified flow where the turbulence is controlled by fluid-wall and fluid-fluid interactions; the second is a developping stratified flow where interfacial interactions have the main role in turbulence production. These flows are realized in rectangular channels with the following dimensions:

-internal flow in a channel 12 m. long, 0.1m.deep, 0.2m.large

-developping flow in a channel 18m.long,0.6 m.large, 1. m. deep, where the mean water depth is near 0.2 m.

The kinematic analysis concerns the monophasic regions of the flow and the interfacial two phase region.

In the monophasic regions, longitudinal and vertical mean velocity components, turbulence intensities and Reynolds shear stress were measured ,by laser doppler anemometry in gas phase. In the two phase region, a new measurement method, using LDA, was perfected to obtain 1st and 2nd moments of the longitudinal velocity in liquid. Capacitive probes were used to obtain instantaneous interfacial height

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from which liquid time fraction and statistical wave characteristics were determined.

Main features of air and water flow are displayed by the examination of dimensionless 1st and 2nd moments profiles. In the mono-phasic regions near the walls and in the gas phase near the interface the classical shear flow behaviour is shown off. On the other hand, the liquid region under the waves exhibits particular features: turbulence intensities and shear stress profiles are showing the important role of turbulence transport from the wavy region; a consequence of this fact is the failing of Boussinesq concept for shear stress in this region, and the existence of secondary flow (which could be measured in internal flow).

A very crude scaling of Reynolds tensor component equations allows to confirm the main role of transport under the wavy region and suggests a functional formulation for shear stress, linked with the turbulent fluxes issued from the waves.

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EFFECTS OF DIFFUSER SPACING AND

SUBMERGENCE DEPTH ON OXYGEN TRANSFER

EFFICIENCY USING THE SMALL OXYGEN BUBBLE

REOXYGENATION TECHNIQUE

by

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ABSTRACT

The turbine, of dams with deep reservoirs and low level intakes may discharge water with unacceptably low dissolved oxygen concentration (DO) during the summer and fall months of the year. This is caused by stratification of the reservoir and the subsequent natural depletion of DO in its hypolimnion. Hence reoxygenation of the turbine discharges may be necessary to maintain a healthy environment for fish and other acquatic organisms in the tailrace. One reoxygenation technique is to inject small bubbles of gaseous oxygen into the reservoir with porous diffusers. The diffusers are located on the bottom of the reservoir, just upstream from the turbine intake. Oxygen in the bubbles rising from the diffusers dissolves and enriches the water entering the turbine.

A pilot scale study of the injection technique was performed by TVA to demonstrate feasability of the method and to develop design criteria. An oxygen transfer efficiency was defined as the ratio of mass of oxygen dissolved to the mass of gaseous oxygen injection. The study included field tests to determine the effects on oxygen transfer efficiency of diffuser pore size, diffuser spacing, diffuser submergence depth, and oxygen flux. This paper presents results of the field tests.

The test procedure consisted of collecting samples of the bubble plume gas at the water surface and analyzing them for oxygen content. Bubbles leaving the diffusers contained pure oxygen, but when they reached the water surface, they contained both oxygen and other gasses picked up from the water--mostly nitrogen. The fraction of oxygen not dissolved was used as an indicator of oxygen transfer efficiency because an accurate oxygen balance could not be obtained in the field tests. The oxygen fraction in the escaping

bubbles was correlated with the oxygen transfer efficiency on the basis of laboratory test data for which a complete oxygen balance was possible.

In these tests, diffuser pore sizes ranged from 1.2 to 20 microns. The diffuser spacing ranged from a single, isolated diffuser (hollow cylinder, 18 inches long by 3 inches OD) to a battery of 136 of the same, mounted about 5 inches apart. Submergence depths ranged to 43 feet. Oxygen fluxes ranges to 0.8 acfm/ft^2.

Test results indicated that transfer efficiency decreased with increasing pore size, increased with increasing spacing, and decreased with increasing oxygen flux. The transfer efficiency increased with increasing submergance depth, but became independent of submergance depth at a point which depended on oxygen flux and diffuser spacing.
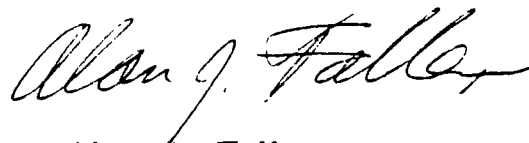
ABSTRACT

International Symposium on Gas Transfer at Water Surfaces

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Laboratory experiments with small-amplitude O(0.1 cm) monochromatic plane waves on water (wave length O(20 cm)) and weak shear , O(0.5 s^{-1}), clearly demonstrate the generation of convective longitudinal vortices as predicted by the Craik-Leibovich (Craik, 1977; Leibovich and Paolucci, 1981) mechanism for the generation of Langmuir circulations. The shear may be produced by wind, a forced surface film motion, or wave-driven shear as predicted by Craik (1982).

The initial occurrence of longitudinal rolls is rapidly followed by deepening of the shear layer, the generation of larger-scale rolls, and transition to turbulence. The experiments and theory taken together show that with almost any observable surface waves there will be mechanically generated convective overturning with longitudinal .rolls (the Langmuir circulations) and turbulence. Gas transfer will then be limited only by the thinnest layer at the surface in which diffusion may be pres; med to dominate. But even there the Langmuir circulations will be important through their tendency to concentrate surface films into lines parallel to the shear , thus presenting a significantly non-uniform surface layer .

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EVALUATION OF TURBULENCE LEVEL IN FLOWING WATER
NEAR THE AIR-WATER INTERFACE

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A general research program is being carried with the objective of developing materials and methods for the inexpressive gross evaluation of turbulence intensity near air-water interface in flowing waters.

It is thought that with one such additional parameter formulas for the prediction of reaeration coefficients could be significantly improved. The method is based on the dependence of the solubility of a solid immersed in a liquid upon the level of turbulence of the liquid. A number of floating probes of known weight dumped in a stream of water could be (partially) recaptured downstream, dryed and weighted, thus giving a gross information on the average rate of dissolution of the solid in water.

A report is presented of a series of tests carried out with floating probes of salts and sugar compunds in a tank of water subjected to convective turbulence. Turbulence is induced by submerged jets; the geometry of the apparatus and the flow were made such that near the surface the observed pattern duplicated that which is visualy observed in flowing streams of water. Probes made out of sugar compounds revealed good sensibility to changes of turbulence levels. Further tests will be conducted in a long channel with bottom shear generated turbulence.

ABSTRACT for

International Symposium on

Gas Transfer at Water Surfaces

PREDICTION OF NON-REACTIVE WATER SURFACE
GAS EXCHANGE IN STREAMS AND LAKES

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A model is formulated for the water surface exchange of a non-reactive or weakly reacting gas such as oxygen in streams and lakes. The model incorporates a molecular layer at the water surface, vertical turbulent diffusion due to bottom shear and wind shear, and the enhancement of surface exchange by wind waves.

The mathematical model gives an equation for the gas exchange coefficient, K_s (m/s) which includes molecular transport in the surface layer and turbulent transport below. The predictive equation is

$$K_s = \left[\frac{\delta}{D_m} + \frac{1}{KU_c^*} \ell n \; (KPe) \right]^{-1} \tag{1}$$

where δ = thickness of molecular surface layer,

D_m = molecular diffusivity of dissolved gas in water,

K = Von Karman's constant,

U_c^* = sum of bottom and water surface shear,

Pe = shear Peclet number = $U_c^* \, h/D_m$,

and h = water depth.

$K_s/h = K_2$ is the more commonly used "reaeration coefficient."

A comparison of the predictive equation with flume observations reported in the literature indicates that the molecular surface layer does exist, controls surface exchange in most cases, and may be described by the equation

$$\delta = A_1 \, \nu/U^*$$ (2)

where ν = kinematic viscosity of water,

U^* = bottom shear velocity in flume, and

A_1 = a constant, $\cong 10$.

Wind-wave flume measurements of K_s available in the literature are used to expand Eq. 2 to incorporate wind shear and the effect of wind waves. The surface layer thickness is then described by the equation

$$\delta = \nu \left[\frac{U^{*2}}{A_1^2} + \frac{U_s^{*2}}{A_2^2} + A_3 \int_0^\infty \phi f \, df \right]^{-1/2}$$ (3)

where U_s^* = wind shear velocity

ϕ = energy spectrum of wind waves,

f = wave frequency,

A_2 = a constant $\cong 14$, and

A_3 = a constant $\cong 2.3 \times 10^{-8} \, \text{sec}^{-1}$.

The three terms in Eq. 3 represent the contributions of bottom shear, wind shear, and the circulation under wind waves, respectively. Under high winds, i.e. 12 m/sec, the wave spectrum term in Eq. 3 will contribute only about 5 percent to K_s. If wind velocity is less than about 6 m/sec, however, the wave spectrum term can assume an importance equal to that of the wind shear term in computing K_s. Separate consideration of wind effects on the surface molecular layer and on waves in addition to bed induced shear improves the predictive capabilities beyond available theories.

The superposition form given in Eq. 3 is chosen because the theory is adding the impact of various sources of turbulence, and turbulence characteristics sum with the square of shear velocity or velocity components.

PREDICTION OF GAS EXCHANGE RATES IN WIND-DOMINATED NATURAL SYSTEMS

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The results from laboratory and field investigations on the processes controlling gas exchange across the air-water interface are presented and used to develop a predictive relationship for gas exchange rates in wind-dominated natural systems. Recent laboratory measurements of the exchange rates of several gases and of parameters characteristic of the fluid turbulence suggest that gas transport can be adequately described by a surface renewal model based on fluid turbulent velocities and length scales.

In the field, the rate of gas exchange in south San Francisco Bay is primarily controlled by wind speed. However, application of published models, which characterize fluid turbulence based on the wind friction velocity and water depth, predicts gas exchange rates which are 2-3 times lower than observed rates. Furthermore, they do not predict the observed functional dependence of gas exchange on wind speed.

The discrepancy between the success of the turbulence approach in the laboratory and its failure in the field is probably due to the absence of adequate means to measure or predict from wind speed the necessary parameters of fluid turbulence. Attempts to use salt dissolution rates as a technique to characterize fluid turbulence have proved unsuccessful to date.

Compilation of our field data with previous measurements of exchange rates in wind-dominated systems suggests that average exchange rates can be predicted to within 20% based on wind speed alone. Until measurements of the necessary turbulence parameters can be accomplished these empirical relationships based upon wind speed must suffice.

ABSTRACT

Field Experimental Techniques for Reaeration Studies
by Edward R. Holley[*] and Nobuhiro Yotsukura[**]

This paper is concerned primarily with gas exchange measurements in rivers with secondary attention given to estuaries, lakes, and reservoirs. Also, the focus is on reaeration problems, with attention being given first to traditional DO measurements and then to tracer gas measurements.

One of the first approaches was based on the mass balance of oxygen with surface reaeration being evaluated as the residual after measuring DO distributions and then accounting for other sources and sinks of DO. The accuracy of reaeration determination with this method is limited by the accuracy of evaluation of the other sources and sinks, some of which are unsteady and therefore prevent testing during steady-state periods. A disturbed equilibrium method has also been used with DO measurements being taken first under natural conditions and then with a steady-state injection of catalized sodium sulfite, which lowers the DO concentration. The change in DO concentration between the two conditions is used to determine the reaeration, assuming that all sources and sinks except the surface transfer are unaffected by the sodium sulfite. The method has been used only for small streams where the sodium sulfite became mixed relatively quickly across the full stream width.

Most studies have assumed that DO concentrations are uniform across the width of a river and have used 1D representations. The data of Churchill et al. shows that the deficit may vary as much as 15% across the width under natural conditions (no BOD loads). The importance of natural transverse variations in a given river can be estimated using Holley's result that the amount of variation of deficit across the width is related to the ratio of a characteristic transverse mixing time to a characteristic reaeration time.

There have been relatively few reaeration measurements in wide estuaries, lakes, and reservoirs where the flow pattern is highly two-dimensional and/or where a significant part of the reaeration is associated with wind induced turbulence. One method that has been used is a floating dome with surface gas transfer being determined by the change of pressure in the gas trapped between the dome and the water surface. Problems with this method include heating of the dome by incident radiation, keeping the gas space under the dome sealed from the atmosphere when surface waves are present, and possibly disturbing the natural turbulence structure at the surface where the gas transfer is taking place.

Tracer gas techniques were developed in an effort to measure gas transfer without interferences from the various natural sources and sinks of DO in rivers. In Tsivoglu's method, a bottle containing dissolved radioactive krypton, tritium, and Rhodamine WT is broken below the water surface. Using the Rhodamine as a location tracer, the difference in measured concentrations of krypton and tritium, a conservative tracer, can be related to the surface desorption of krypton. In the USGS method, hydrocarbon gases are bubbled through the depth of the river and Rhodamine WT is used as a conservative tracer. The injection time may be short (15-30 minutes) to give a moving cloud of tracer gas. The method is then similar to the krypton method. In another technique,

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the hydrocarbon tracer gas is injected long enough to give steady-state concentrations. In small streams with complete transverse mixing, the difference in tracer gas concentrations between cross sections can be related to the surface exchange.

The krypton method suffers from public concern about the introduction of radioactive materials into the environment. The hydrocarbon-gas methods suffer from the inconvenience of setting up the bubbling apparatus in the river and from needing to correct for loss of Rhodamine WT dye. Both the krypton and the hydrocarbon gas methods have been used primarily in small streams where transverse mixing could be achieved in the study reach. Investigations are currently underway on using the steady-state hydrocarbon gas method with an unmixed plume in larger rivers. The tracer gas methods appear to hold much promise for future measurements.

(For each of the methods, the practical aspects of actually executing the tests under field conditions will be addressed.)

ABSTRACT

GAS TRANSFER RATE COEFFICIENT MEASUREMENT
BY A STABLE ISOTOPE KRYPTON TECHNIQUE
I.   TREATMENT PLANT STUDIES

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A new pair of tracers for gas transfer measurement have
been developed for use in turbulent, open systems. Stable
isotope krypton (Kr), with atmospheric composition, and lithium
(Li) salts replace the radioactive tracers ^{85}Kr and ^{3}H, respectively,
as the gas and dispersion tracers in the direct tracer method
developed by Tsivoglou, et. al (1965, 1967, 1968). The primary
application of this technique has been in the precise determination
of oxygen transfer rate coefficients ($^{\alpha}k_La$) in respiring wastewater
treatment systems and natural water bodies.

A complete system of dosing, sampling and analysis has
been developed to make this new, non-radioactive tracer method
a viable field testing procedure. The field equipment and techniques,
and the calculations, will be discussed in this paper. The
analytical methods will be described in Paper II.

It is proposed that this new pair of tracers can be used
under operating conditions in a wastewater treatment plant employing
any common form of oxygen transfer equipment: coarse or fine
bubble diffused air, turbine or mechanical surface aeration.
Further, with the addition of a fluorescent dye to track the
tracer cloud, the method may be applied to large, surface water
bodies: rivers, lakes and impoundments. The technique is also
applicable to the measurement of transfer rate coefficients
for other gases, once appropriate relative transfer rates have
been established.

Two field tests of the stable krypton/lithium tracer method
have been completed to date. These tests have measured: the

$\alpha K_L a$ of (1) a coarse bubble, diffused air system in an operating, municipal activated sludge plant and (2) a fine bubble, dome diffused air system in a manufacturer's, clean water, testing tank. A third test is scheduled in an operating, municipal/paper indusry, activated sludge plant, with mechanical surface aeration.

The precision of the rate coefficient measurements has been determined. The precision of the Kr measurement by isotope dillution mass spectrometry (+/- 0.05%, s.d.) and the precision of the Li measurements by flame atomic absorption spectrophotometry (+/- 3%, s.d.) are discussed in Paper II. Based on the clean water test data, where dispersion was not a factor, the precision of the krypton transfer rate coefficient ($K_L a_f$-Kr) was better than +/- 0.5%, s.d. The overall precision of the $\alpha K_L a_f$-Kr measurement for the wastewater treatment plant was better than +/- 3%, s.d. In calculating the oxygen transfer rate coefficient ($\alpha K_L a_f$) from these data, the precision proved to be limited by the precision (+/- 5%, s.d.) of the literature value for the krypton to oxygen transfer rate ratio (0.83 +/- 0.04, s.d.; Tsivoglou, 1967). Refinement of this ratio is required to improve the precision of the direct tracer measurement for oxygen.

BUBBLES PRODUCED BY BREAKING WAVES

by

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ABSTRACT

Bubbles produced by breaking waves are involved in many processes at the air-water interface. In particular, bubbles are suggested to play an important role in gas transfer across the interface, and in producing spray droplets. However, this sequence of events -- wave breaking, air entrainment, and droplet production -- has not been systematically studied. In the present study, simultaneous measurements of breaking waves, bubbles, and spray at different wind velocities were conducted.

The size and velocity of bubbles and spray were measured with optical sensors. Their size spectra are found to be closely related. This provides further evidence of the bubble bursting production mechanism.

Bubble population is found to increase drastically with wind stress; the critical stress for bubble inception is also deduced. A simple model including mechanism of entrainment is proposed to predict the bubble distribution as a function of depth.

Time series of bubble flux shows intermittent property. The intermittency is closely related to the frequency of wave breaking; the latter in turn is related to wind stress and wave groupiness. Statistical and spectral analysis on the bubble fluxes and waves are performed. Cross spectral analysis shows higher coherence between wave and bubble flux at higher wind velocities (≥ 13 m/s). For lower wind velocities the bubble flux is intermittent due to only occasional wave breaking.

The population distribution per breaking interval (between breaking waves) shows gradual change from relatively uniform distribution for strong breaking to a skewed distribution for weak breaking. The spreading of the distribution is also wider for lower wind velocities, indicating that wave grouping plays a significant role in the breaking processes.

Turbulent Structure and Mixing Near Gas Liquid Interfaces

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Summary

1.   Turbulence structure

In boundary-layer flows of a fluid over another fluid much denser (or more viscous) than itself, or over a solid surface, the production and dissipation of turbulent energy occurs very close to the surface where the mean velocity gradients are greatest; turbulent energy is transported away from the surface by the turbulence itself (one can think of pairs of vortices inducing such motions, or think in terms of 'bursting' motions). Turbulence can also be generated by many other means, by thermal convection, by bubbling motions, by mechanical agitation or wave action on the surface, or by breaking of internal waves. In most of these cases the production and dissipation of turbulence is more evenly distributed through the fluid. The differences and similarities between these classes of turbulent flows will be discussed.

Now at the liquid side of a gas-liquid interface, in the absence of breaking waves or a downward heat flux, no turbulent energy is produced because the mean velocity gradient is smaller. However the turbulence which is produced by the flow field (e.g. by shear) well below the surface is distorted near the surface because the velocity fluctuations normal to the surface are zero, and the scale of the fluctuations decreases toward the surface. Horizontal fluctuations within a thin viscous sublayer may be

affected by the resistance to surface straining motions by surface tension. The effect of wave and surface heat flux on the turbulence structure will also be discussed.

2.   Turbulent mixing

Mixing in a turbulent flow between a fluid and one or more dispersed substances firstly depends on the scale and the intensity of the turbulence, and secondly on the mean or slowly fluctuating velocity gradients, (e.g. caused by shear or waves). The mixing also must depend on the mean and fluctuating distribution of the dispersed substances (e.g. the air dissolved in water). The presence of a second phase (e.g. in the form of spray in air or gas bubbles in water) can also have significant effect on the turbulence and mixing. Depending on how interfaces affect the turbulence and the mean flow, their effects on mixing vary. These will be discussed (as will the first part of this talk) in largely qualitative terms but with some reference to mathematical arguments and to experiments.

Parametrization of air/lake gas exchange

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Previous field data on air/lake gas exchange clearly show a strong wind speed dependence, despite the large scatter of data. But nevertheless these data are not appropriate to parametrise the exchange rates, mainly due to the following reasons. Firstly, the sampling periods were too long, so that the gas exchange rates obtained were a mean value over various conditions. Secondly, and more seriously, the parameters controlling gas exchange (windspeed, stability, waves) were measured only imperfectly. The only parameter known in some experiments was the windspeed, mostly only measured on stations ashore.

Therefore in autumn 1982 we started an investigation on Lake Sempach, Switzerland, in order to try a parametrization of air/lake gas exchange. The gas exchange rate is measured with the Tritium/He^3 method, furthermore oxygen profiles can be measured rapidly with a jojosonde. In the middle of the lake a boje is anchored, measuring automatically all important meteorological and limnological parameters, and additionally the waves with three different optical wave measuring systems.

We do not believe, that it will be possible to obtain a parametrization of air/lake gas exchange during all the time with high time resolution (a few days). Therefore the aim of our investigation is twice: Firstly, to measure gas exchange under extreme conditions (long period of low wind speeds, resp. short stormy period). Secondly, to measure continuosly, all important parameters controlling the gas exchange to compare them (espcially the waves) with wind tunnel results and to test parametrizations predicted from lab results under natural conditions.

The Transfer of Mercury at the air/water interface

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The geochemical cycle of mercury have been of major interest

during many years. However, until recently only few basic data

governing the exchange of mercury at the air/water interface

has been known.

A large portion of the mercury in the atmosphere is elemental.

The Henry's law constant for elemental mercury (Sanemasa, 1975)

was used by Fogg and Fitzgerald (1979) to conclude that the

rainwater concentration of mercury must consist of other species

than Hg^O.

In the last few years, we have performed a series of determina-

tions of the Henry's law constants for different Hg^{2+} species:

Compound	$\underline{H} = [HgX_{(g)}]/[HgX_{(aq)}]$	Temp	$[Cl^-]$	Ref
CH_3HgCl	$1.9 \pm 0.2 \cdot 10^{-5}$	$25^O C$	0.7 M	1
CH_3HgCl	$1.6 \pm 0.2 \cdot 10^{-5}$	15	1.0	1
CH_3HgCl	$0.9 \cdot 10^{-5}$	10	$0.2 \cdot 10^{-3}$	1
$HgCl_2$	$2.9 \cdot 10^{-8}$	25	$0.2 \cdot 10^{-3}$	2
$HgCl_2$	$1.2 \cdot 10^{-8}$	10	$0.2 \cdot 10^{-3}$	2
$Hg(OH)_2$	$3.2 \cdot 10^{-6}$	25	$0.2 \cdot 10^{-3}$	2
$Hg(OH)_2$	$1.6 \cdot 10^{-6}$	10	$0.2 \cdot 10^{-3}$	2
$(Hg^O$	0.3	20	0	3)

1. Iverfeldt and Lindqvist (1982); 2. Iverfeldt and Lindqvist (1980)

The table show that listed mercury compounds are effectively scavenged from air by rain. From these constants and other considerations, Brosset (1981) proposed a mercury cycle where Hg^0 is emitted from ocean water to the atmosphere. He further proposed that the elementary mercury is subjected to atmospheric oxidation processes and transformed to water soluble Hg^{2+} species.

In a preliminary investigation, we have shown that Hg^0 may be oxidized by ozone. (To be published). The laboratory studies show that the ozone induced oxidation is slow in air, but that the rate is increased by several orders of magnitude having a water phase present, cf. cloud and raindrops in the atmosphere.

To get a more complete picture of the mercury cycle we have also performed in situ experiments using benthic chambers to investigate sediment/water exchanges in an unpolluted coastal water (Iverfeldt et al., to be published). A rather large part of the total mercury in water above the sediment was found to be volatile, probably Hg^0. The pore water contained relatively less volatile mercury. We do not know, if the volatile Hg is produced only in the sediment or/and at the sediment/water interface by a change in redoxpotential or by bacterial degradation (cf. Spangler et al, 1973).

The sediment/water interface could be compared to the interface between oxic surface water and anoxic subsurface water in a permanent anoxic fiord (Framvaren, Norway). A very active bacterial layer is found in the redox boundary (Skei, 1981).

Extremely high amounts of volatile mercury was also found just above this boundary. (To be published).

Knowing that the ocean is covered with a surface layer with high bacterial activity, a hypothesis may be stated, that Hg^o emitted from the ocean to the atmosphere is partly produced in the surface microlayer.

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Optical water waves measuring techniques

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We focused our interest on optical wave measuring techniques
because of the importances of capillary waves for gas exchange
and knowing the difficulties to measure them with wire gauges.

Any optical method obvisiously has the advantage not to be in contact
with the water surface and therefore not to interact with the waves.
We developed a refraction technique similar to the ones already used
by other workers. The system measures the slope of the waves. A
He-Ne-laser beam pierces the water surface vertically from above. The
optical reciever consists of a Fresnel lens and a focusing screen, one
focal length distant, so that the displacement on the screen only
depends on the slope and not the height of the waves. Finally the spot
on the screen is imaged on a dual axis position sensitive photo diode.
The resulting electric signal is slightly nonlinear due to the optical
geometry and non linearities of the photo diode. The cutoff frequency
of the detector together with the electronics is about 100 kHz. Thus
the frequency response of the system is limited only by the diameter
of the laser beam. Tests with different diameters show, that all wave
frecencies occuring can be measured without any damping.

The fast response of the detector enables us to measure correlations
with only one wave measuring unit in the following way: The laser beam
oscillates horizontally (0.5 to 30 mm) over the water surface at the

sampling frequency (about 1 kHz) of the time series. Two time series, 0.5 to 30 mm distant, are put on the computer simultaneously. Phase velocities of capillary waves are thus determined.

Finally, the possiblities of visualisation techniques based on the same optical geometry as the spot method with the laser are discussed. The first step done in this direction are photographs of a 20 cm diameter area showing the slopes of waves indicated by different colours. With this method it will perhaps be possible to calculate two dimensional wave number spectras.

Wind/wave-tunnel experiments on the Schmidtnumber- and wave field dependence of air/water gas exchange

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Gas exchange experiments have been carried out in order to study the influence of parameters controlling gas exchange without breaking waves: friction velocity u_*, Schmidtnumber $Sc = \nu/D$ for the gas studied, and the wave field.

We use 3 different wind/wave tunnels for our experiments: Two circular ones of different sizes and the the large wind/wave facility of I.M.S.T Marseille, where the experiments have been carried out in cooperation with L. Merlivat and L. Memery from CEN Saclay. The circular tunnels have the advantage of a homogenous wave field of unlimited fetch in contrast to the short fetch waves in all linear tunnels.

Different tracers are used in order to study the dependence of the exchange rate on the Schmidtnumber: CO_2 and heat in the small circular tunnel, CO_2, He, CH_4, Kr and Xe in the large circular facility and Rn and He in the I.M.S.T. tunnel. Wave slope spectras are obtained with an optical refraction method using a He-Ne-Laser and a position sensitive photodiode.

With a smooth water surface the experimental results agree well with theories treating the water surface as a rigid wall: The $Sc^{-2/3}$ dependence and correct absolute values of the exchange rate are obtained. When waves occure a strong increase in the transfer velocity is observed as well as a change of the Schmidtnumber dependence to $Sc^{-1/2}$.

Both results cannot be explained with existing theories (surface increase and periodic dilation of the viscous sublayer by waves). The increase of the gas exchange rates through the waves is different in the 3 tunnels due to their different wave fields. Several wave parameters are discussed in order to parameterize the influence of waves on the exchange process. Moreover, the windtunnel results are compared with field data.

MEASUREMENTS OF WIND EFFECTS ON WATER-SIDE CONTROLLED GAS EXCHANGE IN RIVERINE SYSTEMS

by

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ABSTRACT

The traditional approach toward the analysis of gas transfer at the surface of streams or rivers has been limited to consideration of turbulence generated by bottom shear in the flowing water. The effect of wind has been simply neglected. However, for wider open rivers with moderate slopes and more tranquil flows, including inflow into lakes or reservoirs and approaches to estuarine conditions the wind effect must be expected to become increasingly important and a transition to purely wind-controlled conditions (as considered in oceanographic work) will take place.

A simple criterion on the relative importance of streamflow versus wind generated gas exchange is developed on the basis of the respective near-surface turbulent energy dissipation rates ε in the water. Open channel experimental data by Nakagawa et al. (1975) are used for ε under pure streamflow conditions, while ε for wind conditions is computed on the basis of similarity in the wall layer of the wind driven turbulent boundary layer in the water with estimates of the roughness height from Kondo (1975).

Data from two riverine gas exchange experiments with concurrent detailed wind measurements are analysed. Correlations between wind shear velocities and observed exchange velocities (K_L) appear to be consistent with the dissipation based criterion. The data also demonstrate the strong micro-meteorological sheltering effect of stream banks and vegetation on gas exchange in small streams.

PREDICTION OF DISSOLVED GAS TRANSFER IN SPILLWAY AND OUTLET WORKS STILLING BASIN FLOWS

by

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An empirical model is presented that predicts the oxygen and nitrogen transfer to and from the flows through hydraulic structure stilling basins. The model may be applied to a wide variety of structures ranging from open chute hydraulic jump basins to flip buckets and plunge pools and from hollow-jet valve to fixed cone valve to slide gate controlled outlet works basins. The model may be used to evaluate both the structure's reaeration potential and the structure's potential for nitrogen supersaturation development. The present model is a refined and expanded version of a model first developed by the author in the mid-70's. The present model is better suited to handle low Froude number stilling basins and is analytically more direct. The model is based on data collected at over 24 different field structures. Parameters considered include dissolved gas concentrations in the flow entering the structure; water temperature; barometric pressure; the velocity, cross sectional shape, and orientation of the flow entering the stilling basin; stilling basin length, width, depth, and shape; and tailwater depth. Included is an example application.

A New Way to Study CO_2/Water Equilibria

by
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Naval Research Laboratory

Washington D.C.

A unique method has been used to study the rate of establishment of an equilibrium between CO_2 in an air stream, and water of varying salinities. It consists in bubbling air through a thermostatically controlled 4 foot length of glass tubing containing the water in question, collecting the effluent in a syringe, then expelling it through an infrared analyzer for the CO_2 measurement.

The equilibrium was studied in two ways: 1) The water was brought to near equilibrium with zero parts per million (ppm) CO_2 initially, then exposed to air containing 350 ppm CO_2, and 2) The reverse, with 350 ppm initially and then with 0 ppm CO_2. The results can be interpreted either in terms of percent equilibrium vs time, or volume of CO_2 absorbed or released as a function of time. As expected, the time for a given water to reach equilibrium increased with salinity. Also equilibrium with 0 ppm CO_2 and seawater was asymptotic, in contrast with the more readily obtained equilibrium with 350 ppm CO_2. Among the unexpected results was the sigmoid shape of the plot of percent equilibrium with time with water initially having near-zero CO_2 tension and then aerated with 350 ppm CO_2. The 50% point on this curve corresponds to a pH of 8.25. The rate of the establishment of equilibrium varied linearly with the air flow rate but not with the volume of water in the tube.

These experiments were conducted as a prelude to measurements of CO_2 uptake by microorganisms but the technique may be useful to those interested in air/sea interactions. The control of temperature is critical; temperature variations greater than 0.07 C reduce the accuracy of the measurements. Also important are the maintenance of a constant flow rate and a constant bubble size. Methods for controlling these variables have been developed (the hard way) so that the system is now highly refined and gives extremely reproducible results.

DISTRIBUTION OF BUBBLES NEAR THE OCEAN SURFACE

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Extended Abstract

Crowther has recently offered an interesting hypothesis that the number of bubbles near the air-sea interface is only a function of the rate of work of the atmosphere on the surface, the surface tension and the bubble radius. Interestly, no consideration was given to the dynamical significance of g, the acceleration due to gravity, which according to Phillip's model of an equilibrium wind-wave field, including breaking waves and extensive bubbling, uniquely defines the wave height spectrum.

A simple model, not explicitly derived in terms of the statistical transport equations utilized by Garrettson and Crowther, is formulated for the generation and 'spectral' transport of bubble mass. A subrange in which there is no mass convergence due to coalescence or dissolution is considered. From mass continuity arguments, the change of radius due to pressure, and the hydrostatic balance, it is readily deduced that the mass (and volume) flux per radius increment is both distributed as a negative exponential with depth and as r^{-3} with radial size. However the model of Crowther, as demonstated, is not unique but is only one of a set of possible similarity solutions.

Based on arguments for the radial forces on a cavity, there exists an outer scale, for bubble production by shattering comparable to the wavelength associated with a minimum phase speed of gravity-capillary waves. A revised dimensional analysis including, g, and this outer shattering scale, leads to a result, identical to Crowther's indicating the similarity function, associated with Crowther's model, is a constant in the problem variables.

An analysis of various data sets for bubble densities and distributions, or deduced properties from acoustic resonance, establishes that the wind dependence, vertical distribution, spectral shape and tentatively, the influence of surfactants agree with the model's predictions. However, for agreement in order of magnitude, it is necessary to consider the relatively sparse nature of active bubble production in breaking waves compared to the total surface area, as well as the relatively sparse nature of large shatterable cavities within a whitecap. Intuitive arguments for these characteristics result in agreement within a factor of 10, but are considered weak due to lack of detailed experimentation on the structure and life cycle of breaking waves.

A MODEL OF INTERFACIAL GAS TRANSFER FOR A WELL-ROUGHENED SEA

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Extended Abstract

Deacon has recently proposed a model for wind-driven gas transfer across a sea surface if the airflow is aerodynamically smooth. In this case of transitional or fully rough flow, it is well-known, at least from laboratory measurements, that the gas flux significantly exceeds that predicted from an extension of smooth wall considerations. At the same time, by analogy or direct comparison with the limited extent of bubbling in breaking waves or peaked small waves, the flow separation associated with rough wall flow is hypothesized to occur over a small fraction of the total area. A key question is whether moderate local turbulence near sparse regions of flow separation can transfer gas more efficiently than weak, but global, turbulence for smooth wall flux.

A model is presented for the flux of a non-reactive, low solubility, low diffusivity gas, like O_2, through this air-sea interface in the presence of patches of waves over which the flow is separating. The development is based in the work of Yaglom and Kader for rough wall transfer of heat and mass, but is applied here to a compliant rather than solid surface. In order to estimate the surface (roughness) Reynolds number, it is necessary to quantify the rms height of the roughness elements. An extension of the Charnock relationship for surface roughness is provided which accounts for the contributions from surface root mean square elevation and slope for waves whose phase speed exceeds the minimum phase speed of gravity-capillary waves. The areal extent of the transfer is modelled in a manner similar to Cardone and Wu, but is normalized in terms of the threshold stress for flow separation.

Comparison of the model with various data sets, including the stress dependence of Charnock's constant, the areal coverage of whitecaps and the gas flux in laboratory and recently reported field experiments, confirms the general validity of the formulation. However, in all cases there is considerable experimental scatter or limited representativeness so that it is uncertain whether the model is correct in detail or only in its general trends.

Stationary and Self-Propelled
Weir Aerators

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Several weir types, sharp-crested, broad-crested, tooth-shaped, and tooth-shaped orifice have experimentally been tested in a hydraulic flume. Sizes of weirs, the flume length and depth, and the water flow rate have been varied over a wide range. The maximum capacity of the test model is 10,000 m^3/d. The efficiency of oxygen transfer has been related to the geometric and hydraulic characteristics of the studied systems. The efficiency of oxygen transfer by the use of weirs reaches 3 kg/kW·L.

A self-propelled modification of weir aerators has been developed. This aerator consists of a weir box with a weir or orifice, and a propeller type pump located on floats. The floating structure is connected by means of a hinged arm to a central pile. When the pump is activated a jet of water is discharged through the weir or orifice. The jet aerates and mixes the water and propels the floating structure around the central pile. Rotation of the floating structure around the pile increases the service area of the aerator. The major parameters of this aerator type, oxygen transfer, velocity of rotation, and mixing capacity have been evaluated.

Weir aerators can be used for water and wastewater treatment, aeration of stagnant and stratified lakes, rivers, etc. The advantages of stationary weirs are best utilized in high rate processes such as activated sludge process, aerobic stabilization of sludge, postaeration, and other. An important feature of self-propelled aerators is their ability to mix large volumes of water. Such aerators can be used for biological ponds, lakes, etc.

ABSTRACT

The Structure of Turbulence on Both
Sides of the Air-Water Interface

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In this paper we discuss the structure of turbulence in the vicinity of an air-water interface as it relates to gas transfer. Because the molecular diffusion coefficient of gas in the liquid phase is much lower than the gaseous coefficient, the transfer of gases across the air-water interface is dominated by the resistance of the boundary layer in the water. Even for hydrodynamically rough flow this remains true because of the large Prandtl number in the water. That is, the erosion of the viscous boundary layer implied by rough flow does not necessarily mean any significant commensurate thinning of the diffusive boundary layer.

However, in the presence of active wind-wave breaking the analogy between transfer across the air-water interface and heat transfer at solid srufaces is no longer valid and the structure of the turbulent boundary layers on both sides of the interface becomes important.

Therefore in the first part of this paper we discuss the processes responsible for the variability of the molecular diffusion sub-layer in the presence of shear-generated turbulence near solid roughness elements. In the second part of the paper we turn our attention to gas transfer processes when there is active wind-wave breaking.

Frequent use is made of data from laboratories and natural air-water interfaces to illustrate the variability of the structure of turbulence as it pertains to gas transfer.

ABSTRACT

GAS TRANSFER RATE COEFFICIENT MEASUREMENT
BY A STABLE ISOTOPE KRYPTON TECHNIQUE.
II. ANALYTICAL METHODS

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We have developed equipment and techniques for measuring the transfer rate of krypton gas in large bodies of water or wastewater treatment plant mixed liquor. The procedure is critically dependent on the ability to measure precisely the small krypton content of liquid samples, which is accomplished by a somewhat unusual isotope dilution technique. Because the test is conducted under dynamic conditions, it is equally critical to account for gas dispersion by using a lithium salt as a conservative tracer added with the krypton.

The isotope ^{78}Kr is used as the isotope dilution spike because ^{78}Kr constitutes only 0.35% of normal krypton gas. The new technique involves spiking the liquid sample with an amount of nearly pure ^{78}Kr which is approximately equal to the amount to total krypton in the sample, and then measuring the abundance ratio of ^{78}Kr to "total krypton" (^{80}Kr, ^{82}Kr, ^{83}Kr, ^{84}Kr, ^{86}Kr) with a specially designed dual collector mass spectrometer. This ratio, combined with the known amount of ^{78}Kr spike, yields a very precise measure of the krypton content.

Five to thirty STP liters of krypton dissolved in twenty to forty liters of lithium chloride brine (40% w/w) are quickly injected into the system to be studied from two equilibrators, each with a volume of ~85 liters and operable at pressures up to 7 atm. Subsequent to this dump, samples of the liquid are collected at appropriate time in ~250 cc glass bottles and sealed with Poly-Seal caps. Exact liquid content is determined by differential weighing. An unsealing device has been designed and constructed which allows the sample bottle to be opened inside a thoroughly

evacuated chamber. The ^{78}Kr spike is introduced into the chamber before opening the bottle. The liquid is degased by violent stirring, and the evolved gases are dried in dry ice - acetone and liquid nitrogen traps before they are cycled over hot (950C) titanium to remove all but the noble gases. The gas is then put through a process gas chromatograph using helium as carrier gas. The sample stream gas is directed into a mechanical vacuum pump except during the time that the krypton is being eluted, when the flow is switched to pass the gas over a molecular sieve trap operated at 77K, which collects the krypton. After the helium is pumped away, the sieve is warmed and the released krypton is collected for the mass spectrometric analysis. Because the spiking material is added at the time that the bottle is opened, total quantitative recovery is not necessary because it is only the isotopic ratio which must be measured.

The concervative tracer (Li) was determined by flame atomic absorption spectrophotometry (AAS). Experimental results have shown than among the standard procedures for sample preparation and AAS analysis of lithium in mixed liquor, only one protocol gives satisfactory results.

The precision and accuracy of the gas and conservative tracer measurements are discussed.

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Estimation of Volatilization of Toxics for Multimedia Modeling

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Abstract

Multimedia modeling for estimating the concentration of
toxic substances considers the transport, transformation and
reactions of chemicals in air, water and soil, and the rate of
chemical exchange between any two of these three geospheres. The
methods used to estimate the changes in concentrations due to the
volatilization processes between water and air as well as between
soil and air can be of critical importance in a multimedia model.

Many multimedia models utilize simplified approaches (e.g.
fugacity, partitioning) in which simple and easy-to-use governing
equations are used to estimate the exchange rates of
volatilization processes (e.g. Henry's law or two-film theory for
the volatilization between water and air and Fick's law of
diffusion between soil and water).

This paper discusses and compares the governing equations
for modeling volatilization processes in existing toxic substance
multimedia models such as UTM (Unified Transport Model developed
by Oak Ridge National Laboratory), ENPART (Environmental
Partitioning Model developed by U.S. Environmental Protection
Agency and General Software Corporation), TOX-SCREEN (a
multimedia screening model developed by Oak Ridge National
Laboratory) and others (e.g. Mackey's and Neely's Partitioning
Models).

Chemical, physical and environmental factors which affect
the volatilization/evaporation processes of toxic substances are
discussed. Appropriate models for estimating volatilization/
evaporation of toxics at the water surface between water and air
and the interface (containing water, soil and air) between soil
and air are suggested and their complexity, accuracy and useful-
ness are discussed.

Abstract for a paper to be presented to the International Symposium on
Gas Transfer at Water Surfaces at Cornell University, June 13-15, 1983:

The Schmidt Number Dependence of the Gas Transfer Coefficient

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Transfer coefficients for N_2O, CH_4, and He at the air water interface
were measured in an 18 meter wind wave tank at moderate wind speeds. The
transfer coefficient was found to vary with D^a, with the exponent 'a' equal
to 0.47 ± 0.14 (90% confidence interval). The diffusion coefficients used for
N_2O, CH_4, and He were 1.84, 2.32, and 6.12×10^{-5} cm^2/s at 23.5°C. This
result supports models in which the transfer coefficient is proportional
to the square root of the Schmidt number (the ratio of the diffusion
coefficient to the kinematic viscosity of water). The result is contrasted
with that for transfer coefficients at solid boundaries, where the analog
of 'a' assumes a value of 2/3. The difference is attributed to the
boundary constraints which allow tangential convergence of fluid at the
air-water interface, but not at the solid boundary.

ABSTRACT

The Determination of Henry's Constants of Volatile Organics

by Equilibrium Partitioning in Closed Systems

by

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and

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An accurate knowledge of Henry's constant is necessary for modeling gas transfer in a variety of situations. Unfortunately, great accuracy is difficult to achieve using straightforward measurement of gas and aqueous phase concentrations from equilibrated, closed systems. Many of the compounds of current interest are so sparingly soluble -- and of sufficient volatility -- that it is difficult to construct accurate calibration curves with which to assay equilibrium concentrations. This is particularly true of aqueous phase assays. As a result, current methods for determining Henry's constants usually involve the use of a batch, diffused-air stripping tower, wherein it must be assumed that equilibrium is achieved between the gas which exits the tower and the aqueous phase through which it has bubbled (e.g., see Mackay et al., Envir. Sci. & Technol. 13, 333, [1979]). In our paper, we demonstrate that for many compounds of high volatility frequently found in contaminated surface and ground waters, mass transfer limitations exist which invalidate the equilibrium assumption of the batch air stripping method.

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[*] To whom correspondence should be addressed.

ABSTRACT: Lincoff, A. H., and J. M. Gossett, "The Determination of Henry's Constants of Volatile Organics by Equilibrium Partitioning in Closed Systems."

A novel technique is presented -- Equilibrium Partitioning in Closed Systems -- which allows the calculation of Henry's constant from the mere ratio of gas-phase concentrations resulting after equilibration of two closed systems which have been prepared differently. The technique is extremely simple and is free of mass transfer limitations which reduce the utility of other techniques. Since this new method uses only the ratio between gas concentrations of two equilibrated systems, knowledge of the actual gas phase concentrations is unnecessary. This eliminates a major problem associated with the research of volatile compounds in dilute solution: namely, the preparation of calibration curves. Henry's constants can be determined with a mean coefficient of variation less than 5%, solely using peak height data obtained through GC analyses of headspace samples from two equilibrated systems. Knowledge of the actual mass of volatile substance added to the two systems is also unnecessary.

Using both our proposed technique -- and that of Mackay et al. -- Henry's constants for five compounds were measured over a range of temperature (10 - 30°C) and ionic strength (0 - 1 N KCl) typical of natural bodies of water. Mixtures of the five compounds in water were also investigated. The compounds, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, chloroform, and methylene chloride, encompass a wide range of volatility and are all EPA priority pollutants. Results demonstrate that for the more volatile of the compounds, the batch air stripping method significantly underestimates Henry's constants due to apparent mass transfer limitations preventing equilibration of exit bubbles.

Carbondioxid Desorbtion from the Activated
Sludge in the Waste Water Treatment Plants

by: Dejan Ljubisavljević

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Abstract:

It is necessary to study more in detail the desorbtion of
carbondioxid from the activated sludge, in waste water
treatment plants where biological nitrification occurs
(sensitive on the decrease of the pH), and where pure
oxygen is applied as an oxidant.

Experimental results obtained from the laboratory models of
the surface and diffused air aerator are presented in this
article. Desorbtion of carbondioxid was measured with the
help of the pH-meter. Experiments were done both with tap
water only, and with tap water and surface active agents.

Results from the models were compared with the existing
gas transfer theories, and the validity of certain theories
were estimated.

From the carbondioxid desorbtion point of view, the conside-
rations on the results obtained from the field measurements
made at the pilot waste water treatment plant in Buesnaw
(Sttutgart, Federal Republic of Germany) are presented. The
field measurements on the mentioned plant in which biological

nitrification - denitrification occurs were performed by
the author in june 1982.

Among else, alkalinity and pH were analysed on the end points
of the nitrification and of the denitrification parts.
(Different from the carbon oxidation, besides the increase
of the carbondioxid content, nitrification decreases the
alkalinity of the activated sludge).

On the base of the theoretical and experimental considerations
the conclusions were drawen about the efficiency of certain
aeration systems on the desorbtion of the carbondioxid from
the activated sludge.

Some recommendations are propoused about the choise of the
aeration systems for the waste water treatment plants, were
special care is to be taken of the problem of the carbondioxid
desorbtion from the activated sludge.

CURRENT FLUCTUATIONS IN THE SURFACE WATERS OF SMALL LAKES

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The transfer of momentum from the wind to the surface of a lake creates fluctuations in velocity which are an expression of turbulent eddies, surface and internal waves. To know the scaling from the wind stress to the stress at the surface of a lake is important for budgets of energy transfer and models of mixed layer dynamics. An environment in which these processes have not been examined is shallow, naturally eutrophic lakes with small fetches. I used an omnidirectional warm-bead thermistor-flowmeter to measure fluctuations in current speeds throughout the upper mixed layer of three shallow lakes in equatorial Africa with differing exposures to wind. The flow sensor resolved speeds of less than 0.1 cm/sec and frequencies of ca. 5 Hz. The first four statistical moments, probability density functions, autocorrelation functions, and energy spectra have been computed from the current records, the mean and rms speeds have been compared with wind speeds measured two meters above the lakes' surfaces, and Richardson's numbers have been calculated.

Current speeds within 1.5 cm of the surface fluctuated rapidly from 0.3 to 16 cm/sec. The mean speeds were ca. 5 cm/sec and the turbulent intensities (ratio of rms speed to mean speed) were greater than 0.4. The data records showed a graded shift from high frequency, high amplitude fluctuations to lower frequency (ca. 2.3 to 0.3 Hz), smaller amplitude fluctuations from the surface to 10 cm depth. This shift occurred in the absence of thermal stratification. At 10 cm the turbulent intensity was still high (0.25). In thermally stratified water, waves with a frequency of 0.01 Hz were observed within 30cm of the surface. These data illustrate the extreme activity and variety of responses in low energy lacustrine environments.

Abstract for
Physical-Chemical Phenomena and
Molecular Properties (Keynote Paper Topic 1)

D. Mackay, University of Toronto

The transfer characteristics of solutes between water and air are controlled by the solute's equilibrium and transport properties.

The equilibrium properties of aqueous solubility, vapor pressure and Henry's law constant determine the relative concentrations at equilibrium and hence the direction of transfer in any given situation. Partition coefficients to solid or liquid materials in both air and water phases near or at the interface and interactions with dissolved material may also play an important role. Methods of measuring correlating and estimating these properties for gaseous liquid and solid solutes are reviewed and discussed.

Mass transfer rates are conventionally expressed using a "two resistance" approach in which mass transfer coefficients are invoked for each phase. These coefficients are primarily determined by the local hydrodynamic regime but are also influenced by the solute's diffusivity. It is suggested that air and water phase Schmidt Numbers currently provide the best characterization of solute properties and of temperature, when raised to an appropriate power reflecting the exchange conditions. Methods of obtaining and testing such data are discussed.

In view of the large number of solutes of potential interest, it is suggested that a strong case can be made for improving the capability of correlating and estimating these physical chemical properties for compounds which are members of similar chemical classes.

THE EFFECT OF INSOLUBLE AND SOLUBLE MONOLAYERS ON GAS EXCHANGE ACROSS AN AIR-WATER INTERFACE

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A B S T R A C T

Two series of laboratory tank experiments are described in this paper. In the first series the simultaneous transfer of H_2O, SO_2, CO_2 and O_2 was monitored across clean and monolayer covered water surfaces under conditions of low hydrodynamic turbulence. It is known that under certain conditions insoluble monolayers are able to present a specific or barrier resistance to gas transfer, and results presented here for long chain fatty acids and alcohols are in reasonable agreement with previous work for the transfer of H_2O and SO_2, which is under gas phase control in these experiments. For O_2 and CO_2, which are under liquid phase control, the specific resistance of the monolayer cannot be seen against the intrinsically high resistance of the water itself.

Soluble monolayers do not fulfil the stringent requirements necessary to present a direct resistance to gas transfer, but can provide an indirect effect under conditions of high hydrodynamic turbulence. In the second series of experiments, the effect of the surfactant Manoxol O.T. (sodium dioctyl sulphosuccinate) was measured on the transfer of O_2 under high stirring regimes. The results show that surfactant concentrations as low as 0.01 mg l^{-1} are capable of significantly reducing O_2 transfer velocities, and that reduction of nearly 60% can be obtained when the concentration of the surfactant exceeds 10 mg l^{-1}.

The ability of sea surface microlayer material, collected using a Garrett screen, to retard gas transfer was tested in both series of tank experiments. In the quiescent experiments no reduction was evident but significant reductions were noted in the turbulent experiments and the consequences of this finding for air-sea gas transfer are discussed.
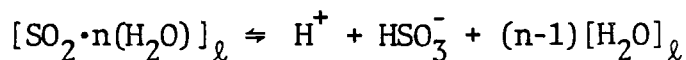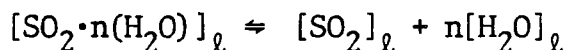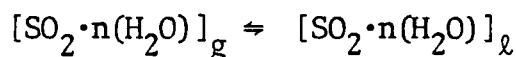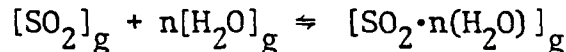
ABSORPTION OF GASES AT CONDENSING

AND EVAPORATING WATER SURFACES

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ABSTRACT

Observations of water vapor condensing on both large droplets (2 mm) and NaCl nuclei (1 μm) in the presence of a trace gas Y, indicate an enhancement in the concentration of Y in the liquid phase during condensation and a depletion of Y during evaporation. A model is proposed wherein homogeneous clusters of gas molecules of the type $Y \cdot (H_2O)_n$ formed in the gas phase may explain these departures from expected mass transfer behavior. When $Y = SO_2$:

$$[SO_2]_g + n[H_2O]_g \rightleftharpoons [SO_2 \cdot n(H_2O)]_g$$

$$[SO_2 \cdot n(H_2O)]_g \rightleftharpoons [SO_2 \cdot n(H_2O)]_\ell$$

$$[SO_2 \cdot n(H_2O)]_\ell \rightleftharpoons [SO_2]_\ell + n[H_2O]_\ell$$

$$[SO_2 \cdot n(H_2O)]_\ell \rightleftharpoons H^+ + HSO_3^- + (n-1)[H_2O]_\ell$$

During condensation or evaporation, a water vapor pressure gradient establishes a gradient in the gas phase hydrate. Mass transfer coefficients, equilibrium constants and heats of solution were calculated for the above mechanism. Further tests with oxygen and NO_2 reveal similar patterns during the condensation-evaporation cycle, and a general model is proposed for absorption water soluble gases.

A COMPARISON OF TURBULENT MASS TRANSFER AT
GAS-LIQUID AND SOLID-LIQUID INTERFACES

by

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For a number of years we have been studying the details of a turbulent
flow close to a solid boundary and have been using this information to develop
a theory for turbulent mass transfer. This work has led to a picture of tur-
bulent mass transfer to a solid boundary which is radically different from
theories currently available in the literature. Only very low frequency velo-
city fluctuations and, therefore, only a small fraction of the turbulent ener-
gy is effective in transferring mass. The fraction of this energy decreases
with increasing Schmidt number. In recent years we have been applying in-
sights gained in this work to the problem of defining the mechanism of tur-
bulent mass transfer at a gas-liquid boundary. This paper summarizes our
progress.

The system in which our experiments are conducted is a 2.54cm x 30.48cm x 9m
enclosed rectangular channel. Liquid flows along the bottom of the channel
and air flows concurrently. The rate of oxygen absorption is determined by
measuring the change of the oxygen concentration of the liquid film at dif-
ferent distances downstream. The wave properties are measured by a parallel
wire conductance probe. The shear stress fluctuations at the wall are
measured by a flush mounted thermal probe. The film varies in height from .05
to .55cm. Air velocities from 4 m/s to 14 m/s have been used. The viscosity
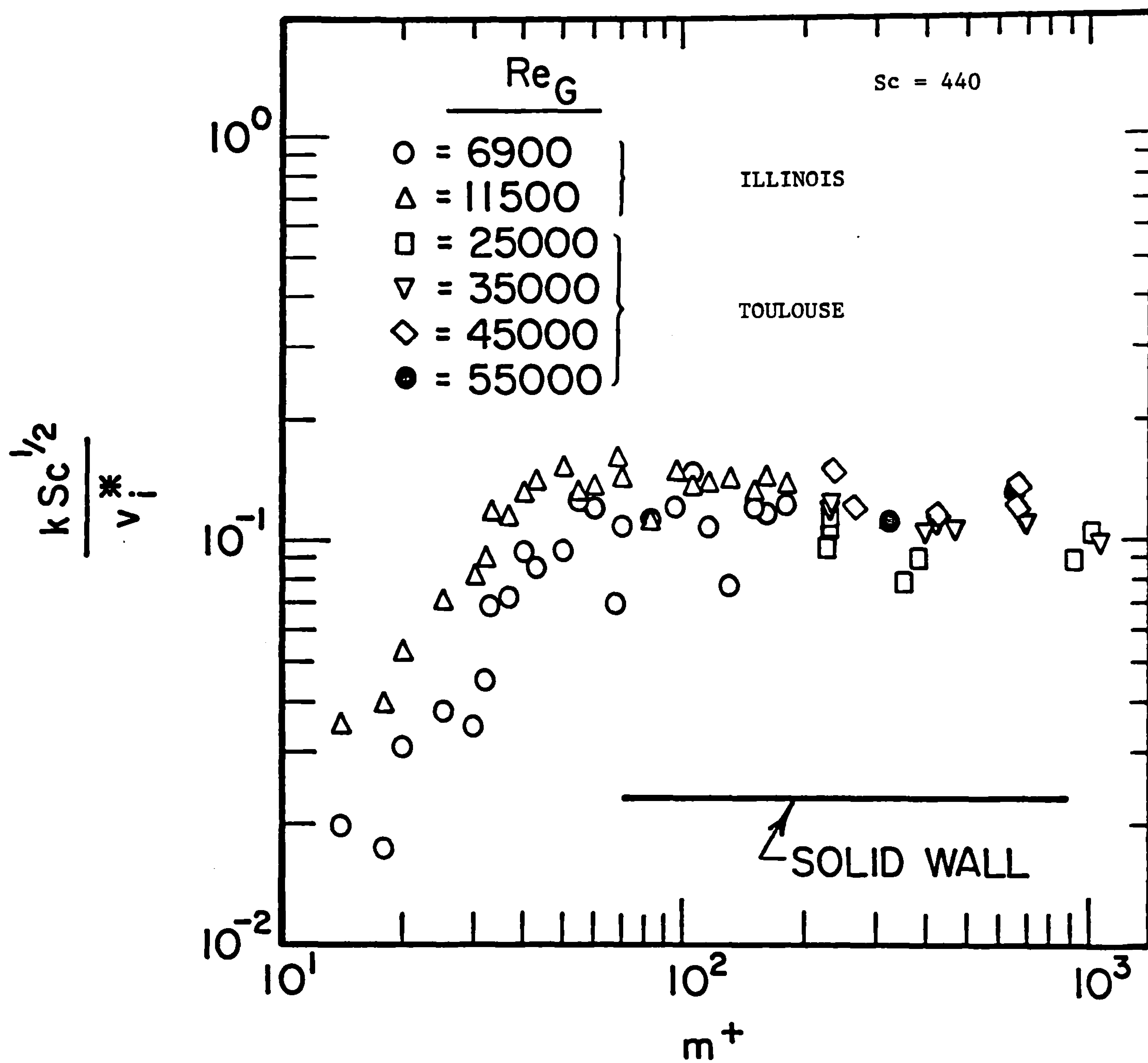of the liquid can be varied using water-glycerine solutions.

Figure 1.

Measurements of the mass transfer coefficient obtained with water are shown in Fig. 1. Here the friction velocity is defined in terms of the interfacial stress, $v_i^* = (\tau_i/\rho_L)^{1/2}$ and the height of the liquid layer has been made dimensionless using the friction velocity and the kinematic viscosity, $m^+ = m\, v_i^*/\nu$. It is noted that for $m^+ > 45$ the dimensionless mass transfer coefficient is approximately constant, $k\, Sc^{1/2}/v_i^* \approx 0.1$. For comparison, measurements obtained in a 10cm x 20cm x 6m channel at the University of Toulouse (Tsacoyannis, 1976) with flowing liquid layers much thicker than ours (1cm to 3.5cm) are also shown. It is of considerable interest that such good agreement is obtained in widely different systems, provided the results are plotted in the manner shown in Fig. 1. These results suggest that the velocity fluctuations controlling mass transfer are independent of the liquid depth for thick films and are caused by interfacial shear. Three mechanisms are being explored as being responsible for these velocity fluctuations close to an interface: turbulence generated at the interface, turbulent velocity fluctuations transmitted by gas flow shear stress fluctuations, and waves.

From extensive experiments we have found that turbulent mass transfer at a solid boundary is given by the equation

$$k/v_w^* = 0.8\ Sc^{-.704}\ .$$

It is noted that this relation is similar to what is found for a gas-liquid interface in that the mass transfer coefficient is related to flow variables through the friction velocity. This suggests that the shear at a gas-liquid interface is producing turbulence by processes similar to what occur at a solid-liquid interface. Support for this is obtained from the measurements of Suzanne (1977) which indicate a maximum in the turbulence intensity in the liquid near a gas-liquid interface.

However, as shown in Fig. 1, the magnitude of the mass transfer coefficient is smaller for the solid-liquid interface. A possible explanation for this can be obtained from an analysis of the relation between the concentration fluctuations and velocity fluctuations close to a boundary. This relationship for a clean gas-liquid interface, where the normal velocity varies linearly with distance from the interface, is quite different from the case of a solid-liquid boundary where the normal velocity varies quadratically in y. For a gas-liquid interface the concentration boundary layer does not act as a filter; this means that mass transfer at a clean gas-liquid interface is being affected by velocity fluctuations of all frequencies, and not just by very low frequencies, as is true for a solid-liquid interface.

The sharp drop off in $k\ Sc^{1/2}/v_i^*$ noted for $m^+ < 40$ can be explained if for small film heights, turbulence generation at the interface can be inhibited by the nearness of the solid boundary. In this region the inflexible boundary distorts the flow field and influences the scales of the turbulence produced at the interface. Consequently, $k\ Sc^{1/2}/v_i^*$ is a function of the gross flow parameters film height and gas Reynolds number for small m^+.

For very thin films measurements from our wall shear stress probes indicate that fluctuations in the gas flow are causing fluctuations in the shear stress transmitted to the liquid film by the gas flow. This provides another source of velocity fluctuations in the liquid near the interface. By using measurements on turbulent shear stress fluctuations of air at a solid boundary, we have carried out an analysis to estimate their influence in gas-liquid mass transfer. We find that the velocities scale with v_i^*. This suggests that these fluctuations should give a contribution to k which increases linearly with v_i^*.

A tentative explanation of the results in Fig. 1 is that mass transfer is controlled by an additive effect of gas shear stress fluctuations being transmitted to the liquid and of turbulence being created in the liquid by the shear field interface. As m^+ increases the creation of turbulence in the liquid becomes relatively more important.

It is well known that surface waves on freely falling films can cause an increase of mass transfer over predictions for laminar flow. A simple analysis of the influence of waves on velocity fluctuations in gas-liquid flows indicates a different scaling for k than what is given in Fig. 1. This, in addition to the observation that the same results are obtained in systems with widely different wave properties (our data and the data of Tsacoyannis), would indicate that the results in Fig. 1 are not explained by a simple wave mechanism.

Nevertheless, we have not ruled this out as a possibility. Consequently, we are currently carrying out experiments which relate mass transfer rates to wave properties. We hope to be able to give a report on these at the Conference.

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10/19/82

GAS EXCHANGE ACROSS AN AIR-WATER INTERFACE : RESULTS OF EXPERIMENTS AND MODELING OF BUBBLE CONTRIBUTION TO GAS TRANSFER

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ABSTRACT

Gas exchange experiments have been performed in a wind-water tunnel filled with fresh water or sea water. Transfer velocities have been measured in a range of wind speed extending from 3m/s to 14 m/s. The air-liquid interface was covered either with normally developed wind waves or mechanically generated waves in addition. For u < 9 m/s a linear variation of the transfer velocity, k_L, with wind speed (and also friction velocity) is observed for all gases. Two distinct relationships link k_L and u, depending on the presence of artificially generated waves. In this last case, a mean enhancement of the order of 30 % is observed. For higher wind speeds (u > 9 m/s), a sudden jump of the values of k_L is observed. This observation is interpreted as being the result of the onset of breaking waves which create bubbles through which mass transfer takes place. No difference for gas exchange either in fresh water or in sea water has been identified from the whole set of experiments.

A first theoretical approach to gas transfer by bubbles is undertaken. Certain parameters which are neglected by smooth air-water interface modelings are studied. It is found that transfer velocity increases when solubility decreases. Further, bubble overpressure leads to water supersaturation at equilibrium, this supersaturation being more significant for less soluble gases. If the transfer velocity remains roughly constant for a variable concentration gradient far from equilibrium, its range of variation becomes infinite near equilibrium. Finally, an effort is made to incorporate surfactants into the modeling.

Because the notion of transfer velocity is not useful near equilibrium, attention is turned directly to the flux itself : the flux is a linear function of the concentration gradient. At least for tracers, the coefficients of this function are entirely defined by the physico-chemical properties of the gas and by the bubble distribution. Results of numerical applications are presented for helium, radon, argon and carbon dioxyde.

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+   +
+

In Situ pH Measurements as an Indicator of CO_2 Gas Transfer in
Glacial Melt Waters

by

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In situ pH measurements in glacial melt waters from glaciers in Washington, Alaska, and Switzerland, during 1977-1981 have firmly established that CO_2 gas transfer across the air-water interface is the dominant process controlling hydrogen ion activity in these dilute waters. Detailed understanding of this phenomenon is critical to : 1) evaluating "acid-rain" pH observations from snow in the high Arctic, 2) understanding the roles of regelation and subglacial precipitation in controlling the basal sliding of glaciers, 3) correctly evaluating thermodynamic mineral stability diagrams for rock weathering in glacier hydrologic systems, and 4) understanding the nature and kinetics of CO_2 cycling in the high alpine environment in an effort to further knowledge of the global CO_2 budget.

During initial spring snow melt, melt waters in the stream exitting the glacier terminus were often oversaturated with respect to P_{CO_2}, and rapidly increased pH during outgassing at $0^{\circ}C$ and ambient atmospheric pressure. This appears to be a result of CO_2 purification within the glacier by a presently undetermined process. Not surprisingly, after years of purification, summer melt waters from "old" glacier ice in the ablation zone of a temperate glacier are usually undersaturated by 10 to 100 times with respect to atmospheric P_{CO_2}, and rapidly lower their pH values to achieve equilibrium upon encountering the atmosphere. Especially during summer, proglacial stream waters sometimes show pH increases from rock weathering with the rate limited by the transfer of CO_2 across the air-water interface to drive the weathering reactions.

dpH/dt experiments demonstrate that glacial waters achieve equilibrium without agitation within 2 to 3 hours in 0.25 dm^3 polythene beakers at in situ pressures and temperatures. The change in pH is exponential with time, driven by the P_{CO_2} gradient between the sample and the atmosphere. By comparison, melt waters in the shallow, wide proglacial streams generally achieve pH equilibrium in 10 to 15 minutes, primarily hastened by enhanced gas transfer across the often turbulent stream surface.

THEORETICAL AND EXPERIMENTAL EVALUATION OF OXYGEN TRANSFER AND TOTAL OXYGEN REQUIREMENTS IN BIOLOGICAL WASTEWATER TREATMENT

by

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A year long study was conducted to investigate the ability of the two film theory to accurately predict oxygen transfer in the activated sludge process and to evaluate the hypothesis that the efficiency of aeration devices installed in activated sludge systems are not fixed but increase with an increase in the oxygen uptake rate as purposed by Albertson and DiGregorio [1]. Biochemical stoichiometric equations are developed as a function of wastewater composition and the mean cell residence time to theoretically predict oxygen requirements. The theoretical valves are compared with actual valves obtained from an extensive laboratory investigation.

Two laboratory scale activated sludge reactors were operated over a 3 to 20 day mean cell residence time. Various analytical tests were conducted on samples taken from the influent, effluent, and mixed liquor so that complete materials balances could be written. The oxygenation capacity and the overall oxygen transfer coefficient (K_1a) of the diffuser stones (utilized for aeration) was determined in tap water and the waste-water effluent from each of the reactors under steady state and nonsteady state conditions. Presently, data are being obtained and evaluated. Preliminary results indicate that the theoretical valves agree with actual valves and that activated sludge systems operating under a dissolved oxygen limitation yield an effluent with a high nitrite-nitrogen concentration in the range of 200 to 300 mg/l if the influent has a total kjeldahl nitrogen of approximately 450 mg/l.

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THE ROLE OF OCEANIC WHITECAPS IN AIR-SEA GAS EXCHANGE
BY
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The wind dependence of the air-sea gas exchange rate, as expressed by the gas transfer coefficient or piston velocity, k', has variously been described as being linear ($k' \propto U$; Broecker, 1979), quadratic ($k' \propto U^2$; Kanwisher, 1963a), or exponential ($k' \propto e^{U/2}$; Emerson, 1975) in character, and recently, based on a consideration of the Geosecs Radon data (Peng, et al , 1979), it has been stated that no clear relationship can be found between k' and U. Kanwisher (1963a) described the possible role of whitecap bubbles in eliminating the laminar surface layer of the ocean, and Banner and Melville (1976) have discussed the manner in which whitecaps induce separation in the airflow over the waves. A model thus evolves in which each oceanic whitecap can be perceived as a low-impedance vent or duct, effectively penetrating the fluids on both sides of the naviface. It follows from such a model that the piston velocity should be proportional to the instantaneous whitecap coverage, W (Kerman, 1980). Since the wind-dependence of oceanic whitecap coverage has been demonstrat-ed to be of the form, $W \propto U^{3 \cdot 4}$ (Monahan and O'Muircheartaigh, 1980), it follows that the present $k'(U)$ model is of the form,

$$k' \propto U^{3 \cdot 4} \quad \text{(Eq.1)}$$

The discrepancy between the wind dependence of k' reflected in this model and the earlier linear and quadratic descriptions is attributed to the fact that these earlier models were in large measure based on wind flume observations, and such laboratory experiments have unreal-istic "wave ages" or sea states associated with them (Kanwisher,1963b; Monahan, et al,1982). As a working hypothesis the following expression has been adopted, where the cubic approximation (Monahan. 1981) has

$$\overline{k'} = C_g \overline{U^3} \quad \text{(Eq.2)}$$

been introduced as a computational convenience, and the ($\overline{}$) represents a temporal average over a suitable interval - four days according to Peng, et al (1979). This hypothesis has been tested, and a value for the coefficient C_g obtained, with reference to recent tabulations of Radon k' values, e.g., Peng, et al (1979). Since the meteorological data required for the calculation of $\overline{U^3}$ are in all instances lacking, $\overline{U^3}$ has been estimated from a judicious combination of mean monthly $\overline{W}$ (i.e. $\overline{U^3}$) values (Spillane, 1982) based on the data compilation of Hellerman (1978), and the day-of-measurement $\overline{U}$-values reported by the Radon workers.

The Ratio of Gas-Phase to Liquid-Phase Mass Transfer Coefficients
in Gas-Liquid Contacting Processes

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The objective of the work reported herein was to assess the relative importance of gas- and liquid-phase mass transfer coefficients in diffused aeration, surface aeration and packed columns. Recently, each of these processes has been considered as a possible method to strip volatile halogenated organic compounds from solution (1,2,3,4). When modelling these systems, previous workers (1,3,5,8,14) consistently have assumed a ratio of gas phase mass transfer coefficient to liquid phase mass transfer coefficient (k_g/k_l) of 150 as the criterion to assess the relative importance of gas and liquid side resistances. The value $k_g/k_l \cong 150$ was inferred from average estimates for $k_g(H_2O)$ and $k_l(CO_2)$ at the air-sea interface by Liss and Slater(6) and thereafter applied to volatilzation/absorption at air-water interfaces for treatment processes(1,3,4,5,8,14) as well as natural processes(8,9,10,11). However, it is likely that this ratio depends significantly on the type of system or process and possibly also within a given system depending on the flow conditions.

Laboratory experiments were carried out modelling diffused aeration, surface aeration, and packed columns in which the following compounds were stripped out of solution while oxygen was absorbed (stripped in packed column) simultaneously: CCl_2F_2, $CHCl_3$, CH_3-CCl_3, CCl_4, $CHCl=CCl_2$ and $CCl_2=CCl_2$. The surface aeration device consisted of a baffled cylindrical glass vessel with a liquid volume of 7.3 liters; a ring-guarded stirrer with three pitched blades was used. The bubble aeration

device consisted of a glass column 22.5cm in diameter; the diffuser was a ceramic perforated plate and the liquid volume was 18 liters. Packed column experiments were carried out in the same glass column. The packing material was 1/2-inch ceramic berl saddles with a packed height of 40cm. In all experiments non-adsorbing materials were used: glass, teflon, stainless steel and ceramic. Organic compounds were determined by gas chromatography, and oxygen was monitored continuously with a probe. The procedure for surface and diffused aeration consisted of analyzing the change in organics concentration with time. In the packed column experiments five replicate influent and effluent samples were analyzed after reaching steady state. In each experiment an overall mass transfer coefficient, $K_l{\cdot}a$, for each of the compounds was obtained by using an appropriate model (accounting for partial gas phase saturation in bubble aeration(12)). Linear regressions of $1/K_l{\cdot}a$ vs. $1/H_c$ were carried out to estimate $k_g{\cdot}a$ and $k_l{\cdot}a$ according to the concept of additivity of resistances:

$$\frac{1}{K_l{\cdot}a} = \frac{1}{k_l{\cdot}a} + \frac{1}{H_c{\cdot}k_g{\cdot}a} \tag{1}$$

Although both k_g and k_l depend somewhat on diffusivity. the approach is reasonable because the diffusivities of the halogenated organics differ little (Table 1). Oxygen data were not included in the regression analysis. Henry's Constants, H_c, were also measured(15) except for CCl_2F_2 and O_2 (Table 1).

Fourteen surface aeration experiments were carried out at varying stirring rates from 131 to 376 rpm(13). The results of the regression

analysis are presented in Table 2. It is evident that the ratio k_g/k_l decreases with increased stirring. At low agitator speeds k_la increases faster than k_ga. At higher speeds both values increase approximately proportionally, reaching what appears a limiting value of $k_g/k_l \approx 20$; the correlation coefficients are in general >0.95 in the latter range. Also, the validity of the regression can be judged by comparing the measured $K_la(CCl_2F_2)$ values with the predicted k_la's: these should agree closely, which indeed is the case.

Fourteen packed column experiments were carried out(7) varying the gas flow rates from 2 to 16 lit/min. The results are presented in Table 3. The ratio k_g/k_l increases with increasing gas flow rate, but is substantially smaller than in surface aeration. While all correlation coefficients exceed 0.92, the predicted k_la's differ substantially from the measured $K_la(CCl_2F_2)$ values at low gas flows. This is because the gas phase resistance is more important than the liquid phase resistance, i.e. the slope of the regression $(1/k_ga)$ is large and the $K_la(CCl_2F_2)$ contributes little to the regression. To account for this, the data will be reanalyzed to obtain K_ga values instead of K_la values.

Six preliminary bubble aeration experiments have been carried out at varying gas flow rates from 1.7 to 7.7 lit/min. Results are shown in Table 4, and in this case the ratio k_g/k_l appears to decrease with increasing gas flows. Negative predicted k_ga values can be attributed to insufficient mixing. An additional set of experiments will be conducted to resolve this difficulty before the Symposium.

In summary. the data presented indicate strongly that k_g/k_l ratios vary from system to system and also with flow conditions within a given system. It is dangerous to assess the relative importance of gas and liquid side resistances based on a generally accepted value of $k_g/k_l \simeq 150$.

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REAERATION MEASUREMENT IN SWAMP STREAMS
RADIOTRACER CASE STUDIES

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Reaeration in swamp-like streams is particularly difficult
to characterize due to the unusual variability of swamp stream
hydraulics and the difficult access for field survey crews. The
normal regulatory tendency is to use "conservative" (low) estimates
of reaeration rates when confronted with a swamp stream situation.
Probably due to the difficulty in studying swamp streams, there
is little published data on swamp stream reaeration.

This paper presents the results of radiotracer (krypton - 85
and tritium) studies of reaeration in several different swamp
streams. These swamp streams are located in Georgia, Louisiana,
North Carolina, and South Carolina with flows ranging from a few
cubic-feet per second (cfs) up to about two-hundred cfs. Flow
velocities in the study segments range from less than 0.05 feet
per second (fps) up to about one fps with measured reaeration rates
from about 0.05 to over 1.0 (per day, base e, 20°C).

In addition to the tracer-measured reaeration rates, some
energy dissipation data are presented indicating that these swamp
streams are relatively efficient in utilizing available head for
mixing and resulting reaeration. Interim recommendations
are provided concerning reaeration predictions for swamp-like
streams and further study needs are identified.

EXCHANGE RATES OF GASEOUS SULFUR COMPOUNDS BETWEEN OCEAN AND ATMOSPHERE

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Biological activity plays an important role in the gaseous sulfur compound exchanges between ocean and atmosphere. Indeed, this activity evolves organic sulfur compounds, one of which is dimethyl sulfide (DMS). This gas is rather insoluble and volatile, it escapes from the water, oxidizes in the atmosphere to give SO_2 and then sulfates.

Two cruises, in the Indian and Pacific Oceans, were undertaken to measure DMS at the ocean-atmosphere interface. Measurements were taken in the water and in the air at heights of 1, 10, and 17 m above the ocean surface. The results obtained during these voyages show a good correlation between surface water and atmospheric concentrations. These concentration gradients from surface water layer to atmosphere enable us to determine the diffusion coefficient in the first 17 meters altitude over ocean, and consequently the ocean-to-atmsophere transfer coefficient (or piston velocity). These parameters depend mostly on meteorological factors (wind scale and sea state, etc,..).

From these parameters, gaseous sulfur compound oceanic production in the atmosphere could be estimated to be about 30×10^6 tons of sulfur per year.

THE SIGNIFICANCE OF GAS-LIQUID EXCHANGE
IN WATER QUALITY MODELING & ASSESSMENT

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Environmental problems, in which gas-liquid exchange plays a major role, concern aesthetics, eutrophication and toxicity. These are not only of environmental importance, but also are of economic significance. in view of the costs of treatment and control methods which are invariably required to address such problems.

Rational water quality management requires the application of mathematical models which describe the spatial and temporal distribution of the relevant water quality constituents. These models contain transport, transfer and kinetic components. While the transport factors are fairly well established for many natural water systems, little fundamental basis exists for the quantification of the kinetic interactions and transfer routes. These coefficients are either assigned empirically or calculated from observations in the prototype systems. The one notable exception is the gas-liquid transfer process, for which at least some theoretical basis exists for the determination of the relevant coefficient. An objective element is thereby provided in the important process of the validity of the water quality model. Furthermore, the fundamental nature of the gas transfer relationships permits extrapolation to other environmental conditions, an element which is an integral part of the planning process. The coefficient, which quantifies the process, is one which may be determined without recourse to water quality measurements in the prototype and thereby, provide for the validation of water quality models and the subsequent application in water resources management.

The specific constituents considered are oxygen, carbon dioxide, ammonia, sulfur dioxide and volatile organic chemicals. whose concentration in natural waters is effected by the discharges of municipal, agricultural and industrial wastewaters, as well as been natural runoff and drainage. The first three gases are important because of their roles in chemical and biological cycles. Ammonia is toxic to aquatic organisms, as are many volatile synthetic chemicals. Carbon dioxide. an integral element in the pH-acidity-alkalinity balance of a natural water systems, is important in acid mine drainage and dry and wet deposition from teh atmosphere.

A brief description of general elements of water quality models is first presented. A review of the gas transfer relationships relating to dissolved oxygen, carbon dioxide, ammonia, sulfur dioxide and volatile organic chemicals follows. The various viological, chemical and physical factors which affect these constituents are discussed, including the significance of the gas-liquid exchange. The types of models. commonly employed in the analysis of dissolved oxygen and reactive toxics, are reviewed. For the analyses of pH and inert toxics, the general structure of the models are suggested. For each constituent, a practical methodology of environmental analysis and examples of practical applications are presented.

ABSTRACT

Transfer Coefficients of Smooth Transitional and Rough Flows

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Many constituents, which are susceptible to transfer through the
air-water interface, are of environmental importance. Factors which
affect the exchange rate across this boundary are the air and water
velocities, the relative smoothness-roughness of the surface, and the
physio-chemical characteristics of the interface and of the transferable
constituents. Fluid motion exerts a shear at the interface, which
establishes the structure of the boundary layers in both media. The
dynamic features of these interfacial regions, defined the viscous
sublayer and roughness height, influence the transfer between air and
water. Velocity functions are developed for both smooth and rough
surfaces. Relationships between the transfer coefficient and these
hydrodynamic parameters are established for each regime. A transition
function is also proposed for the momentum transfer which is used as a
basis to formulate the mass transfer relations. The overall transfer
coefficient is expressed in the usual manner of resistances in series,
involving both the film and surface renewal concepts. The latter is
predominant for smooth flow and the former for rough flow. In the
transition, the viscous sublayer and thus the diffusional sublayer are
eroded with a simultaneous growth of roughness effects and cavities, the
latter imparting an additional resilience to transfer. A constituent is
characterized by the solubility and partial pressure (Henry's Constant)
and by its diffusivity and viscosity of air and water (Schmidt Numbers).
Both liquid and gas film control are included in the applications. The
proposed model yields reasonable and consistent correlation with
transfer data from a number of laboratory systems. Extrapolation of the
relationships to prototype conditions are considered.

INTERNATIONAL SYMPOSIUM ON GAS TRANSFER AT WATER SURFACES

Cornell University

Ithaca, New York

June 13-15, 1983

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CARBON DIOXIDE GAS TRANSFER AT GAS/WATER AND OIL/WATER INTERFACES

AS A FUNCTION OF SYSTEM TURBULENCE

For processes which are not rate limited by chemical reactions, interfacial mass transfer will be controlled by the fluid mixing. This applies to transfer across both the gas/water and the oil/water (e.g., petroleum spill) interfaces. As they involve environmental water bodies, such processes are therefore often controlled by the degree and nature of the turbulence underlying the interface. Efforts in our laboratories have been directed towards the use of the pH-dependent laser-induced fluorescence (LIF) of fluorescein compounds to characterize the mass transfer of CO_2 (an acid)

across both the gas/water interface and the oil/water interface. The photo-diode monitoring of the LIF intensity in dilute fluorescein solutions ($\sim 10^{-8}$ - 10^{-7} $\underline{M}$) as a function of depth allows the calculation of the CO_2 flux across the interface as well as across any internal solution surface. Fine structure superimposed on the average signal has been found to be caused by the mixing of turbulent eddies of fluid particles of dissimilar net CO_2 content. Turbulence has been generated by means of an oscillating grid. Mass transfer measurements have been made under conditions of varying turbulence intensity, length scale, and distance to either the gas/water or the oil/water interface. (In the latter case, the oil phase is maintained saturated at a constant CO_2 level.) Experimental data will be presented and conclusions will be drawn for gas transfer at the air/sea and oil slick/sea interfaces.

MEASUREMENTS OF THE FLUCTUATING PRESSURE IN THE TURBULENT BOUNDARY LAYER OVER PROGRESSIVE, MECHANICALLY GENERATED WATER WAVES

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The structure of the pressure and velocity fields in the air above mechanically generated water waves was investigated in order to evaluate their contribution to the transfer of momentum and energy from wind to water waves.

Two wave-height gauges, an array of two X hot-film probes, a specially designed high-sensitivity pressure instrument, and five piezocrystal pressure transducers mounted on the roof of the Stanford wind-water wave facility were used to monitor the water-wave height and the velocity and pressure fields in the air.

The pressure and velocity measurements in the air boundary layer were performed in a transformed Eulerian wave-following frame of reference at preselected distances from the wave surface. Seven different wind speeds were examined in the range 140.59-402.04 cm/sec, with 1 Hz, 2.54 cm amplitude, mechanically generated water waves.

Measured acoustic and other pressure waves associated with the traveling upstream-reflected water wave were found to alter the wave-induced pressure behavior. These components are an order of magnitude greater than, and comparable to, the actual wave-induced pressure.

The nonlinearities of the propagating water wave and the drift current seem to introduce pressure components at frequencies other than that of the main wave. Wave-wave resonant interactions and wave-turbulence nonlinear interactions are also responsible for the strong wave-induced pressure harmonics.

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The wave-induced composite pressure coefficient, at the fundamental mode, shows in general an exponential decay behavior, but the rate of decay is different from that predicted by potential flow theory.

The relative wave-induced pressure phase remains fairly constant throughout the boundary layer, except at $c/\dot{U}_{\delta_0}$ = 0.780 and 0.677. This phase difference was found to be about 130° during active wave generation, pressure lagging waves.

The momentum and energy transfer rates supported by the waves were found to be dominated by the wave-induced pressure, but the transfer of the corresponding total quantities to both waves and currents may or may not, depending on c/U_{δ_0}.

The contribution of the wave-induced Reynolds stresses to the transfer processes is negligible.

INVASION OF FOSSIL FUEL CO_2 TO THE SEA

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ABSTRACT

Our knowledge of gas transfer at water surfaces can be applied to environmental problems such as the uptake of fossil fuel CO_2 by the ocean. CO_2 exchange rates across the sea-air interface have been successfully estimated from radon profiles in the upper few hundred meters of the ocean measured during GEOSECS cruises. The amount of anthropogenic CO_2 uptake is estimated by the one-dimensional box-diffusion model of Oeschger et al. (1975). The zonal variations of CO_2 exchange rates and vertical mixing rates as derived from GEOSECS tritium measurements are included in these model calculations. The results of these calculations and the amount of fossil fuel CO_2 reaching major active carbon reservoirs will be discussed.

R E A E R A T I O N   OF   T U R B U L E N T   W A T E R

E.J. Plate and R. Friedrich

The reaeration of oxygen depleted turbulent water through the water-atmosphere interface has been studied extensively, but the phenomenon has not been fully explained. The most logical qualitative explanation is the surface renewal theory according to which the water layer very nearest the interface is enriched by molecular processes and then swept into the interior of the water by turbulent eddies which penetrate the surface and remove the enriched layer. In the interior of the water body, the oxygen rich water is mixed with its surroundings. The process of surface renewal is diffuclt to be quantified, and even more difficult to investigate experimentally, because it is non-stationary and involves measurements near the surface which cannot be conducted by standard transducers, such as hot wire anemometers.

It has been our belief that in order to solve the reaeration problem one has to rely on circumstantial evidence, in particular on the action of turbulence. Therefore we set up a program of studying reaeration on interfaces at which the turbulence has been generated by many different mechanisms. From these experiments we hope to amass a body of experimental data against which theories can be checked! The following experimental set ups have been used: a stirred tank, with turbulence generated by an arrangement of parallel horizontal rods located near the bottom of the tank, which could be rotated about their axis; a wind wave tank with standing water, in which the surface turbulence was generated by the shear of the wind and the wind waves, and a wind wave tank with flowing water, in which waves and currents acted as turbulence generators. Quantities which were measured included velocities, turbulence intensities and spectra, wind waves, and optically visible turbulent cells.

Whereas the tank experiments lend support to the surface renewal theory in the form given by Fortescue and Pearson (1967), one finds that the wind wave results require a different explanation. Theoretical and experimental arguments will be presented which we hope will help towards establishing a unified surface renewal theory without conflict between experimental data and theory. The importance that this theory may have in evaluating reaeration in environmental and chemical engineering problems justifies extension and continuing experimental and theoretical efforts.

VOLATILIZATION OF CHLORINATED HYDROCARBONS FROM WATER

By

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ABSTRACT

The distribution and the fate of organic compounds in the
waters of our environment are determined by the interactions of
a number of complex chemical, physical, and biological processes.
One of the most important physical processes for many compounds
is volatilization which is the transport of the compound from the
water across the water-air interface into the air.

This report considers two aspects of volatilization: (1) the
concentration dependence of the volatilization coefficient; and
(2) laboratory measurements that permit estimation of the
volatilization coefficients of organic compounds in streams without
actual introduction of the compounds into the stream. The discussion
of these two aspects is based on laboratory measurements of the
volatilization characteristics of 1,1,1-trichloroethane and
1,2-dichloroethane. Both these compounds are on the U.S. Environmental
Protection Agency list of priority pollutants, and both are significant
contaminants in surface and ground waters.

Volatilization coefficients for the chlorinated hydrocarbons and absorption coefficients for oxygen were measured in a stirred tank in the laboratory. The general procedure consisted of stripping the water with nitrogen gas to reduce the dissolved oxygen concentration, adding water containing sufficient dissolved chlorinated hydrocarbon to give the desired concentration, stirring the water at a constant rate, and measuring concentration as a function of time. Hydrocarbon concentrations were determined by a strip-and-trap procedure followed by gas chromatographic analysis with a flame ionization detector. Oxygen concentrations were determined using the Winkler technique.

Experiments for each of the compounds at constant mixing conditions over a wide concentration range showed that the volatilization coefficient was independent of concentration. This result confirms the assumption that the volatilization process follows first-order kinetics analogous to the kinetics for the absorption of gases such as oxygen.

Simultaneous measurements of the volatilization coefficient for each of the compounds and the oxygen absorption coefficient over a wide range of mixing conditions showed that the ratios of the chlorinated hydrocarbon and the oxygen coefficients were independent of mixing conditions. The fact that these ratios are constant makes it possible to estimate the volatilization coefficients for these compounds for a given stream from estimates of the oxygen absorption coefficient.

VOLATILIZATION OF FISSION PRODUCTS

IN NUCLEAR REACTOR BUILDINGS

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Fission products released from a nuclear reactor core are distributed throughout the containment vessel: in the reactor building atmosphere, in the cooling system, on building surfaces, and in pooled waters that may form in the building. Of particular concern are the volatile radionuclides, especially the short- and long-lived radioisotopes of iodine, which influence markedly the cost and methods of cleanup. The potential for volatilization following a specific accident depends on the conditions under which a contaminated pool of water formed and the thermo- and hydrodynamic conditions for volatilization from the pool. The potential for volatilization also is dependent on the competing processes, such as adsorption, precipitation, and rainout in sealed buildings. A study to identify and model competing processes that influence volatilization of fission products in pooled waters is underway. The model is designed to incorporate these competing processes into a prediction of volatilization as a function of water quality parameters, reactor building conditions, introduction of abatement agents and time.

Input to the model is the likely distribution of fission products in a reactor accident of given severity. The model compiles a data base of pertinent literature data for the several processes included in the numerical model. Laboratory experiments are underway to acquire necessary data not in the literature and a scale model of the TMI-2 containment vessel has been constructed for feedback and verification experiments to improve the model.

Processes under study include: volatilization from liquid- and solid-gas interfaces, rainfall in the saturated-humidity enclosed vessel, precipitation of solids from the pooled water, adsorption from the liquid phase on

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Abstract (Continued)   A. Riojas and P. Kruger

building surfaces, gas-phase adsorption on building surfaces, liquid-phase

adsorption onto suspended solids, gas and aerosol absorption by sprays and

condensation, and gas absorption by falling films.

DEPENDENCE OF MASS TRANSFER
ON ENERGY DISSIPATION DURING SURFACE AERATION

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It has been reported previously that the oxygen mass transfer rate constant ($K_L a$) is proportional approximately to the specific energy dissipation ($P/V(W/m^3)$) in streams (1), large-scale surface aeration as practiced in wastewater treatment (2), and in laboratory studies of surface aeration (3). The objectives of this paper are three-fold: to compare the proportionality coefficients relating $K_L a$ to P/V in several kinds of systems observed; to present experimental evidence that the values of $K_L a$ for volatile organic solutes are approximately proportional to that of oxygen; and to assess whether the values of the proportionality coefficients are consistent with mass transfer models such as the surface renewal theory. Significant relations between the value of $K_L a$ for oxygen and the value of P/V have been reported for streams (1), large-scale surface aerators (2), and a laboratory-scale surface aerator (3). The dependence of $K_L a$ on (P/V) demonstrates a near-linear proportionality for each of the several systems. Differences between the systems can be explained qualitatively in terms of the method of energy dissipation. In large-scale surface aerators the energy dissipation is concentrated at the air-water interface; therefore, the value of $K_L a$ is relatively large compared to the other contacting systems, for a given specific energy input. Conversely, the value of $K_L a$ for a given energy input is relatively low in streams because energy dissipation occurs largely at or near the stream bed. The laboratory experiments reported here represent an intermediate case because the agitator used was conceived as a combination surface aerator and mixer, with energy input to mix the bulk liquid as well as to promote air-water contact.

The value of $K_L a$ for volatile organic solutes (CCl_2F_2, CCl_4, $CCl_2=CCl_2$, $CHCl=CCl_2$, CH_3CCl_3, and $CHCl_3$) was found to be proportional to that of oxygen over a wide range of power inputs. The coefficient of proportionality, $\beta_i = (K_L a)_i / (K_L a)_{O_2}$ was in the range of 0.55 to 0.65 for the organic solutes

studied. The proportionality coefficient β was found to depend on the ratio of diffusivities to the 2/3 power, in accordance with the boundary layer and film-penetration models. Nonetheless, the observation that $K_L a$ is proportional to specific energy input seems inconsistent with mass transfer theory as applied to a plane air-water interface. The surface renewal theory predicts a significantly weaker dependence of $K_L a$ on P/V, e.g., $K_L a \propto (P/V)^{0.3}$ if the surface renewal rate is estimated as suggested by Davies and Khan (4). Similarly, boundary layer analogy approaches predict $K_L a$ proportional to (P/V) raised to an exponent in the range 0.2 to 0.3, when the characteristic average velocity is evaluated using either the Blasius Relation or Kolmogoroff-Turbulence Theory (5).

It appears that specific energy input is a useful predictor of mass transfer at the air-water interface in natural systems as well as engineered surface aeration contactors.

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OPTIMUM APPLICATION OF THE RADON DEFICIT METHOD TO OBTAIN AIR-SEA GAS EXCHANGE RATES

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The deficit of ^{222}Rn relative to radioactive equilibrium with the dissolved ^{226}Ra in the ocean's mixed layer is caused by ^{222}Rn escape into the atmosphere and allows to determine gas exchange rates at sea. The extensive spot observations of radon deficits by W. S. Broecker and coworkers (see Peng et al., J. Geophys. Res. **84** (1979) 2471) give averages of this rate. We persue a different approach, in which momentary gas exchange rates are obtained in intensive and carefully controlled field observations and are used to adapt gas exchange parameterizations resulting from laboratory and/or theoretical investigations to field conditions.

We made ^{222}Rn-deficit observations during JASIN 1978 ($\sim$59°N, 12.5°W) and FGGE 1979 ($\sim$2°S, 22°W), employing a precise and fast-acquisition, automatic radon measuring system (B. Kromer and W. Roether, "Meteor" Forsch.-Ergebnisse A, in press). The FGGE gas transfer velocities average considerably lower than those for JASIN, despite little difference in average wind velocity, while the range is similar to that observed in laboratory experiments. The JASIN/FGGE difference is ascribed to considerably steadier winds met during FGGE. On the other hand, our ^{222}Rn-deficit time series showed a surprising degree of variability, which we believe to be caused by ^{222}Rn redistribution in the mixed layer during the period between generation and escape into the atmosphere, i.e., a few days.

At present we are preparing the next generation of field observations. The most important requirements are anticipated to be (i) careful bookkeeping of the mixed-layer ^{222}Rn deficit; and (ii) adequate monitoring of the external variables. Ingredients for (i) are

- Obtaining repeated ^{222}Rn deficit observations ($\sim$10 min repetition) over periods of days or longer, the short-term ^{226}Ra variability being monitored by salinity and silica concentration, with continuous control of system performance and with on-line evaluation.

- The observations are preferably to be carried out while drifting with the horizontal mixed-layer flow. The local structure of the mixed layer and thermocline is to be monitored by temperature and salinity profiling and vertical current shear is to be assessed. Verification of the absence of mixed-layer fronts in the observation area is desirable.

- A suitable observation area is to be selected.

As for (ii), meteorological variables have to be measured, but furthermore also waves, and perhaps surface slicks, which play an added role; improved understanding of the effects of waves would help in outlaying the necessary measurements.

On the basis of our JASIN and FGGE results, we estimate the achievable precision in gas transfer velocities in such an observational program as ± 20% under favourable conditions, and the temporal resolution as 10h. The necessary measurements and their precisions can be outlined, and criteria can be given for the selection of an observation area.

EFFECTS OF EVAPORATION AND CONDENSATION

ON AN ABSORPTION PROCESS

by

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Dr. Burton A. Segall
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Dr. Charles R. Ott

ABSTRACT

Research was conducted to investigate the effects of evaporation and condensation on a gas phase controlled absorption process. Individual droplets of distilled water of known weight and temperature were dropped through a counter-flowing gas mixture that contained a known concentration of ammonia and water vapor. The rates of evaporation and condensation of water vapor were varied by modifying droplet temperature and the water vapor content of the air/ammonia gas mixture. The droplets were collected after passing through the gas mixture for each set of conditions and the collected solution was analyzed for ammonia concentration. The resulting concentrations were then compared. Theoretical Diffusion Prediction Equations were also derived to predict the effects of increased evaporation and condensation rates on absorption.

The experimental results indicate that absorption rates increase with increases in condensation rate and decrease with increases in evaporation rate. The experimental trends showed good similarity with the trends projected by the derived Diffusion Prediction Equations.

The intent of this paper is to present an overview of the test methods used, the results obtained, and the conclusions drawn. Potential applications and implications of the results are also discussed.

The theoretical Diffusion Prediction Equations are presented along with the similarities between the experimental absorption trends and those projected by the Prediction Equations discussed. Due to assumed time constraints, detailed derivation of the Prediction Equations is presently considered outside the scope of this presentation.

ON THE EXCHANGE OF OXYGEN AND CARBON DIOXIDE BETWEEN OCEAN AND ATMOSPHERE
IN AN EASTERN BOUNDARY CURRENT. J. J. Simpson, Marine Life Research Group,
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Simultaneous measurements of temperature, salinity, dissolved oxygen, pH, nitrate,
phosphate, silicate and chlorophyll-a were made continuously while underway from R.V.
New Horizon during July 1979. The observations were made over a region of the northern
California shelf bounded by Pt. Arena to the north and Pt. Reyes to the south, off the
southern California coast near Pt. Conception and enroute between these two areas. In
addition, discrete titration alkalinity and total carbon dioxide determinations were
made with the GEOSECS titrators approximately every 15 minutes during the underway
survey. Water for these measurements was drawn from a depth of 3 meters via the un-
contaminated seawater system of R.V. New Horizon. From these data the spatial distribu-
tions of dissolved oxygen, percent saturation of dissolved oxygen, partial pressure of
carbon dioxide and the P_{CO_2} departure from atmospheric equilibrium were calculated.
These measurements show that the oceanic concentrations of dissolved oxygen and the
partial pressure of carbon dioxide in a coastal regime depart radically from equilibrium
values. The spatial coherence and phase between these distributions cannot be explained
solely by physical dynamics. The data support the hypothesis that the dynamics of gas
exchange in an eastern boundary current are largely controlled by biological processes.
The latter are clearly influenced by the physical dynamics associated with such features
as offshore jets, upwelling fronts and intrusions of warm Central Pacific water onto the
shelf. The spatial distributions of chlorophyll-a and nutrients independently support
this conclusion. The global distribution of biological productivity and its significant
impact on the air-sea exchange of oxygen and carbon dioxide demonstrate the need to
develop reliable remote sensing techniques to monitor synoptically global gas exchange
processes and their possible effects on climate.

REAERATION AND WIND INDUCED TURBULENCE SHEAR

IN A CONTAINED WATER BODY

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Reaeration in contained bodies of water (such as lakes and ponds) is mainly achieved by the oxygen transfer at the air-water interface and its subsequent transport into bulk fluid. The action of wind induces shear and causes turbulence at the air-water interface which can significantly enhance the reaeration process.

The process of atmospheric reaeration (it is, in fact, reoxygenation) can be simply defined as the physical absorption of atmospheric oxygen in water. However, the primary resistance to oxygen absorption in water takes place at the water side of the air-water interface. Detailed experiments were conducted to study the relationship between reaeration and wind induced turbulence in a laboratory size wind-water tank facility. In this paper, the results of the turbulence measurements and their correlation to reaeration coefficient will be presented.

The reaeration and turbulence measurements were made simultaneously. Hot-film anemometer and surface floats were used to measure fluctuating and mean components of the water drift. Spectral analyses were made on the fluctuating components. These results indicate that there is a definite similarity existing between the wind induced water drift below the water surface and flow past 'solid walls'. This is indeed interesting in so far as the transfer theories developed for the 'solid walls' may be applied to mass transfer occurring at the water side of the air-water interface.

Using the observed similarity and starting from the eddy cell theory of

mass transfer proposed by Lamont (1970) for gas transfer in pipe flows,

an expression is derived relating reaeration coefficient and wind shear

velocity. Laboratory data seems to agree well with the derived expression.

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THE SIGNIFICANCE OF GAS TRANSFER
ON THE DISSOLVED OXYGEN BALANCE

By: John P. St. John, Thomas W. Gallagher, and Donald J. O'Connor

Dissolved oxygen is widely used as both a specific and general measure of water quality conditions in the streams, rivers, lakes and estuaries of the country. Sufficient levels of dissolved oxygen are necessary to support fish life and reproduction, and to maintain a balanced biological community. Each state is obligated by the law to develop and enforce water quality standards, and all such standards contain specific numerical requirements for dissolved oxygen. The vast majority of municipal and industrial wastewater treatment plants in the United States were built primarily to protect the dissolved oxygen resources of the nation's waterways.

In many critical cases, calculations are performed to relate the effect of specific wastewater discharges to dissolved oxygen conditions in the receiving waters. The purpose of such calculations is to determine the specific level of wastewater treatment which is necessary to achieve or maintain the local disolved oxygen standard. The calculation procedure consists of the application of a water quality model which incorporates relevant transport, transfer, and kinetic terms associated with the dissolved oxygen balance. Several of the kinetic factors are associated with the utilization of oxygen for stabilization of carbonaceous and nitrogenous materials present in the receiving waters. A particularly important factor, however, characteristic of such models is the atmospheric reaeration coefficient which defines the rate at which atmospheric oxygen is transferred through the air-water interface to replenish that which is utilized in the stabilizaton of waste materials.

Many of the transport and kinetic factors incorporated in the mathematical modeling framework are measured or empirically determined from field water quality data. The atmospheric reaeration coefficient, however, is generally estimated from one of a number of formulations which have been developed over the years by a variety of theoretical and/or empirical means. Many of the more empirically based equations were developed from data collected for specific ranges of those hydraulic and physical characteristics which have a bearing on the gas transfer process. Such formulations often give widely different estimates of the atmospheric reaeration coefficient when applied in a problem context. Their differences can seriously affect the calculation of the oxygen balance, lead to a misinterpretation of the effect of the wastewater discharge on the oxygen resources of the waterway, and result in an improper determination (too great or

small) of the required degree of waste treatment. Hence, accurate knowledge of the reaeration coefficient as representative of the gas transfer process is required for proper environmental and economic decision making.

The proposed paper will illustrate the importance and significance of the gas transfer process, as represented by the atmospheric reaeration coefficient, on the oxygen balance and on the decision making process, that is, on the proper determination of the degree of required waste treatment. An example stream situation will be presented and described. Wastewater inputs to the stream will be described, and characteristic water quality profiles, particularly dissolved oxygen will be shown. The mathematical water quality model used for analysis of data will be described as well as procedures for evaluation of kinetic coefficients. It will be demonstrated that it is possible to correlate a particular set of water quality (dissolved oxygen) data with different estimates of the reaeration coefficient. It will then be shown that the different reaeration coefficients, when modified for and used to project water quality impacts at critically low stream flows, yield markedly different results. The degree of waste treatment necessary to maintain the equivalent level of dissolved oxygen in the stream as calculated with the different reaeration estimates will be indicated. The practical significance of gas transfer and the importance of atmospheric reaeration in the specifications and design of wastewater treatment facilities will be discussed.

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Experimental Studies of

Surface Wave Breaking and Air Entrainment

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Physical processes of air entrainment and subsequent air bubble generation
from breaking of steep surface gravity waves under controlled situations will
be described and discussed in this paper.

It is generally known from actual field measurements that wind-wave
breaking in lakes and oceans contributes by far the most significant portion
of air/gas/particle transfers cross the water surface; and yet, the underlying
physio-chemical processes are only poorly understood. To a large extent, this
slow progress made so far might be attributed to the highly nonlinear complex
wave breaking process itself, which has defied full understanding of physicists
and applied mathematicians despite a long history of both theoretical and
experimental investigations.

Recently, a close interplay between experimental and theoretical studies has
lead to an important breakthrough on the physics of deep-water wave breaking
as a consequence of a new type of three-dimensional wave instability and
subsequent bifurcation (for details see Su (1982), Su et al. (1982), McLean (1982),
Saffman & Yuen (1980, 1982)). This breakthrough now provides, in turn, a sounder
foundation for us to study the gas transfer resulted from such wave breaking
processes.

In this paper, we shall present some preliminary experimental results conducted
in a large-scale wave tank, which exhibits clearly the three-dimensional wave
plunging and spilling that cause air entrainment and bubble generation/transport
in the deep water. The rapid and complex physical processes involved are recorded

by photographic techniques. These experimental results are then used to delineate general characteristics of the physical mechanisms involved.

Finally, we discuss the relationship of our results with previously published results and oceanic observations.

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Conceptual Models on Gas Exchange[*]

The characteristically high Sc number process of mass transfer at
free, turbulent gas/liquid interfaces implies complicating as well as
simplifying factors in the development of general predictive methods.
The simplifications arise due to the thinness of the concentration bound-
ary layer that often occupies only a minute fraction of even the smallest
turbulent eddies present. The convective field can therefore be con-
siderably simplified into elementary flows, hence convective diffusion
solutions become readily available. The difficulties arise in relating
the characteristic parameters of these flows to the turbulence state in
the bulk (i.e., to measurable turbulence properties). Since these flows
within the concentration boundary layer are not directly observable their
nature must be deduced by the mass transfer response of the interface
(i.e., through conceptual mass transfer models). This process is often
further complicated by the need to crudely estimate the bulk turbulence
(lack of simultaneous turbulence and mass transfer measurements).
Although considerable progress has been achieved along these lines during
the past fifteen years or so certain controversial aspects remain, primarily
due to the incomplete definition of mass transfer "regimes" within the
broad context in which such turbulent interfaces are encountered. A
critical, comparative evaluation of available conceptual models will be
presented in an effort to identify strengths, weaknesses, and possible
additional research needs.

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Abstract for International Symposium on Gas Transfer at Water Surfaces, Cornell, June 1983

ENTRAPMENT AND TRANSPORT OF BUBBLES BY PLUNGING WATER

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Free surface penetration by plunging water gives rise to gas entrainment and transport of bubbles in the submerged flows. The phenomenon is found in a variety of practical circumstances. In chemical engineering it is exploited as a convenient method of dissolving gases in liquids. In environmental engineering,weir flows provide for reoxygenation of rivers and waste-waters. In oceanography there is much interest in the transport of bubbles from breaking waves (which appear as spilling or plunging flows depending on wind conditions and water depth). Factors affecting the efficiency of gas transfer into the liquid include entrainment flux, sizes of bubbles, their residence times and dispersion throughout the liquid. Our studies,outlined below, are particularly relevant to the last of these.

Using still photographs and high speed movie film, we have observed that submerged plunging flows transport bubbles in discrete clusters. We attribute this behaviour to bubble entrapment by large transient vortices travelling in the free shear layer between the submerged flow and surrounding bubbly

The existence of such vortices is well-documented — they are often referred to as large eddies or 'coherent structures'. However their inhibiting influence on bubble dispersion has not

been widely appreciated and our paper will help to fill this gap in understanding.

We shall describe elements of a recently developed general theory of bubble motion in unsteady, non-uniform, high Reynolds number flow. The theory is based on inviscid analyses of the forces arising from pressure gradient, acceleration and vorticity-lift, together with a simple drag law. Errors in previous formulae for interfacial forces will be identified. Having introduced the general theory, we shall concentrate on the practically relevant special case of bubble motion in line vortex flow. A laboratoratory experiment will be described which quantitatively confirms the theoretical predictions of bubble entrapment.

We shall report on recent progress towards a computer simulation of the bubbly free shear layer. Our simulation makes use of a discrete vortex method to model the fluctuating large eddy structure; bubble trajectories are calculated using the new general theory. Exploratory tests to date show indications of bubble entrapment by transient vorticity concentrations. We would hope to present results of more detailed calculations now in progress. Also measurements of local gas and liquid flows in a controlled experiment on the bubbly downflowing free shear layer.

ANOMALOUS NEON-HELIUM RATIOS
IN THE ARCTIC OCEAN

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Abstract: Dissolved rare-gas studies in the ocean have become increasingly important in the last decade. The subjects of the present study, oceanic helium and neon, have the atmosphere as their major source. The heavier and more abundant helium isotope ^{4}He, is sometimes augmented at the sea-floor due to the injection of a sedimentary-crustal (radiogenic) component. Both helium and neon are often found in the ocean in excess of their solubility equilibrium values due to the forced dissolution of air bubbles in wave action (air injection) in the upper layers. Because there is apparently no mechanism to alter the neon concentrations in the ocean, neon can be used to strip off the air injected helium component. In a recent study of the Baffin Bay (Top et al., 1980) however, this procedure gave rise to negative helium excesses! What seemed to be a suspicion then, of the constancy of the neon concentration became a certainty in the later studies at two Arctic locations. The data confirming the anomalous He/Ne ratios are presented. The source of the anomaly appears to be at the surface. The ice formation is thought to be primarily responsible for the relative enrichment of neon. As well, differential diffusion of neon and helium in ice, and ice melting are discussed as potential contributors to the observed effect. The great potential of Ne/He ratios in the Arctic Regions (and probably Antarctic) as a tracer for the newly formed bottom water is proposed.

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On the Exchange Rate of Organic Gases
Between Air and Falling Water Drops

by

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Abstract

The exchange rate of organic gases between falling water drops and
air has been studied as a function of drop size and concentration in the
gas phase. The study was carried out using the UCLA Rain-Shaft, a unique
facility consisting of a 35 meter high and 50 cm diameter shaft which
allows a quantitative determination of the amount of gas scavenged by
water drops after reaching their terminal velocity. Following a success-
ful study on the exchange rate of SO_2 between air and falling water drops
(Walcek et al., 1981: J. Atmos. Sci., 38, 871-876) using the same facility,
we determined the rate of absorption of the organic gases: acetaldehyde,
formaldehyde, methylene chloride and chloroform by water drops of 300 to
2500 μm equivalent radius, falling at terminal velocity in air as a function
of gas concentration. The concentration of the organic gas in the gas phase
and in the water were determined using gas chromatographic techniques. The
results of our experimental study are compared with and discussed in
light of the results derived from our theoretical model for forced convec-
tive gas absorption by falling water drops which exhibit internal circulation.

A New Optical Bubble Measuring Device

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Encouraged by the good experience with optical wave measuring systems we developed an optical method to measure bubbles in the water.

A He-Ne-Laser beam pierces the water surface vertically from below. The light scattered by bubbles crossing the beam is collected in 4 detectors at different depths ranging from 0.1 - 0.5 m. Two sets of this arrangement are used with differnt laser beam diameters (1 and 5 mm) for the following reasons. Firstly, the dynamics in bubble size and even more in intensity detected beeing proportional to the square of the bubble radius is too large for only one detector. Secondly, the large bubbles are rare if compared with small ones, and a larger sampling volume is therefore necessary to obtain good statistics.

The first measurements with this device are carried out in the large wind/wave facility of the I.M.S.T Marseille, simultaneously with He- and Rn gas exchange experiments. We obtained bubble spectra at four water dephts in the wind speed range from 11 to 13.8 m/s. First bubbles are observed at 12 m/s. The spectras are compared with other wind tunnel results. The total number of bubbles is about a factor 3 smaller than in the wind tunnel of the Sonderforschungsbereich Meeresforschung, Hamburg.

With a simple model we estimated that even at the highest possible wind speed of the large facility (13.8 m/s) no noticeable enhancement (< 10%) even of the He gas exchange is possible.

LABORATORY OBSERVATIONS ON TRANSFER OF ATMOSPHERIC OXYGEN

INTO STRATIFIED SEA WATER

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ABSTRACT

Laboratory sea water was stripped of most of its dissolved oxygen by bubbling nitrogen through it in a column filled with marbles. The sea water, starting with dissolved oxygen concentrations of 0.5 to 1.0 mg/L, was held in a round plastic container, 56 cm high and 34 cm in diameter at the top, in a water table with sea water 14 cm deep at a temperature of 12-18°C. Water samples were taken at the surface, 10, 25, 40 cm and at the bottom of the container periodically for dissolved oxygen determinations. Within 4 days, dissolved oxygen concentrations reached 7 mg/L at all depths, when only sea water was present; but when a 2-cm layer of fresh water covered the sea water, dissolved oxygen in the bottom half of the container, starting at 1.0 mg/L, ranged from 0.3 to 0.6 mg/L after 5 days. In deoxygenated sea water (0.5 mg/L), covered with a 1-mm layer of South Louisiana crude oil, dissolved oxygen was near 1 mg/L at the bottom of the container, 3 mg/L at 25 cm depth, and 5 mg/L at 10 cm and at the surface after 5 days. Results suggest that stratification with fresh water can be at least as effective as a thin layer of oil in retarding the transfer of atmospheric oxygen downward in sea water. They are in line also with observations of vertical dissolved oxygen distributions found in deep, partially-restricted marine inlets receiving substantial fresh water runoff.

Moisture and Heat Transport in a Stably Stratified Boundary Layer Over a Water Surface

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A laboratory experiment in which a stably stratified boundary layer was formed by blowing warm, dry air over a water surface is described. The experiment was carried out in the air-sea interaction facility of d'Institute de Mechanique Statistique de la Turbulence (I.M.S.T.), Marseille. Velocity, temperature and humidity fluctuations were measured by means of hot (and cold) wires and a microwave refractometer. In order to obtain high bulk Richardson numbers, Ri_b, $[\equiv (g/\rho_0) (\Delta\rho L/U^2)$ where $\Delta\rho$ is the density difference across the depth L of the boundary layer, U is the free stream velocity, g is the gravitational acceleration and ρ_0 is a reference density] low wind speeds ($\leq$ 0.7 m/s) were used. Under these conditions, the water surface remained smooth. Particular attention was given to a situation in which the Ri_b was so strong($\sim$0.4) that the boundary layer turbulence, tripped by means of vortex generators at the entrance to the tunnel, was rapidly suppressed. However as the flow evolved downstream and the boundary layer thickened (and hence Ri_b diminished), bursts of turbulence occurred close to the water surface, causing rippling of the water. Most of the momentum, heat and moisture transport occurred during these bursts. Classified averaging of the momentum, heat and moisture flux formed from the time series of the velocity, temperature and humidity fluctuations showed remarkable similarity to the intermittency observed in the neutral boundary layer (at a much smaller scale) by previous workers. The results also have similarities to bursting observed in river estuaries and in the sea.

An Assessment of Tracer Techniques for Measuring Reaeration Rates in Large River Systems

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NCASI had the opportunity to investigate tracer techniques for the estimation of stream reaeration rates during its study of mathematical water quality modeling on the Ouachita River basin. Data was first collected which allowed for the examination of the variablity of measurements of stream reaeration rates which were subsequently used to assess uncertainty in the calibration and verification of four water quality models. This study was followed by a comparison of hydrocarbon and radiotracer techniques on the same river reach.

The major conclusions from these studies were two fold:

(a) The precision of the radiotracer measurement was directly related to the amount of gas lost during the experiment. Thus, the precision of the measurement is ultimately limited by an ability to follow the dye and conservative tracer, the precision of the krypton to oxygen transfer ratio, and the temperature correction factor.

(b) The hydrocarbon tracer techniques produced reaeration rates higher than that obtained by the radiotracer technique and selected empirical equations. This difference was two large to be accounted for by variability in the radiotracer method.

METHYL CHLORIDE AS A GAS-TRACER IN REAERATION

STUDIES ON SOME NEW ZEALAND RIVERS

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Many New Zealand rivers receive waste inputs with significant oxygen demands from sources such as dairy factories and wood-pulp mills. In order to have effective models of dissolved oxygen profiles in these rivers it is necessary to have accurate estimates of the reaeration coefficient, K_2. This paper describes a gas-tracer technique using methyl chloride, that has been developed and successfully tested in several rivers and streams. Methyl chloride is a stable substance not found in significant background concentrations in New Zealand waters, that can be detected down to 1×10^{-12} g by a gas-chromatographic technique. In this study, values of K_2 and an analagous gas transfer coefficient for methyl chloride, K_{CH_3Cl}, were measured simultaneously in laboratory experiments over the temperature range 5 - 35°C. The results indicated a temperature dependence for the transfer coefficient ratio, K_{CH_3Cl}/K_2, which was fitted empirically to an expression based on the absolute rate model for diffusion, giving

$$\frac{K_{CH_3Cl}}{K_2} = 4.323 \exp(-530.97/T)$$

where T is the absolute temperature.

Results are given of applications of the methyl chloride technique in several

rivers, in which rhodamine-WT was used as a conservative tracer to correct

for dispersion and dilution. The measured reaeration coefficients range from

0.2 to 16.6 day^{-1} (base e) and are compared with values calculated using the

O'Connor-Dobbins formula. The experimental results correlate well with the

calculated values but are generally about 50% greater than the predicted

values of K_2. It is concluded that for K_2 values greater than about 1 day^{-1}

the methyl chloride method gives values having a much better precision than

those calculated from empirical expressions, and provide estimates of K_2

with an uncertainty of about $\pm$ 10%. The major source of error in the tracer

technique appears to be associated with estimating peak concentrations of

the dissolved methyl chloride. Empirical expressions can give rise to

errors of $\pm$ 50% in their estimates of K_2 in streams having irregular cross-

sections, or where estimating mean depths is difficult. Rivers in which K_2

was 1 day^{-1} or less had comparable uncertainties between measured and

calculated values of the reaeration coefficient, because of the small

change in the ratio of methyl chloride : rhodamine-WT peak concentrations,

with distance downstream.

WIND EFFECT ON AIR-WATER OXYGEN TRANSFER
IN A LAKE

by

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The paper will report results obtained from field experiments conducted in a lake in Northern New Jersey to investigate the effect of wind on the air-water oxygen transfer process. Mass transfer and boundary layer theories were utilized to formulate theoretical prediction models for the reaeration coefficient, K_2.

Parameters considered in model formulation include wind velocity, wind shear velocity, effective mass diffusivity, and water depth. Equations of linear, nonlinear, and dimensionless forms were examined. Statistical methods such as analysis of variance and residual analysis were employed to determine model adequacy.

Results indicate that wind speed is a limiting factor in affecting lake reaeration. Below a "critical" wind speed (4.2 m/s at 10 m), there is no significant wind effect on K_2. Above another "critical" wind speed (6.5 m/s at 10 m), K_2 varies nonlinearly with wind speed. Between these two limits, K_2 assumes a fairly linear relationship with wind speed, as shown in the following dimensionless equation:

$$\frac{K_2 H^2}{\nu} = 1.63 \times 10^{-5} \left(\frac{UH}{\nu} \right)^{1.136}$$

where K_2 = reaeration coefficient in sec^{-1}, H = water depth in meters, ν = water viscosity in m^2/s, and U = wind velocity at 10 meters in m/s.

An investigation was made later to test some of the proposed reaeration equations using data collected for the Occoquan Reservoir in Northern

Virginia. Two years of water temperature and dissolved oxygen data taken at various depths and at six stations throughout the lake were available for the analysis. Wind recorders were obtained from two locations in the vicinity of the lake.

The Occoquan data indicate that the wind is responsible for keeping dissolved oxygen levels near or above saturation for the upper 1 to 3 meters of the lake even though the lake is strongly stratified and dissolved oxygen levels dip to zero near the bottom of the lake. The proposed lake reaeration equation was also found to be adequate in predicting surface reaeration coefficient.