

A mixing length model for the aqueous boundary layer including the effect of wave breaking on enhancing gas transfer

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Abstract. A mixing length model for air-water gas transfer is developed to include the effects of wave breaking. The model requires both the shear velocity induced by the wind and the integrated wave dissipation. Both of these can be calculated for tanks and oceans by a full spectrum wave model. The gas transfer model is calibrated, with laboratory tank measurements of carbon dioxide flux, and transported to oceanic conditions to yield air-sea transfer velocity versus wind speed.

1. Introduction

Mixing length theory has been applied to the air boundary layer to model the transport of water soluble compounds such as water vapour, aerosols, SO₂, SO₃ and NH₃ [1, 2]. Wind-generated waves on the air-sea interface enter this problem only in that they modify the wind stress ($\tau = \rho_a u_{*a}^2$) and the principal scaling velocity for the mass flux, i.e., the friction velocity u_{*a} . The wind profile very near the surface is controlled by molecular viscosity, ν , and is linear in height, z ; whereas away from the surface (wall units, $zu_*/\nu = z^+ > 100$), the profile is proportional to the logarithm of height. Mixing length parameterization of the eddy viscosity/diffusivity provides the simplest way to model the profiles (of wind/contaminant) with the observed smooth transition from linear to logarithmic in flow over a smooth wall [3]. To deal with transitional and rough boundaries, [4] and [1] proposed additive mixing lengths, introduced by the surface roughness, for momentum and mass respectively; thereby providing a general model for air-phase limited gas transfer through smooth, transitional and rough surfaces [5].

Sparingly soluble gases such as O₂, N₂, CO₂, CO, CH₄ and the inert gases are under water-phase control. The aqueous boundary layer is also ventilated by the water turbulence generated by the wind stress acting on the surface but, unlike the air-phase, it is also mixed directly by the turbulence produced in wave breaking. Here the turbulent velocities injected may be an order of magnitude larger than those due to the wind stress. This leads to ventilation of the aqueous boundary layer and entrainment of air bubbles to depths comparable to the wave height. Both of these are related to wave breaking dissipation, D_w , which is the integral over all waves of the dissipation source function in wave models. The bubble-mediated transfer further depends on the solubility of the entrained gas, being greater for lower solubility [6]. While it is generally accepted that wave breaking enhances the transfer of gases that are limited in the water-phase, it is not known to what extent or how D_w affects the mass transfer velocity.



The principal problem in the experimental determination of the effect of wave breaking on gas transfer lies in the extreme difficulty of measuring D_w and u_{*w} . However, a wave model with properly formulated source functions for wave dissipation and wind input can be used to estimate both D_w and u_{*w} . Such a wave model has been developed and proven for gravity waves [7] and is extended to include capillary-gravity and capillary waves for the full spectrum calculations required here. With this wave model, careful and precise laboratory measurements of mass transfer velocities can be transported to the field.

2. The mixing length model

Modeling the average properties of the boundary layers at the air-water interface requires closure of the Reynolds equations. The simplest closure represents the diffusivity of the turbulence in analogy to molecular viscosity:

$$(\nu + \nu_t) \frac{dU}{dz} = u_*^2$$

where constant flux layers on both sides of the interface are assumed. In describing the turbulent boundary layer, ν_t , the eddy viscosity is taken to be $\nu_t = \kappa u_* z$, leading to the usual logarithmic “law of the wall”; κ is von Kármán’s constant. In the context of gas transfer this is not adequate because the main resistance to gas transfer comes from the thin diffusive layers on either side of the interface. The concept of mixing length is particularly useful as it provides a physical picture of the eddy sizes that are dominant in the mixing process. It may be thought of as the average vertical distance eddies travel before losing their characteristics (velocity, temperature, etc.) to the average surrounding flow. Formally, it is related to the eddy viscosity:

$$\nu_t = l_u^2 \frac{dU}{dz}$$

where in the logarithmic layer: $l_u = \kappa z$.

Clearly, there is a need to have a smooth transition between the viscous sub-layer, having a linear profile, and the logarithmic layer. This was suggested by [8] and modified by [4], and used to good effect in several descriptions of boundary layers on smooth solid walls:

$$l_u = \kappa z [1 - \exp(-zu_*/13\nu)]^2$$

The corresponding mixing length for passive scalars:

$$l_g = Sc_t^{-\frac{1}{2}} \kappa z [1 - \exp(-zu_* Sc^{0.33}/13\nu)]^2$$

where Sc_t is the turbulent Schmidt number and is a function of the Monin–Obukhov stability index, ζ . Thus the universal behaviour of diabatic boundary layers is built into the mixing length. The molecular Schmidt number dependence, $Sc^{0.33}$, is determined from the smooth flow values (at $U_{10} = 2$ m/s) of mass transfer velocity of water vapour and carbon dioxide.

To deal with flows that are rough or transitional – those in which the thickness of the viscous boundary layer is less than the height of the roughness elements – [2] introduced a non-zero mixing length at the surface, l_{us} :

$$l_u = l_{us} + \kappa z [1 - \exp(-zu_*/13\nu)]^2$$

which leads to the following (fitted) relationship between the roughness length, z_0 and l_{us} :

$$l_{us} = z_0 [3.35 \exp(-0.1\{0.25 / \text{Re}_*\}^4) \exp(-0.96\{\text{Re}_* / 0.25\}^{0.33}) + 0.449]; \quad \text{Re}_* > 0.11$$

$$l_{us} = 0; \quad \text{Re}_* \leq 0.11$$

where $\text{Re}_* = z_0 u_*/\nu$ is the roughness Reynolds number. l_{us} increases from zero to $1.61z_0$ at $\text{Re}_* = 0.25$; then decreases exponentially to $0.449z_0$ in fully rough flow.

The ratio of surface mixing lengths for gases to that for momentum is necessarily a function of the other relevant non-dimensional numbers, i.e., the molecular Schmidt number and the roughness Reynolds number:

$$l_{gs} = 0.684 \text{Sc}^{-0.5} \text{Re}_*^{-0.47} l_{us}.$$

where the empirical coefficients are set by comparison with the data of [9] and [15].

3. Wave breaking and enhancement of gas transfer of water-side limited gases

Wave breaking is a source of vertical turbulent energy to the aqueous boundary layer that acts to disrupt the thin viscous sub-layer near the surface. The integrated (over all wavenumbers) variance dissipation rate, D_w , provides an unambiguous connection with the effect of wave breaking on the mixing length. The full spectrum wave model is used to obtain D_w in the laboratory tank, the ocean, and the large circular flume of Heidelberg University's Aeolotron (figure 1).

D_w is a strong function of wind speed and a weak function of fetch – compare 230 km (black circles) with 4 km (black squares) oceanic fetches. The dissipation rates for the laboratory tank (length, width, height = 32.2 m, 0.76 m, 0.85 m) with water depth of 0.225 m, as used in the measurements of CO_2 flux, are given for a fetch of 14.3 m (black diamonds). The tank dissipation rates are much smaller (up to a factor of 30) than those computed for oceanic fetches. They permit transporting the precise laboratory measurements to the field. In order to compare with data from Heidelberg University's Aeolotron [10], D_w was computed for its circular shape (green diamonds). Note that the Aeolotron's (water depth of 1 m) dissipation rates are much larger than the linear tank's at low wind speeds because of the homogenous quasi-infinite fetch of the Aeolotron. At higher wind speeds the waves become depth-limited in both cases; the deeper Aeolotron being about three times larger.

D_w (units of viscosity, m^2/s) can be thought of as an eddy viscosity associated with wave breaking. Flow mixing effects of wave breaking, such as mass transfer of gases and emulsification of oils, can be parameterized in terms of a "wave dissipation number," $W_d = D_w/\nu$.

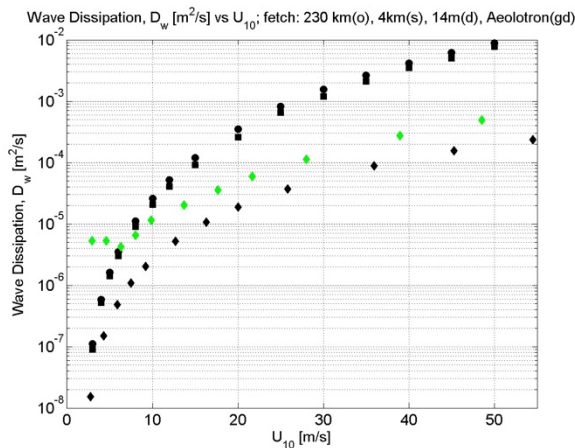


Figure 1. Modelled wave dissipation versus wind speed. Ocean at 230 km (black circles); ocean at 4 km (black squares); linear tank (black diamonds); circular flume (green diamonds).

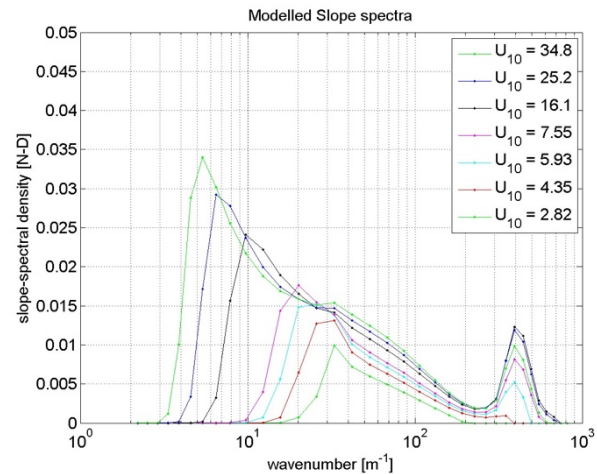


Figure 2. Modelled slope spectrum in the linear tank for various wind speeds in m/s.

Figure 2 shows the modelled slope spectra versus wavenumber for various U_{10} in m/s. The spectra have two modes: a wide band extending across the gravity wave spectrum to wavelengths of about 10 cm, and a narrow band centred on the capillary-gravity minimum phase speed waves (wavelength 1.73 cm in clean fresh water). These small breaking waves (micro-breakers) mix the thin aqueous boundary layer very effectively and provide a scaling length for the mixing length due to breaking.

The additive mixing lengths due to wave dissipation, l_{uw} and l_{gw} , may now be determined by comparison of the mixing length model with the laboratory CO_2 transfer velocities [11]. Figure 3 compares the measured and modelled transfer velocity versus tank centreline wind speed, with and without D_w .

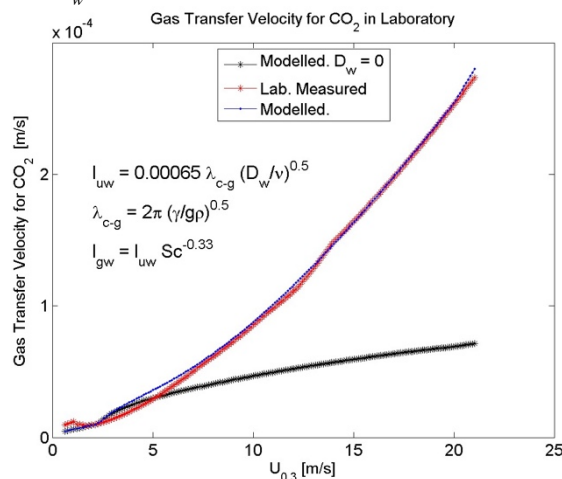


Figure 3. Measured and modelled gas transfer velocity in linear tank versus centerline wind speed.

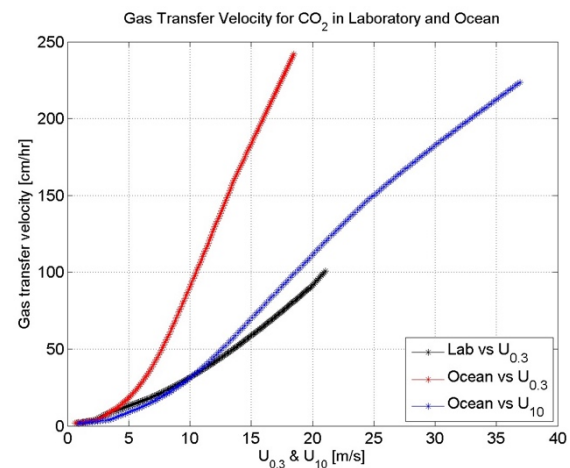


Figure 4. Modelled gas transfer velocity in the laboratory and ocean versus wind speed.

l_{uw} is scaled with the center capillary-gravity wavelength, $\lambda_{c-g} = 2\pi(\gamma/g\rho)^{0.5}$, where γ is the surface tension and ρ the water density. To obtain a close fit between measured (red line) and modelled (blue line) gas transfer velocities, the additive wave dissipation mixing lengths for velocity, l_{uw} , and gas, l_{gw} , are:

$$l_{uw} = 0.00065 \lambda_{c-g} (D_w / \nu)^{0.5}$$

$$l_{gw} = l_{uw} Sc^{-0.33}$$

The coefficient and exponents have been determined empirically. The black line, representing the modelled gas transfer velocity without any wave dissipation, illustrates the enormous impact of wave dissipation on the transfer of sparingly soluble gases.

Figure 4 compares the modelled gas transfer velocity in the laboratory (black line) and ocean (red line) using the corresponding wave model calculated D_w and u_* . The effect of the increased wave dissipation in the ocean is about a factor of two when plotted against $U_{0.3}$. While the laboratory transfer velocity shows a quadratic dependence on $U_{0.3}$, the oceanic transfer velocity is quadratic at low U_{10} , and approximately linear above 20 m/s.

4. Schmidt number dependence

The Schmidt number dependence of the mixing length model is tested by comparison with measurements in the same laboratory tank (figure 5) at Schmidt numbers of 600 [11] and higher [12]. Measurements are in red; model in blue.

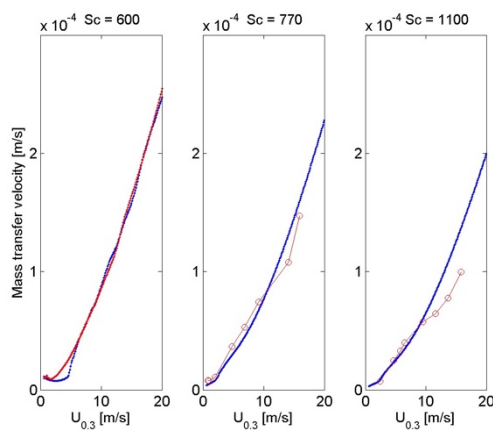


Figure 5. Measured and modelled gas transfer velocity in linear tank versus centerline wind speed for various Schmidt numbers.

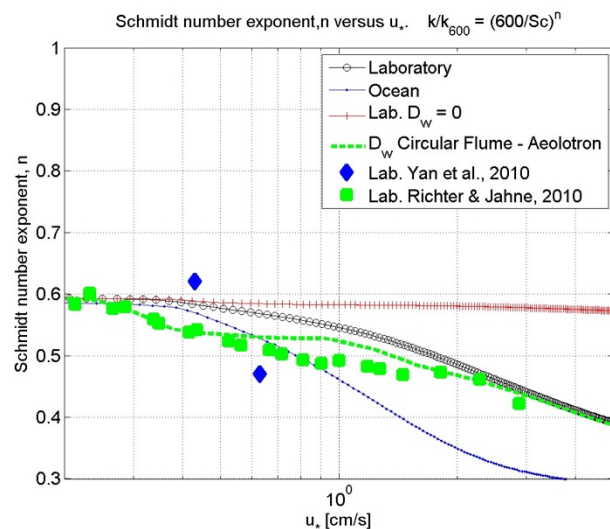


Figure 6. Measured and modelled Schmidt number exponent versus friction velocity in the water.

The Schmidt number exponent, n , is defined by the gas transfer velocity = aSc^{-n} . This exponent is plotted against friction velocity in figure 6 for the model with D_w values of zero (red line), linear tank (black line), Aeolotron (green dashed line) and ocean (blue line). The Aeolotron measured values (green squares [10]) are in close agreement with the modelled (green) line in the low and high thirds of $\log(u_*)$. Overall, both measurements and model show a downward trend with increasing u_* and D_w , showing decreased sensitivity to Schmidt number as the surface turbulence intensity increases. Applying laboratory measured Schmidt number dependencies to the field will lead to gross errors especially at high winds.

5. Carbon dioxide transfer on the oceans

The CO_2 transfer laboratory experiments [11] also explored the effect of ambient current on the gas transfer velocity. They found that the imposed current contributed 1.03% to the effective friction

velocity. This yields a simple prescription for calculating the gas transfer velocity in the presence of ambient (at depth of 10 m) currents. Figure 7 shows the modelled CO_2 transfer velocity versus U_{10} for various ambient currents plotted with the measurements of [13] and the model of [14]. The mixing length model can be used to calculate the oceanic transfer velocities for any sparingly soluble gas provided that the wave dissipation rate, the friction velocity and the ambient current are known.

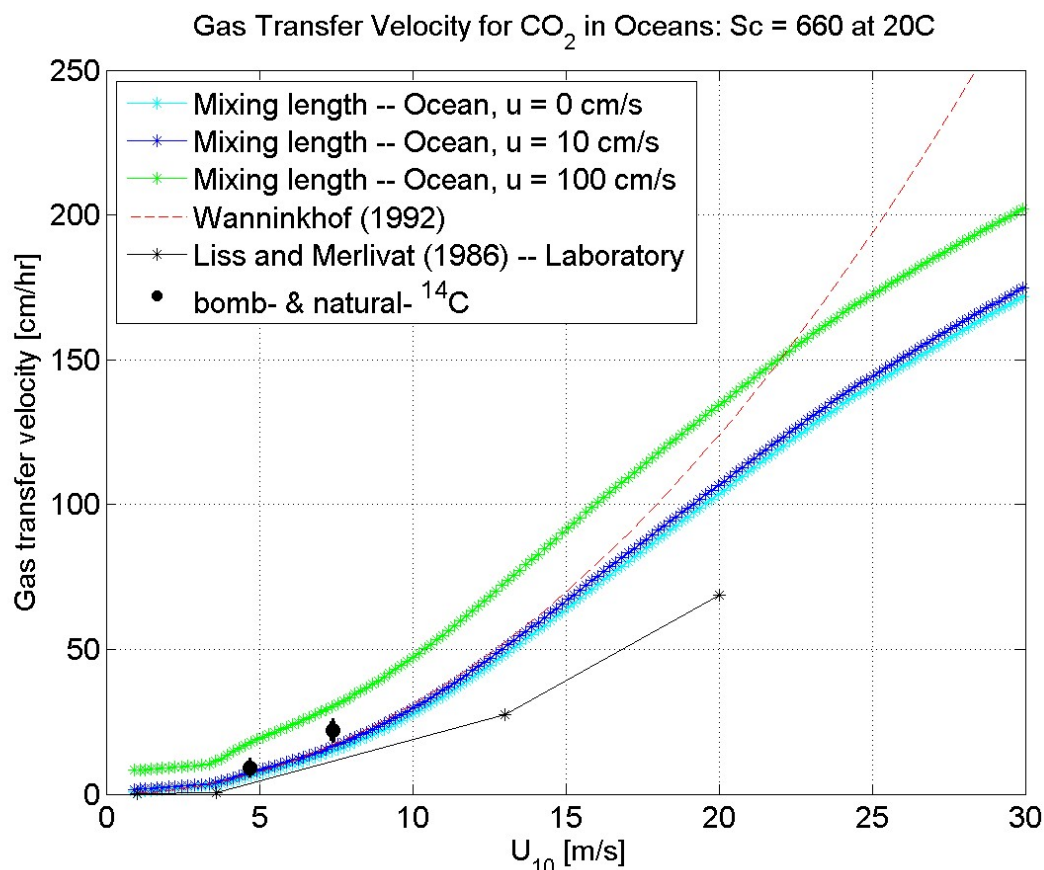


Figure 7. Modelled CO_2 transfer velocity in oceans at 20°C versus wind speed, with “ u ” the ambient current.

6. Summary

The mixing length model provides a means of calculating mass transfer velocities for ‘contaminants’ that are limited in either phase. The various empirical coefficients that define the relationship between mixing lengths for momentum and passive scalars were set by comparing with the wide Schmidt number range data of [15] for Schmidt number dependence and to the evaporation data of [9] for the roughness Reynolds number dependence. The model, thus established for the air boundary layer, is applied to the water boundary layer with the important role of wave breaking in mixing the sub-layer included through the integrated wave dissipation rate. Ocean transfer velocities of carbon dioxide are found to be less than linear in the 10-m neutral stability speed at high winds, not quadratic or cubic as has been suggested. They are further enhanced by the upper ocean ambient currents. The model is general and can be used for all sparingly soluble gases and any gas-liquid interface.

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