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Authors
Turney, D E
Smith, W C
Banerjee, S

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A measure of near-surface fluid motions that predicts air-water gas transfer in a wide range of conditions

Damon E. Turney
Bren School of Environmental Science and Management, University of California, Santa Barbara, California, USA

Walter C. Smith
Department of Mechanical and Environmental Engineering, University of California, Santa Barbara, California, USA

Sanjoy Banerjee
Department of Chemical Engineering, University of California, Santa Barbara, California, USA

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[1] Air-water gas transfer impacts many important biogeochemical processes, yet current understandings involve large uncertainty. This arises because the process depends on a complex interaction between molecular diffusion and fluid motions that has not been adequately characterized. Here we show the first experimental support for a mechanistic model that relates near-surface motions to gas transfer coefficients over a range of flow conditions, including those leading to breaking wavelets. We find that the square root of the root mean square surface-velocity divergence varies linearly with gas transfer coefficients, as predicted by theory, and also with mean square surface slope. Besides advancing the understanding of the mechanisms governing air-water gas transfer, these results suggest easy-to-measure parameters that could, with further investigation, provide gas transfer coefficients in field settings. **Citation:** Turney, D. E., W. C. Smith, and S. Banerjee (2005), A measure of near-surface fluid motions that predicts air-water gas transfer in a wide range of conditions, *Geophys. Res. Lett.*, *32*, LXXXXX, doi:10.1029/2004GL021671.

1. Introduction

[2] Early interest in the subject of air-water gas transfer arose from the need to understand the aeration of anoxic waters, and has continued due to the need to track dissolved pollutants, greenhouse gases, and other geochemical compounds. A large amount of literature exists on the subject, including recent reviews [*Banerjee and MacIntyre*, 2004]. In spite of this body of work, the mechanisms that drive the process remain poorly understood and consequently predictions have large uncertainty. For example, widely used predictive models of the gas transfer process commonly differ by factors of three or more, and contain poorly understood non-linearities [*Banerjee and MacIntyre*, 2004]. This translates to uncertainties of at least 300% in recent attempts to calculate a net oceanic CO_2 uptake [*Donelan et al.*, 2002; *Takahashi et al.*, 2002]. Such uncertainty is due to the highly variable nature of correlating factors, e.g., wind, waves, surfactants, and thermal convection or stratification. The purpose of this letter is to report experimental support for a mechanistic model of air-water gas transfer that accurately predicts the rates in a wide range of conditions.

[3] Previous attempts to develop mechanistic models of the process [*Danckwerts*, 1951; *Komori et al.*, 1993; *Siddiqui et al.*, 2004; *Zappa et al.*, 2001] have relied on surface-renewal models. However, these models are limited by ambiguity in defining their central parameter — the time-scale of renewal — and consequently much tuning of parameters is needed for predictions to agree with measurements. An alternative model, termed the "surface divergence" model, has been developed [*Chan and Scriven*, 1970; *McCready et al.*, 1986]. This model recently was shown to agree with data from a grid-stirred tank without wind [*McKenna and McGillis*, 2004] and with direct numerical simulations at low wind speeds [*Banerjee et al.*, 2004]. This letter builds on these results by showing experimental support for the model at low and intermediate wind speeds, with breaking wavelets arising at the intermediate wind speeds. This is an important advance, since similar conditions are ubiquitous in the environment and yet it is not clear how they affect air-water gas transfer.

2. Conceptual Model

[4] The gas transfer coefficient, k, is defined as

$$k \equiv \frac{N}{(c_b - c_{eq})} \tag{1}$$

where N is the gas flux density across the interface, c_{eq} is the equilibrium concentration at the interface, and c_b is the bulk concentration. Because the molecular diffusivities, D, of most gases in water are $\sim$O(10^{-9} m^2/s), the main resistance to transfer lies in a very thin layer, $\sim$O(10 μm), on the water side of the interface [*Jahne and Haussecker*, 1998]. In this layer a combination of molecular diffusion and convective liquid motions control the gas transfer rate.

[5] Reliable models have been proposed for very low wind speeds where wavelets do not break [*Banerjee et al.*, 2004]. However, when short wavelets appear, gas transfer coefficients become more sensitive to wind speed and the situation is poorly understood. This transition is usually reported to occur when the ten-meter-height wind speed, U_{10}, is greater than 3.5 m/s. In this wavelet regime, molecular diffusion and near-surface motions should still

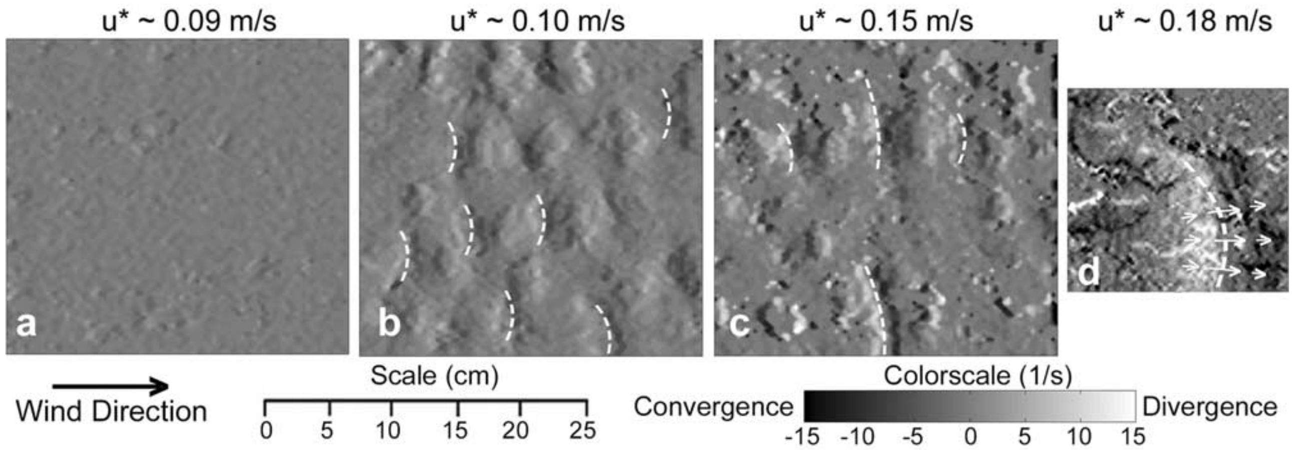

Figure 1. (a–d) Plan view images of instantaneous surface divergence under progressively higher wind stress. Example wave crests are drawn in with dashed white lines, as determined from the raw overhead photographs. The camera had a smaller field of view for $u^* \sim 0.18$, 0.19, and 0.21 m/s, as seen in (d). Example surface velocity vectors are shown in (d), but note that the actual density of DPIV velocity vectors for each image was 237 × 253.

control the transfer rate but much uncertainty exists as to which motions are important and how to model predictions. The surface divergence model, mentioned earlier, suggests that a useful measure is the instantaneous surface divergence,

$$\gamma = (du'/dx + dv'/dy) \tag{2}$$

where u′ and v′ are the interface-tangential velocity fluctuations. The root mean square (rms) surface divergence is $(\overline{\gamma^2})^{1/2}$, where the overbar denotes an ensemble average. In the thin liquid layer near the surface where the main resistance to transfer exists, γ is equal to the interface-normal-velocity gradient [*Banerjee and MacIntyre*, 2004]. A simplified form of the surface divergence model is

$$\bar{k} = C\sqrt{D\left(\overline{\gamma^2}\right)^{1/2}} \tag{3}$$

where $\bar{k}$ is the average gas transfer coefficient and C is a constant ~O(1) [*Chan and Scriven*, 1970; *Csanady*, 1990; *McCready et al.*, 1986; *Banerjee*, 1990]. The term $(\overline{\gamma^2})^{1/4}$ is termed "the square root of the rms surface divergence". As mentioned earlier, equation (3) was recently verified in direct numerical simulations and in a laboratory with grid-stirred turbulence. The strength of this model is its mechanistic origin and the scaling arguments that suggest $(\overline{\gamma^2})^{1/4}$ generically accounts for all motions, e.g., wave, turbulent, or viscous motions. In this report we experimentally test equation (3) under windy conditions for the first time, including intermediate wind speeds with short breaking wavelets, sometimes called microbreaking waves.

3. Experimental Setup

[6] The experiments were conducted in a linear wind-wave channel of height 31 cm, width 71 cm, and length 11.5 m. Water height was constant at 9.5 cm. The water surface was continuously cleaned with a surface vacuum during experiments and for 30 minutes prior to experiments. Bulk water velocity was steady at 1 cm/s, co-current with the wind.

[7] The gas transfer coefficient, $\bar{k}$, was measured by the streamwise gradient in dissolved oxygen concentration at steady state, similar to previous studies [*McCready and Hanratty*, 1985]. The equation $\bar{k} = \Gamma/\Delta x \ln[(\overline{c_1} - c_{eq})/(\overline{c_2} - c_{eq})]$ gave $\bar{k}$, where Γ is the volumetric flow rate per unit width, Δ*x* is the streamwise distance between samples, $\overline{c_1}$ is the time-averaged concentration upstream, and $\overline{c_2}$ is the time-averaged concentration downstream.

[8] Images of surface slope, *s*, were obtained similar to previous studies [*Jahne and Riemer*, 1990], where a light source with an intensity gradient is placed beneath the waves and overhead images give measurements of slope. These images were collected at 125 frames per second. The term $\overline{s^2}$ denotes the mean square surface slope.

[9] Floating glass microballoons, of diameter 75 μm and effective density 0.18 g/cm^3, acted as interfacial flow tracers. Just before images were collected they were dispersed on the water surface. At low surface concentrations such as those used here, microballoons have been shown to change the surface conditions only negligibly [*Kumar et al.*, 1998]. Images collected at 125 frames per second were fed into particle imaging velocimetry (PIV) calculations [*Sveen*, 2004] to map the surface velocity field. Near-surface velocity obtained in this way was confirmed to agree with that from side-view images of neutrally buoyant particles.

[10] The airside friction velocity, u^*, was calculated by fitting time-averaged airside velocity profiles to a logarithmic law assumption, i.e., $u^*/\kappa = d\overline{U}/d\log(z)$ where $\overline{U}$ is the time-average wind speed, *z* is height above the mean surface level, and κ is the von Karman constant. U_{10} was calculated from u^* (and conversely) using correlations of *Smith* [1988], which, for our wind speeds, were recently reviewed and recommended [*Yelland et al.*, 1998].

4. Results

[11] Examples of surface divergence fields are shown in Figures 1a–1d, where it is seen that well-organized patterns emerge above $u^* \sim 0.10$ m/s. The pattern is periodic and in-phase with wave crests. Convergence zones appear

just ahead of the crests and divergence zones just behind, confirming some results from side-view studies of micro-breaking waves [*Peirson and Banner*, 2003]. The patterns are not parallel-crested but are crescent shaped, similar to infra-red imagery captured in other studies [*Zappa et al.*, 2001].

[12] The raw images of flow tracers, not shown here, afford additional qualitative information. For u^* greater than $\sim$0.10 m/s, the tracers occasionally collect just downwind of a wave crest and "surf" along with the wave, i.e., travel at the crest velocity. This is evidence that water moves down the front of the wave at a speed equal to, or slightly greater than, the crest speed. This is a defining characteristic of wave breaking [*Peirson and Banner*, 2003]; Bubbles are not generated by this breaking. Such small wavelength breaking, which is ubiquitous on the ocean and on lakes, is often termed "microbreaking". In our experiments it begins to occur at wavelengths of 5 cm (u^* $\sim$0.10 m/s), simultaneous with the development of surface divergence patterns. We use the particle "surfing" behavior as an operational criterion for microbreaking.

[13] For each friction velocity a collection of 300 sequential surface-velocity fields and 3750 sequential surface-slope fields were used for a calculation of $(\overline{\gamma^2})^{1/4}$ and $\overline{s^2}$ respectively. The results are shown in Figure 2a where it is seen that the measures have similar shape, and show a change in behavior at $u^* \sim 0.10$ m/s when microbreaking begins. In Figure 2b, it is seen that $(\overline{\gamma^2})^{1/4}$ varies linearly with $\overline{s^2}$. It is also seen that values of $(\overline{\gamma^2})^{1/4}$ level off at 0.5 $(1/s)^{1/2}$ for lower wind speeds. This offset is due to small random PIV errors in γ, which are significant only at the lower wind speeds due to the $\frac{1}{4}$ exponent in $(\overline{\gamma^2})^{1/4}$. A correction for this effect is described in detail in the online supplemental material[1]. All figures after Figure 2a use this corrected $(\overline{\gamma^2})^{1/4}$ data. Uncertainty in the final values of $(\overline{\gamma^2})^{1/4}$, $\overline{s^2}$, and $\overline{k}$ are estimated by repeat experiments.

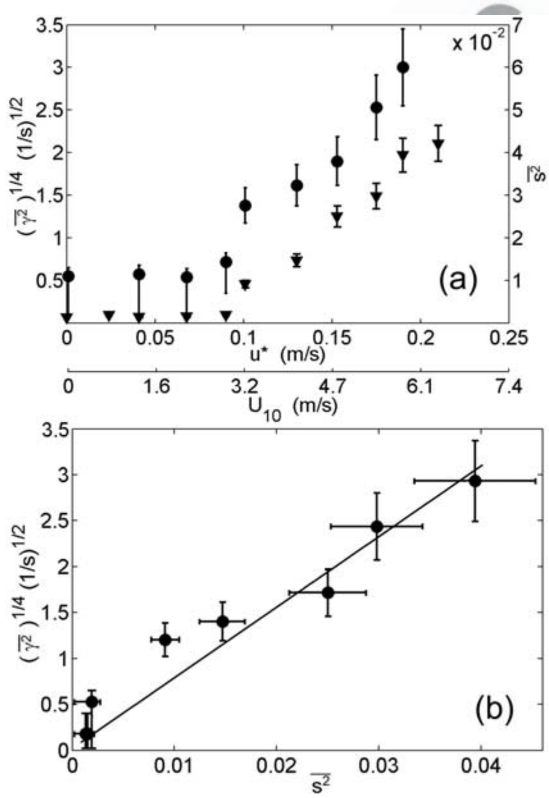

Figure 2. (a) The square root of rms surface divergence (circles) and the mean square slope (diamonds) are plotted versus friction velocity. A vertical offset, due to noise variance, is seen to affect the first few $(\overline{\gamma^2})^{1/4}$ values. (b) The linear relationship between $(\overline{\gamma^2})^{1/4}$ and $\overline{s^2}$ is plotted with a linear regression, $r^2 = 0.93$.

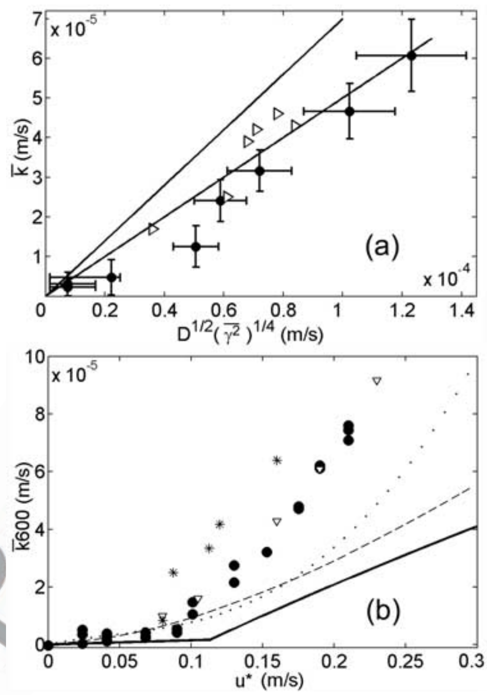

Figure 3. (a) The development of the gas transfer coefficient $\overline{k}$ with $D^{1/2}$ $(\overline{\gamma^2})^{1/4}$. A linear regression gives $\overline{k}$ = 0.45 $D^{1/2}$ $(\overline{\gamma^2})^{1/4}$, r^2 = 0.95. The solid lines are the prediction of equation (3), with C = 0.7 and 0.5. Circles are data from this study. Right-pointing triangles are "cleaned II" data from the oscillating-grid tank study of *McKenna and McGillis* [2004]. (b) Gas transfer coefficients normalized to Sc of 600, $\overline{k}600$, versus u^* (u^* is calculate from U_{10} as described in methods), compared with other experimental data and common oceanic parameterizations: *Liss and Merlivat* [1986] is the solid line; *Nightingale et al.* [2000] is the dashed line; *Wanninkhof and McGillis* [1999] is the dotted line; data of *Komori et al.* [1993] are the diamonds; data of *Siddiqui et al.* [2004] are the asterisks.

[14] In Figure 3a the surface divergence model is compared with our laboratory data. Values of $\overline{k}$ are plotted against $D^{1/2}$ $(\overline{\gamma^2})^{1/4}$ along with the grid-stirred tank data of *McKenna and McGillis* [2004]. Equation (3) is also plotted with C = 0.5 and C = 0.7, values suggested by direct numerical simulations in non-breaking conditions [*Banerjee et al.*, 2004] and by theory [*McCready et al.*, 1986]. Figure 3a shows that $D^{1/2}$ $(\overline{\gamma^2})^{1/4}$ is a measure that can predict $\overline{k}$ in a wide range of conditions, i.e., in grid-stirred tanks, at low wind speeds, and at intermediate wind speeds with breaking wavelets. There does exist an anomalous point in our data at

[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2004GL021671.

$\overline{(\gamma^2)}^{1/4} \sim 0.5$ and this will have to be the subject of future investigation.

[15] Figure 3b shows $\overline{k}$ values from laboratory experiments as well as oceanic parameterizations. The data exhibit large variability, which is to be expected since u^* is only indirectly connected to $\overline{k}$. In spite of this variability, Figure 3b suggests a change in gas transfer behavior at $u^* \sim$0.10 m/s, near the onset of breaking wavelets. Apparently, in both laboratory and oceanic studies, the organized surface-normal motions of microbreaking waves, seen in Figure 1, dominate the air-water gas transfer process at intermediate wind speeds. Note that, in Figure 3a, $\overline{k}$ values from flow conditions of widely different origin and character collapse to a single line.

[16] The gas transfer coefficients in Figure 3b are normalized to a Schmidt number of 600 ($Sc = \nu/D$ where ν is viscosity). This is done because this is the only way to compare our results to data reported in the literature [*Jahne and Haussecker*, 1998; *Jahne et al.*, 1987; *Wanninkhof and McGillis*, 1999]. However, if the surface divergence model is accurate then normalization should only involve D, not Sc. Experiments from *McCready et al.* [1986] confirm that viscosity does not have a simple effect on $\overline{k}$.

[17] Turning now to measurements of mean square wave slope, linear relationships between $\overline{k}$ and $\overline{s^2}$ have been found in previous studies [*Jahne et al.*, 1987], and were confirmed here; data are in the online material. In light of our experiments, this result can be expected based on the combination of Figures 2b and 3b, showing that $\overline{s^2}$ is linearly correlated with $\overline{(\gamma^2)}^{1/4}$ and $\overline{(\gamma^2)}^{1/4}$ is linearly correlated with $\overline{k}$. The hydrodynamic reason for the linear correlation between $\overline{s^2}$ and $\overline{(\gamma^2)}^{1/4}$ is unclear at present, but the relationship in Figure 2b provides some insight. A connection between $\overline{s^2}$ and $\overline{k}$ is intriguing since surface roughness measurements, such as slope, may be gathered over large spatial areas using satellite remote sensing. We caution that in field conditions, with fetch, swell, and other complexities, the relationship between $\overline{s^2}$ and $\overline{(\gamma^2)}^{1/4}$ could easily be different than Figure 2b. However, even if our laboratory wave conditions are much different than the real ocean, there is no reason to expect the surface divergence model, equation (3), to fail in field settings, as long as the interface is clean and bubbles are not present.

5. Summary

[18] Our results support the surface divergence model of air-water gas transfer in low and intermediate wind speeds, with microbreaking wavelets. Taken with the results of *McKenna and McGillis* [2004] and *Banerjee et al.* [2004], the surface divergence model agrees with experiments over a wide range of conditions. Linear relationships are found between $\overline{k}$ and $\overline{(\gamma^2)}^{1/4}$, and also between $\overline{s^2}$ and $\overline{(\gamma^2)}^{1/4}$, explaining previously observed correlations between $\overline{s^2}$ and $\overline{k}$. Microbreaking waves commence forming at $u^* \sim$0.10 m/s, equivalent to $U_{10} \sim 3.5$ m/s, and significantly increase the surface-normal motions in the concentration boundary layer, as seen in Figure 1. These motions dominate the gas transfer process at intermediate wind speeds, likely causing the regime change seen in Figure 3b.

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S. Banerjee, Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, USA.

W. C. Smith, Department of Mechanical and Environmental Engineering, University of California, Santa Barbara, CA 93106, USA.

D. E. Turney, Bren School of Environmental Science and Management, University of California, Santa Barbara, CA 93106, USA. (dturney@bren.ucsb.edu)