MacIntyre, S. W. Eugster, and G.W. Kling. 2001. The critical importance of buoyancy flux for gas flux across the air-water interface. In Gas Transfer at Water Surfaces, edited by M.A. Donelan, W.M. Drennan, E.S. Saltzman, and R. Wanninkhof. AGU

The Critical Importance of Buoyancy Flux for Gas Flux Across the Air-water Interface

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Physical processes at the air-water interface that affect gas flux include turbulence from wind shear, penetrative convection due to heat loss, micro-wave breaking, and large scale wave breaking. While considerable effort has been expended to parameterize the gas transfer coefficient due to the contributions of wind and surface waves, the contribution of buoyancy fluxes to turbulence at the air-water interface has not received the same attention. In addition, the rate of mixed layer deepening is sensitive to heat loss. Without this deepening, gas concentrations quickly equilibrate with those in the atmosphere leading to lower rates of gas flux. Measured gas flux was up to 5 times higher when heat was being lost from the surface layer of an arctic lake and wind speeds were low than when wind speeds were 5 m s^{-1}. At wind speeds less than 5 m s^{-1}, calculated values of gas transfer velocity based on wind speed alone were 2 to 5 times lower than those calculated using the surface renewal model. These observations indicate the critical importance of including buoyancy fluxes in estimates of gas transfer coefficients.

INTRODUCTION.

Empirical models are frequently used to parameterize the reaeration coefficient k used in computing gas flux across the air-water interface. At present, the three most commonly used equations are based on wind speed (Wanninkhof 1992; Liss and Merlivat 1986; Wanninkhof and McGillis 1999). However, a number of physical processes contribute to gas transfer across the air-water interface (MacIntyre et al. 1995). These include penetrative convection due to heat loss, shear due to wind forcing, microwave breaking at moderate wind speeds (Jessup et al. 1997), and bubbles at high wind speeds (Woolfe and Thorpe 1991). While wind contributes to all of these processes, use of the surface renewal model (Higbie 1935; Danckwerts 1951; Soloviev and Schluessel 1994) to calculate k may prove to be more inclusive. In particular, as heat losses from the air-water interface are due not only to evaporation but also to sensible heat loss and long wave back radiation, the turbulence due to buoyant motions as well as wind may be better modeled by surface renewal. In this paper, we present evidence showing the critical importance of heat loss for gas flux.

Background

Gas flux, when estimated indirectly, is obtained from the equation $F = k(C_w - \alpha C)$ where k is the reaeration coefficient, C and C_w are concentration of the gas in air and water respectively, and α is the Ostwald solubility coefficient. The reaeration coefficient depends upon the Schmidt number Sc, characteristics of the aqueous boundary as given by n, and the physical processes at the interface: $k = Sc^{-n} f(u,l)$. Here, the turbulent velocity and length scales u and l are used to represent the physical processes at the interface.

In the large eddy version of the surface renewal model, $k = a_1 (D\ u/l)^{1/2}$. Here, the gas flux depends explicitly on the turbulent velocity and length scales. D is molecular diffusivity of the gas. In the small eddy version, $k = a_2 D^{1/2} (\varepsilon/\nu)^{1/4}$ where ε is the rate of dissipation of turbulent kinetic energy and ν is kinematic viscosity. ε is related to u and l through the expression $\varepsilon = u^3/l$ (Taylor 1935). When written in terms of the Schmidt number and turbulent Reynolds number Re_t, these expressions become $k\ Sc^{1/2} = c_1\ u\ Re_t^{-1/2}$ and $k\ Sc^{1/2} = c_2\ u\ Re_t^{-1/4}$ for the large and small eddy versions respectively. $Re_t = ul/\nu$. ε, u, l, and Re_t can all be obtained from profiles of turbulent microstructure or from surface energy budgets (MacIntyre et al. 1995). The coefficients a_1, a_2, c_1, and c_2 are determined empirically. The time scales for the upper meter to overturn, u/l, is ~ 5 minutes. Within large eddies are many smaller eddies. Overturning of large eddies puts smaller eddies in contact with the diffusive sublayer allowing them to exchange gases at the interface.

A major difference in our calculations of surface energy exchange is that fluxes are calculated not for the aqueous boundary layer, but for the surface layer, defined as that part of the upper mixed layer in which temperatures are within 0.02 ^oC of the surface temperature. By this approach, heat gains and losses in the upper water column are identified.

DIURNAL MIXED LAYERS AND GAS FLUX

Our understanding of the dynamics of the upper mixed layer of lakes and oceans has changed dramatically in the last 15 years due to higher resolution temperature profiles and determination of locations of active mixing (Imberger 1985; Shay and Gregg 1986; Brainerd and Gregg 1993; MacIntyre 1993; MacIntyre 1998). The upper mixed layer is not continuously mixing. Instead, during the day, there is an upper, surface layer that may be actively mixing with a diurnal thermocline below, or the water column may be thermally stratified to the surface. When only a thin upper layer is mixing, the concentrations of gas within the layer may quickly equilibrate with the atmosphere. Not until the upper most layer begins losing heat does the surface layer begin to deepen (MacIntyre et al. *In submission*). The larger turbulent eddies may then bring water whose concentration is different from the atmosphere to the surface where gas exchange can resume.

The importance of weakening of the temperature gradient in the upper part of the water column for gas flux was first noted by Crill et al. (1988). Gas flux from L. Calado, Brazil, was five times higher at sunrise and sunset than at noon. The higher fluxes occurred when the temperature difference in the upper 3 m was reduced. Engle and Melack (2000) show the importance of episodic mixed layer deepening for enhanced gas flux. Surface energy budgets obtained from L. Calado during a two-month period when the lake was seasonally stratified show that buoyancy fluxes were 50 to 100% of the total energy flux at night into the lake (MacIntyre, unpublished data). Buoyancy fluxes ranged from 20 to 100% of the total energy flux at sunrise and sunset, and between 0 and 50% during the day. Typically, the upper mixed layer was 0.5 m deep in the day and deepened at night to 6 m depth. Wind speeds were higher in the day. These data indicate the critical importance of heat loss for mixed layer deepening, circulation, and gas flux.

Comparisons of Diurnal Cycles of u_* and w_*

The diurnal periodicity in mixed layer depth and diurnal variations in u_* and w_* are illustrated over two diurnal periods for a tropical lake (Figure 1). The shear velocity scale $u_* = (\tau/\rho)^{1/2}$ where τ is wind stress and ρ is density of water; the convective velocity scale $w_* = (Bh)^{1/3}$ where B is buoyancy flux and h is depth of the actively mixing layer. w_* is non-zero when a water body is losing heat.

The mixed layer is shallow in the day and deepens beginning in late afternoon. Wind speeds increased above 8 m s^{-1} four times during the 60 hour period ($u_* > 0.008$ ms^{-1}). The first three of these events occurred at night causing the thermocline to downwell. Downwelling does not imply mixed layer deepening. Deepening of the mixed layer and entrainment of thermocline waters occurred beginning in late afternoon when w_* increased and exceeded 0.003 ms^{-1}. Afternoon winds ranged from 4 to 6 m s^{-1} (u_* ranged from 0.004 to 0.007 m s^{-1}), but mixed layer deepening did not occur until the lake began losing heat. The rapid shoaling of the mixed layer at 1000 h on 26 April occurred once incident short wave energy exceeded heat losses. The shoaling occurred despite winds of 7 m s^{-1} and $u_* = 0.009$ m s^{-1}. The upper mixed layer is shallow when w_* equals zero, and deepens as w_* increases. Because values of w_* exceed u_* by a factor of 2 to 3 much of the night, it is essential that they be included in computations of the rearration coefficient.

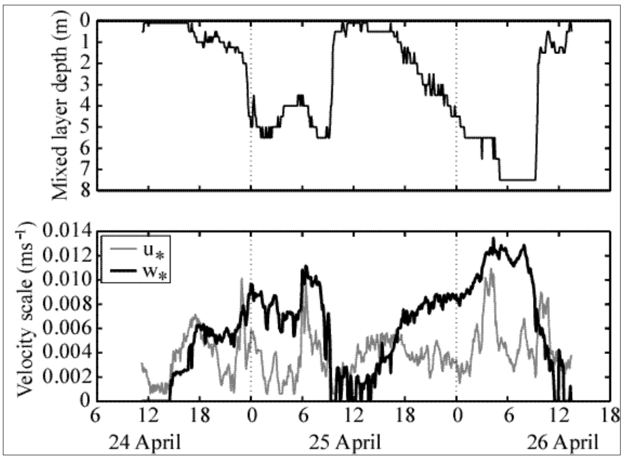

Figure 1. Upper mixed layer depth (upper panel), shear and convective velocity scales (lower panel) over two diurnal cycles in Pilkington Bay, Lake Victoria, East Africa. (from MacIntyre et al. *In submission*). Thermocline downwelling occurs when winds are high, but mixed layer deepening occurs as heat is being lost.

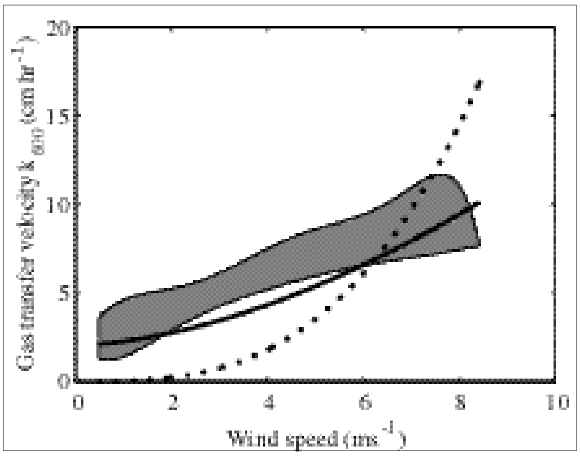

Figure 2. Reaeration coefficient k_{600} computed using the surface renewal model (shaded), a wind based model (••) (Wanninkhof and McGillis 1999), and an empirical model based on tracer studies from several lakes (-) (Cole and Caraco 1998). The small eddy version of the surface renewal model ($k\ Sc^{1/2} = c_2\ u\ Re_t^{-1/4}$) using $c_2 = 0.56$ (Crill et al. 1988) was used to calculate k_{600}. The total energy flux into the surface layer $F_T = (w_*^3 + 1.33^3 u_*^3)$; $\varepsilon = 0.82\ F_T\ /h$ (Imberger 1985); h, u, and Re_t were defined in *Background*. Meteorological data from Pilkington Bay (data from MacIntyre et al. *In submission*. Data are 5 min. averages.)

Comparison of Gas Transfer Coefficients Based on Wind Speed Alone and on Surface Renewal

At moderate wind speeds (6-8 ms^{-1}), when evaporation is likely to be included in a wind based formulation of k_{600}, estimates of k based on wind alone and the surface renewal model give comparable results (Figure 2). However, at wind speeds < 5 ms^{-1}, Wanninkhof and McGillis' (1999) regression equation gives lower estimates of k_{600} relative to Cole and Caraco (1998) and the surface renewal model. The equation developed by Cole and Caraco is based on tracer studies from several lakes (Wanninkhof 1992; MacIntyre et al. 1995; Cole and Caraco 1998). Scatter was high and unexplained in these earlier studies. The data from Pilkington Bay, where w_* is often three times higher than u_* at wind speeds < 6 ms^{-1}, suggest that turbulence due to heat loss may explain a large part of the scatter.

Importance of w for Gas Flux*

Gas flux measurements in Toolik Lake, Alaska, further corroborate the importance of buoyancy fluxes. An eddy covariance tower with sonic anemometer was deployed at Toolik Lake, Alaska, in July 1995. Methods are described in Eugster and Senn (1995) and Eugster et al. (1997). We computed buoyancy flux following MacIntyre et al. (1995). As no thermistor data were available to determine depth of the mixed layer, we assumed it was 1 m deep at all times. Given that time series data of mixed layer depth in other years show mixed layer depths increasing to 6 m at night, this assumption could cause w_* to be a factor of 2 too low. Eddy covariance data were sampled at 20 Hz and 30 minute averages computed from the raw data; data are presented as 9 point running averages of the 30 minute fluxes.

During this study, wind speeds ranged from 1 to 6 m s^{-1} and u_* ranged from 0 to 0.007 m s^{-1} (Figure 3). w_* was non-zero for only a few hours each day. Flux of CO_2 into or out of the lake occurred at all times of day (Figure 3), but gas fluxes were maximal while heat was being lost from the lake. Fluxes increased over the cooling period suggesting that mixed layer deepening was replenishing surface waters.

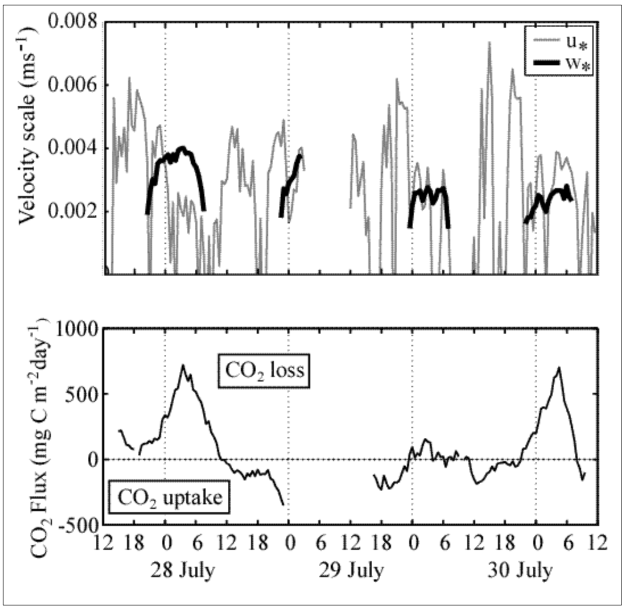

Figure 3. Shear and convective velocity scales (upper panel) and gas fluxes (lower panel) from Toolik Lake, Alaska, during a four day period in July 1995. Maximum gas fluxes are not correlated with wind speed, as represented by u_*, but by whether or not heat was being lost from the surface layer ($w_* > 0$). Gas fluxes are less than 100 mg C m^{-2} day^{-1} at highest wind speeds, but increase above 500 mg C m^{-2} day^{-1} when buoyancy flux led to convective overturning.

SUMMARY

Fluxes of dissolved gases are appreciably higher when the surface layer is cooling. Heat loss contributes to turbulence within the aqueous boundary layer and to mixed layer deepening which entrains dissolved gasses.

The surface area of the world's great lakes totals 997,000 km^2; of the world's large lakes, 686,000 km^2; and of the world's small to moderate sized lakes, 620,000 km^2. However, many of the smaller lakes have higher concentrations of CO_2 and CH_4 and a net flux of CO_2 and CH_4 to the atmosphere (Cole et al. 1994). For instance, in the Canadian Shield, lakes whose surface area is less than 10 km^2 have P_{CO2} values above 500 μatm. Concentrations decrease linearly with lake size, with Lake Superior having P_{CO2} of 100 μatm. If these numbers are extrapolated world wide, the potential for gas flux would be comparable in the three size classes of lakes. While gas flux due to heat loss occurs in all stratified water bodies, it is likely to be especially important in fetch-limited small to moderate sized lakes and wetlands. These data stress the need to incorporate the surface renewal approach into models of gas transfer.

Acknowledgements. Financial support was provided by National Science Foundation Grants DEB93-17986 and DEB97-26932 to SM, DEB93-18085 to GWK and SM, and DEB95-53064 to GWK. WE was supported by NSF grant OPP-9318532 and a Hans-Sigrist Fellowship grant from the University of Bern. We thank J.M. Melack and two anonymous reviewers for critically reading the manuscript and Lorenz Moosmann for graphics.

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CRITICAL IMPORTANCE OF BUOYANCY FLUX

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