

Wind-Driven Surficial Oxygen Transfer

KYOUNG S. RO and PATRICK G. HUNT

USDA-ARS, Coastal Plains Soil, Water, and Plant Research Center, Florence,
South Carolina, USA

MATTHEW E. POACH

Soil Scientist, Meriden, Connecticut, USA

Wind-driven surficial oxygen transfer into stationary water bodies has become increasingly important because the fate of many pollutants in these water bodies is strongly influenced by oxygen mass transfer. There are many existing correlations that can be used for predicting wind-driven surficial oxygen transfer; however, the actual prediction has been difficult because there are large variations among numerous predictive transfer coefficient correlations. As a result, selecting an equation that can relate well to certain application conditions becomes critical for accurately predicting surficial oxygen transfer rates. To facilitate the selection process, this article critically reviews and analyzes many of wind-driven surficial oxygen transfer coefficient correlations published during the last five decades. These correlations are for oxygen and other pertinent gas transfer into nonmoving, open water bodies. Empirically derived oxygen coefficients were evaluated using the data derived from investigations in controlled wind tunnels, floating reaeration devices in open waters, and natural open waters. To compare these gas transfer coefficient correlations, gases were normalized to oxygen, and wind speeds were normalized to 10-m height. Generally, low wind speed did not significantly influence the transfer coefficients; however, the transfer coefficients increased, even exponentially, with higher wind speeds. Recently, a new unified equation was developed based on the gas transfer data published in the last five decades to estimate surficial oxygen transfer into stationary water bodies. Although this new equation satisfactorily fits the 50-

Address correspondence to Kyoung S. Ro, USDA-ARS, Coastal Plains Soil, Water, and Plant Research Center, 2611 West Lucas Street, Florence, SC 29501-1241, USA.
E-mail: kyoung@florence.ars.usda.gov 

year data using wind speed as a major variable, the effects of other environmental factors such as wind direction, solid contents, and precipitation need further research.

INTRODUCTION

Wind-driven oxygen transfer into stationary or slowly moving water bodies such as lakes, lagoons, and estuaries strongly influences the fate of many environmentally important chemicals and oxygen-demanding pollutants. For instance, the information about wind-driven surficial oxygen transfer into surface impoundments is useful in estimating fugitive emission rates. The wind-driven oxygen mass transfer coefficient of the surface impoundments in conjunction with that of ethyl ether can be used to estimate the individual liquid-phase mass transfer coefficients of fugitive chemicals for the U.S. Environmental Protection Agency (EPA) Water 9 emission model (U.S. EPA, 1994). The surficial oxygen transfer information will also improve the process emission model for estimating volatile organic compounds (VOCs) volatilization rates from the surface aeration tanks of municipal wastewater treatment plants (Hsieh et al., 1993). The oxygen transfer by aerators was used to estimate the VOCs volatilization rates based on the proportional relationship of mass transfer coefficients between oxygen and VOCs. The surficial oxygen transfer due to wind-induced turbulence, however, was not considered. Accounting for additional surficial oxygen transfer by the wind blowing over the aeration tank surface would further improve the accuracy of the model.

Wind-driven oxygen transfer also impacts the biological pathways of nutrients in treatment lagoons. For instance, wind-driven surficial oxygen transfer into animal waste treatment lagoons through the water–air interface may play an important role in analyzing the complex biochemical processes responsible for ammonia removal in the lagoons. These treatment lagoons treat animal wastewater with high levels of chemical oxygen demand (COD) and ammonia. Although nitrification is not expected from these highly anaerobic treatment lagoons, Jones et al. (2000) claimed that the amount of atmospheric oxygen transferred into the top surface layer of the lagoons should be adequate to convert substantial amount of ammonia to nitrate/nitrite, subsequently to dinitrogen gas by denitrification. Dinitrogen gas emission from these anaerobic lagoons observed by Harper et al. (2000, 2004) partially supports this hypothesis. Jones et al. (2000), however, were unable to either narrow the oxygen transfer rate or more quantitatively evaluate the nitrification–denitrification process, due to a lack of cohesive information on wind-driven surficial oxygen transfer in the literature.

The wind-driven surficial oxygen transfer information in the literature is conveniently expressed as a product of a thermodynamic driving force and

an overall bulk liquid-phase mass transfer coefficient.

$$M_{O_2} = K_L \cdot A \cdot (C_s - C) \quad (1)$$

where A is the mass transfer area (m^2), C_s the dissolved oxygen concentration in equilibrium with air (kg/m^3), C the bulk water concentration of dissolved oxygen (kg/m^3), K_L the overall bulk liquid-phase oxygen mass transfer coefficient (m/s), and M_{O_2} the oxygen mass transfer rate into water surface (kg/s).

Although the bulk dissolved oxygen concentration and the surface area are easily measured, the task of predicting oxygen transfer using Eq. 1 reduces to the determination of the overall liquid-phase mass transfer coefficients (hereafter it is referred as the transfer coefficient). For liquid-controlled gas transfer processes such as surficial oxygen transfer, the gas-phase mass transfer coefficient is not needed to determine the overall bulk liquid-phase mass transfer coefficient. Classical film-based theories, such as two film, penetration, and surface renewal theories, had been developed to explain the dependency of transfer coefficients on a complex array of hydrodynamic and aerodynamic factors and molecular transport properties of gases (Lewis and Whitman, 1924; Higbie, 1935; Danckwerts, 1951). Although these film-based theories elucidate simple physical pictures of gas absorption processes, transfer coefficients cannot be predicted by these theories alone because of unknown turbulence parameters of film thicknesses and the surface renewal rates of these theories.

Instead of using the film-based theories, Deacon (1977) used a friction velocity as a parameter to characterize the degree of turbulence and assumed the water surface as a rigid smooth wall. He used a semiempirical correlation for predicting liquid-phase controlled gas transfer such as oxygen transfer into water.

$$K_L(m/s) = 0.082 \cdot Sc^{-2/3} \left(\frac{\rho_a}{\rho_w} \right)^{1/2} u_{*,a} \quad (2)$$

where ρ_a is the air density (kg/m^3), ρ_w the water density (kg/m^3), $u_{*,a}$ the air friction velocity (m/s), Sc the Schmidt number (ν/D), and ν the kinematic viscosity of water (m^2/s).

Although Eq. 2 predicted a few values of oxygen transfer coefficients observed at low wind conditions reasonably well (Liss, 1973), the validity of the rigid smooth wall assumption quickly diminishes at higher wind conditions. Its major weakness was that water surface becomes rough with the onset of ripple waves associated with higher wind conditions. Additionally, the friction velocity is not a convenient parameter that can be readily measured by common meteorological instruments.

Other researchers used innovative instruments and experimental systems such as pulsed infrared (IR) radiator/IR radiometer, microwave backscatter,

and grid-stirred tank to investigate gas transfer process at micro scales within the air–water interface boundary layer regions (Brumley and Jirka, 1988; Jahne et al., 1989; Wanninkhof and Bliven, 1991). These theoretical studies improved the understanding of interfacial gas transfer processes; however, these studies were far from complete and comprehensive enough to allow surficial oxygen transfer rates to be predicted by these theories alone.

Because of these limitations of the existing theories, researchers have often relied on empirical relationships to predict transfer coefficients based on few important environmental factors. The applicable empirical equations for predicting oxygen transfer coefficients for treatment lagoons and surface impoundments have been predominately derived from reaeration and other gas exchange studies on ponds, lakes, and estuaries. Many of such empirical equations exist in the literature; however, these equations do not predict similar oxygen transfer rates (Ro and Hunt, 2006). Therefore, selecting an appropriate empirical equation among these equations is very difficult without detailed knowledge of how and under what conditions they were formulated and validated. The objective of this article is to provide detailed information about existing empirical correlations for surficial oxygen and other gas transfers into essentially stationary open water bodies.

We critically reviewed and conducted limited performance evaluations of these equations using literature data. Equations are summarized in tables for each section.

EMPIRICAL EQUATIONS FROM REAERATION STUDIES (TABLE 1)

Wind Tunnels

One of the early reaeration investigations was conducted by Downing and Truesdale (1955) five decades ago. A wind tunnel and a water tank were used to measure the effects of wind on the oxygen transfer coefficients. The oxygen in the tank water was initially removed with either sodium sulfite plus a catalyst (cobalt ion) or with a stream of nitrogen. The water was then allowed to reaerate from the atmosphere, and the dissolved oxygen concentrations in the tank water were measured over time as the atmospheric oxygen was transported into the water (i.e., reaeration). From these measurements, the oxygen transfer coefficients were estimated. As would be expected, the oxygen transfer coefficients increased with wind speed. They ranged from 4.2×10^{-6} to 1.0×10^{-4} m/s for wind speed of 0 to 9 m/s. When the wind speed was less than 3 m/s, the water surface was not noticeably disturbed. Accordingly, the oxygen transfer coefficients were not significantly influenced by low-speed wind.

Although Downing and Truesdale (1955) did not report any empirical formula for their transfer coefficient data, a transfer coefficient formula (Eq. 3) as a function of square of wind speed describing their data was reported

TABLE 1. Empirical Equations from Reaeration Studies

Laboratory Wind Tunnel Studies

$$K_L(m/s) = 0.0276 \cdot U^2 / 86400 \tag{3}$$

where U = wind speed (m/s).

$$K_L(m/s) = 4.19 \times 10^{-6} U^{1/2} \quad \text{for small U} \tag{4}$$

$$K_L(m/s) = 1.80 \times 10^{-6} U \quad \text{for medium U} \tag{5}$$

$$K_L(m/s) = 0.32 \times 10^{-6} U^2 \quad \text{for large U} \tag{6}$$

where U = wind speed at a reference height (m/s),
 K_L = transfer coefficient (m/s).

$$K_L(m/s) = 2.78 \times 10^{-6} \left(\frac{D_i}{D_{EE}} \right)^{2/3} \tag{7}$$

for deep lakes : $0 \leq U_{10} < 5.5$ m/s and $F/D < 14$

$$K_L(m/s) = (1.87 \times 10^{-7} U_{10}^2 - 1.3 \times 10^{-6}) \left(\frac{D_i}{D_{EE}} \right)^{2/3} \tag{8}$$

for deep lakes: $U_{10} > 5.5$ m/s and $F/D < 14$

$$K_L(m/s) = 2.788 \times 10^{-6} \left(\frac{D_i}{D_{EE}} \right)^{2/3} \tag{9}$$

for shallow systems: for $0 \leq U_{10} < 5$ m/s and $F/D > 14$

$$K_L(m/s) = 2.60 \times 10^{-9} (F/D) + 1.277 \times 10^{-7} U_{10}^2 \left(\frac{D_i}{D_{EE}} \right)^{2/3} \tag{10}$$

for shallow systems: $U_{10} > 5$ m/s and $14 \leq F/D < 51.2$

$$K_L(m/s) = 2.611 \times 10^{-7} U_{10}^2 \left(\frac{D_i}{D_{EE}} \right)^{2/3} \tag{11}$$

for shallow systems: $U_{10} > 5$ m/s and $F/D > 51.2$

where D_i = diffusivity of gas in water (m^2/s),
 D_{EE} = diffusivity of ethyl ether in water (m^2/s),
 U_{10} = wind speed at 10 m height (m/s).

$$K_L(m/s) = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} u_{*,a} Sc^{-0.5} \quad \text{for } u_{*,a} > 0.3 \text{ m/s} \tag{12}$$

$$K_L(m/s) = 1.0 \times 10^{-6} + 144 \times 10^{-4} u_{*,a}^{2.2} Sc^{-0.5} \quad \text{for } u_{*,a} < 0.3 \text{ m/s} \tag{13}$$

$u_{*,a}$ = air friction velocity (m/s)

$$\frac{k_2}{(k_2)_0} - 1 = 0.2395 \cdot U_{20 \text{ cm}}^{1.643} \tag{14}$$

(Continued on next page)

TABLE 1. Empirical Equations from Reaeration Studies (*Continued*)

where k_2 = wind-produced reaeration coefficient (h^{-1}),
 $(k_2)_o$ = the transfer coefficient predicted by Bennett and Rathbun,
 $= 0.101 \frac{U_w^{0.607}}{H^{1.689}}$,
 U_w = average water velocity (m/s),
 H = average water depth (m),
 $U_{20 \text{ cm}}$ = wind speed at 20 cm above water surface (m/s).
 For purely wind driven:

$$K_L(\text{m/s}) = 0.0375 \cdot u_{*,a}/86400 \quad \text{for } u_{*,a} < 0.2 \text{ m/s} \tag{15}$$

$$K_L(\text{m/s}) = 1.83 \times 10^{-3} \cdot u_{*,a}^2/86400 \quad \text{for } u_{*,a} > 0.2 \text{ m/s} \tag{16}$$

For pure open-channel flow:

$$K_L(\text{m/s}) = 2.150 \left(\frac{u_{*,a}^3 \times 10^6}{H \cdot 100} \right)^{0.25} / 86400 \tag{17}$$

where K_L = oxygen transfer coefficient at 20°C (m/s),
 $u_{*,a}$ = air friction velocity (m/s)

Field Studies

$$K_L(\text{m/s}) = (3.7 + 0.79 \cdot U_1)/360000 \tag{18}$$

where U_1 = wind speed at 1 m (mph).

$$K_L(\text{m/s}) = 5.2 \times 10^{-6} \quad \text{for } 0 < U_{10} < 3.2 \text{ m/s} \tag{19}$$

$$K_L(\text{m/s}) = 3.69 \times 10^{-5} \cdot U_{10} \quad \text{for } U_{10} > 3.2 \text{ m/s} \tag{20}$$

$$K_L(\text{m/s}) = 5.0 \times 10^{-6} \cdot U_{10} - 8.0 \times 10^{-6} \quad R^2 = 0.69 \quad \text{for } U_{10} > 3.2 \text{ m/s} \tag{21}$$

$$K_L = \frac{k^{1/3} u_{*,a}}{\Gamma_o} S_c^{-2/3} \left(\frac{\rho_a}{\rho_w} \right)^{1/2} \quad \text{for smooth flow} \tag{22}$$

$$K_L = \left(\frac{D u_{*,a}}{k z_e} \frac{\rho_a v_a}{\rho_w v_w} \right)^{1/2} \quad \text{for rough flow} \tag{23}$$

$$\frac{u_{*,a}}{K_L} = \frac{\Gamma S_c^{2/3}}{C_1} + \frac{(z_{o+} S_c)^{1/2}}{C_2} \quad \text{for transitional flow} \tag{24}$$

where k = von Karman constant (about 0.4),

$$C_1 = k^{1/3} \left(\frac{\rho_a}{\rho_w} \right)^{1/2},$$

$$C_2 = \left(\frac{1}{k} \frac{\rho_a}{\rho_w} \right)^{1/2}$$

$$\Gamma = \Gamma_o \frac{u_{*,a}}{u_{*,c}} \exp \left(- \frac{u_{*,a}}{u_{*,c}} + 1 \right) \quad \text{for } u_{*,a} \geq u_{*,c}$$

$u_{*,c}$ = critical friction velocity (m/s), z_e = equilibrium roughness height (i.e., about 0.25 cm),

$$z_{o+} = \frac{u_{*,a} z_o}{v} = \text{dimensionless roughness height.}$$

by the U.S. EPA (Table 3-11 of the EPA/600/3-85/040, Bowie et al., 1985). The U.S. EPA report did not specify the height of wind speed measurement; however, after comparing the equation to the original data of Downing and Truesdale, we concluded that the original wind speed measured at 0.05 m above water surface had been normalized to 10-m height wind speed for Eq. 3.

The data of Downing and Truesdale were also used by Banks (1975) along with the surficial heat transfer data of Hindley and Miner (1972) to develop semiempirical transfer coefficient formulas under three different wind regimes (Eq.s 4–6). In deriving these equations, Banks used the equations of motions previously solved by Liggett and Haditheodorou (1969) to estimate the wind-induced surface water velocity. Then, Banks estimated the power dependency on the wind speed by relating the turbulent diffusivity and the transfer coefficient (Hidy and Plate, 1966; Newmann and Pierson, 1966; Wu, 1968). High wind speed would produce more turbulent conditions and thereby accelerate the gas exchange processes.

Banks did not specify the wind speed regimes in Eqs. 4–6. The figure in his paper, however, allows inference of approximate boundaries for these regions; up to about 3 m/s, 3 to 8 m/s, and more than 8 m/s for the small, medium, and large wind speed regions, respectively. In these wind-speed-region equations, transfer coefficients are dependent upon the one-half, first, and second powers of the wind speed for the small, medium, and large regions. Thus, oxygen transfer increases more rapidly at higher wind speeds. The increase in this dependency on wind speed could be attributed to the progressive generation of ripples, waves, and breaking up waves. Indeed, the breaking up of waves with sputtering liquid droplets was observed by Banks and Chandrasekhara (1963) at wind speed of 15 m/s.

Banks cautioned that the use of these formulas was valid only for shallow lakes because he assumed a constant turbulent diffusion coefficient throughout the water column in developing these equations. The applicability of the Banks equations for shallow lakes was challenged by Lunney et al. (1985). Although Downing and Truesdale obtained their reaeration data with a laboratory tank of low fetch to depth ratio (F/D), Banks' equations derived from the Downing and Truesdale's aeration data should be representative of deep lakes rather than shallow lakes. They hypothesized that for systems of great depth ($F/D < 14$), Ekman depth (Tennekes and Lumley, 1972) would be established. As a result, the system would be separated into wind-induced turbulent upper layer and a relatively calm lower layer (Lunney, 1983).

The effect of F/D was studied with a laboratory wind-tunnel using the volatile gas ethyl ether (Lunney et al., 1985). The transfer coefficient was essentially constant at F/D less than 14 at a given wind speed. It increased with F/D at higher F/D values because the entire fluid was then turbulent at shallow depths. They developed transfer coefficient correlations for deep lakes ($F/D < 14$) and shallow systems ($F/D > 14$) such as surface impoundments (Eqs. 7–11).

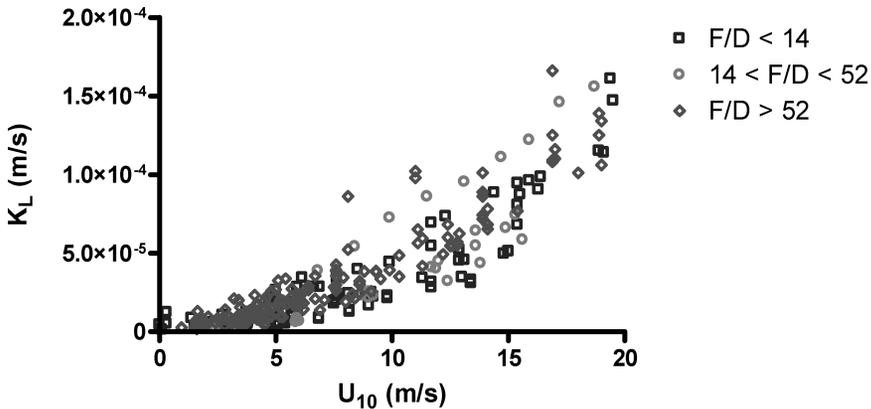


FIGURE 1. Plot of literature K_L (normalized to O_2) with widely different F/D .

Lunney et al. (1985) partially validated the equations just discussed with four suggested values of benzene transfer coefficients by Mackay (1981) assuming F/D greater than 50. Mackay, however, did not provide a detailed explanation how those values were obtained except stating that these values were the results from critically reviewing the existing data. Mackay also suggested values of benzene transfer coefficient for volatilization from tanks (contrast to environment), which were much higher than those used by Lunney et al. (1985). To test their hypothesis that F/D is an important parameter for transfer coefficient formulation, we plotted literature values of K_L (normalized to O_2 at 20°C) against U_{10} (Figure 1). Normalization procedures for K_L and wind speed are discussed later in this review. These data were obtained from gas transfer studies involving wind tunnels and lakes with F/D values ranging from 2 to 603 (Broecker et al., 1978; Cohen et al., 1978; Chu and Jirka, 2003; Clark et al., 1995; Crusius and Wanninkhof, 2003; Downing and Truesdale, 1955; Kanwisher, 1963; Liss, 1973; Lunney, 1983; Ocampo-Torres et al., 1994; Upstill-Goddard et al., 1990; Wanninkhof et al., 1985, 1987; Wanninkhof and Bliven, 1991). Albeit convincing in concept, Figure 1 shows that these literature transfer coefficients are not strongly influenced by F/D .

Equations 9–11 were later used by the U.S. EPA for the WATER9, the wastewater treatment model, in estimating emissions of volatile organic compounds (VOCs) from surface impoundments (U.S. EPA, 1994). These equations were further modified in the U.S. EPA report; the critical wind speed of 5 m/s was reduced to 3.25 m/s. For deep lakes (i.e., $F/D < 14$), the U.S. EPA report suggests the use of Eqs. 12 and 13, developed by MacKay and Yeun (1983), instead of Eqs. 7 and 8. MacKay and Yeun suggested the following empirical equation developed by Smith (1980) to relate the friction velocity ($u_{*,a}$) to environmentally more relevant U_{10} :

$$u_{*,a}(\text{cm/s}) = (6.1 + 0.63U_{10})^{0.5} U_{10} \quad (25)$$

where U_{10} is the wind speed measured at 10 m (m/s).

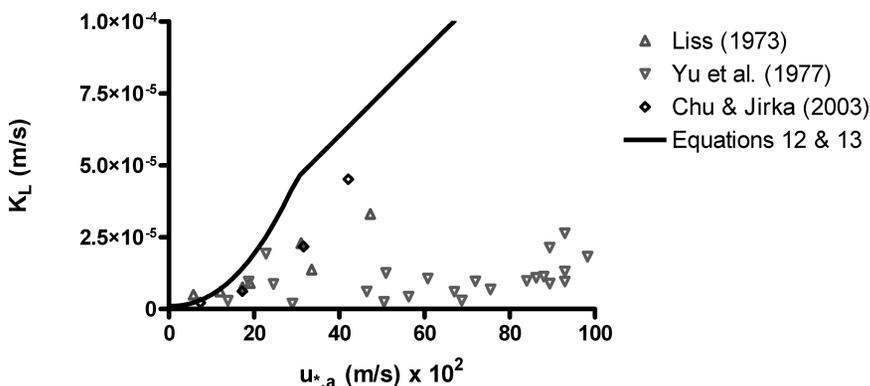


FIGURE 2. Deep lake equation and literature K_L (normalized to O_2 at $20^\circ C$) data.

We tested the predictability of Eqs. 12 and 13 by plotting few literature K_L versus $u_{*,a}$ data representing deep lakes (i.e., $F/D < 14$). These data (normalized to O_2 at $20^\circ C$) were obtained from a wind tunnel with $F/D = 2$ (Liss, 1973) and from a floating pool in a reservoir with $F/D = 6.7$ (Yu et al., 1977). As shown in Figure 2, Eqs. 12 and 13 did not perform well in predicting transfer coefficients determined from deep lakes.

Figure 2 also shows that the deep lake equations (i.e., Eqs. 12 and 13) actually performed better in predicting the transfer coefficients determined from a system representing a shallow lake (Chu and Jirka, 2003). They investigated reaeration characteristics of slow moving streams where both wind and stream flow induced turbulence. The water in a wind tunnel apparatus was deoxygenated by bubbling nitrogen to avoid the uncertainty concerning residual reactants of the chemical deoxygenation method. For stagnant water, they correlated the oxygen transfer coefficient with friction velocity, instead of wind speed. The water channel was 20 m long and 0.8 m deep; their system represented a shallow lake with $F/D = 25$. As shown in Figure 2, their shallow-lake K_L data were actually closer to the deep lake equations than the K_L data representing deep lakes.

In addition to F/D , drift water flow induced by wind can also increase mass transfer. The impact of wind was shown to have much larger (>30 times) effects than small water flow on reaeration (Mattingly, 1977). Eloubaidy and Plate (1972) also observed that the transfer coefficient significantly increased with wind. Mattingly (1977) estimated the reaeration coefficients by applying the non-linear least-square method on the data obtained from a laboratory wind tunnel study (55 cm wide and 27 cm deep for both water and air flows). Their results (Eq. 14) were summarized as a ratio of wind-produced reaeration coefficient to the values of the reaeration coefficient obtained without wind (Bennett and Rathbun, 1972).

Similar to Eq. 14, Chu and Jirka (2003) combined the effects of water flow and wind speed on oxygen transfer coefficients. They reported that the

oxygen transfer was influenced mostly by water flow for $U_{10} < 6$ m/s, and by wind for $U_{10} > 6$ m/s. They developed wind-induced equations (Eqs. 15–16) based on pure wind-driven oxygen mass transfer coefficient data along with other data from the literature (Kraft, 1983; Liss, 1973; Nakayama, 2000). Chu and Jirka reported that Eqn. 16 was compared favorably with the work of Jahne et al. (1987); however, we failed to identify similar observations in their article. Jahne et al. (1987) reported the following simple relationship for a large circular facility based on basic analogy between momentum, heat, and mass transfer.

$$K_+ = \frac{K_L}{u_{*,a}} = \beta^{-1} Sc^{-n} \quad (26)$$

where β is the Stanton number, which is the transfer coefficient/flow velocity, and K_+ is a dimensionless transfer coefficient.

They reported values of β and n for a smooth water surface to be 13.7 and 0.7, respectively. Using $Sc = 530$ for oxygen at 20°C, Eq. 26 predicts the dimensionless transfer coefficient to be 9×10^{-4} . For $u_{*,a} = 0.1$ m/s, Eq. 16 of Chu and Jirka (2003) predicts 4.3×10^{-6} m/s, while Eq. 26 of Jahne et al. (1987) yields 9.0×10^{-5} m/s. It is not clear why the value of the transfer coefficient predicted by Eq. 26 is so much higher than that by Eq. 16.

Chu and Jirka (2003) also developed a water-flow induced equation based on pure open-channel flow, oxygen mass transfer coefficient data (Eq. 17). Applying the superposition principle for the oxygen transfer coefficient equations derived from wind alone (i.e., Eqs. 15–16) and from water flow alone (Eq. 17), a linear, additive oxygen transfer coefficient model was developed.

$$K_L = K_{L,b} + K_{L,w} \quad (27)$$

where $K_{L,w}$ is the wind induced transfer coefficient (Eqs. 15 and 16) and $K_{L,b}$ the water-flow induced transfer coefficient (Eq. 17).

Equations 14 and 27 were compared for a slowly moving stream ($U_w = 0.1$ m/s) with an average depth of 1 m as shown in Figure 3. Equations 25 and 43 were used to convert $U_{20\text{ cm}}$ to $u_{*,a}$. Equation 27 predicted a much higher transfer coefficient than did Eq. 14.

Field Investigations

Unlike the well-controlled environments of the wind tunnel apparatus, the oxygen absorption process in field experiments presents challenges with far more complex arrays of environmental factors. Furthermore, these vary in time and space. These field-condition problems were admirably addressed by the Thames Survey Committee (1964). Floating reaeration tents were designed and made of polythene sheet (about 1 ft in diameter), and field

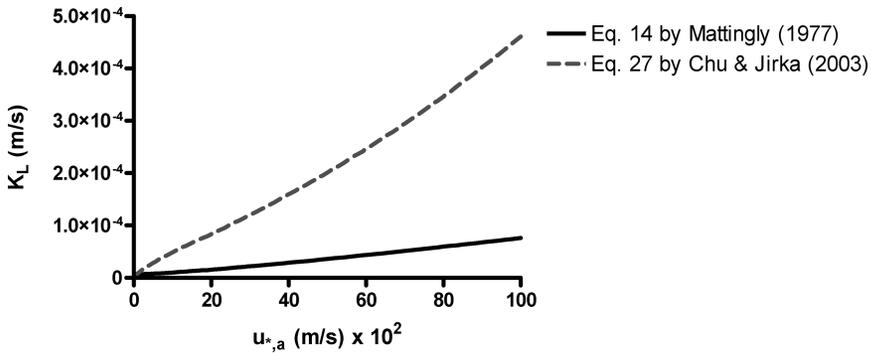


FIGURE 3. Comparison of Eqs. 14 and 27.

aeration coefficients were measured in the Thames Estuary near the London Bridge during 1953–1954. It was assumed that for the duration of the reaeration test (about 2 h) the floating tents would imitate rather than disturb the turbulence of the water surface, which would be induced by wind and other environmental factors. Oxygen transfer coefficients were estimated by comparing the decline of oxygen in the floating-tent headspace with the dissolved oxygen deficit in the water column (i.e., concentration difference in Eq. 1). The resulting oxygen transfer coefficient equation (Eq. 18) was based on more than 40 data points over a 2-year period.

The floating-tent method was validated by simultaneously determining the transfer coefficient based on the rates of change in oxygen concentration both in water and the tent headspace. For the water component, water in 200- and 2000-gal tanks was initially deoxygenated with Na_2SO_3 , and the dissolved oxygen (DO) concentration was measured as the atmospheric oxygen began to absorb into the water. To simulate the turbulence in water induced by wind, waves with variable characteristics were generated with a reciprocating baffle, located at the end of the tank. Values of the transfer coefficient determined from the DO change in the tanks were compared to values obtained from the oxygen mass change in the tent headspace. For calm water as generated by slow stirring of impellers, the two methods produced very similar transfer coefficients. For turbulent water with waves of varying heights, the floating-tent method produced much higher transfer coefficient values. Judging from this discrepancy of the two methods, the accuracy of Eq. 18 appears to be highly questionable.

Reaeration investigations somewhat similar to the floating-tent were conducted at the Spruce Run Reservoir in Clinton, N., in two floating pools; they were 1.8 and 8.1 m in diameter, respectively (Yu et al., 1977, 1983). The oxygen transfer coefficients from the small pool varied from 6.9×10^{-6} to 5.2×10^{-5} m/s for wind speed ranging from 3.6 to 8.0 m/s measured at 4.9 m above water surface. The transfer coefficient from the larger pool varied from $1.9 \times$

10^{-6} to 4.0×10^{-5} m/s for 10-m wind speed ranging from 1.4 to 8.5 m/s. Based on multiple regression analysis, two regions of wind speed were decided; low (less than 3.1 m/s) and high (>3.1 m/s) wind speed regions. A constant apparent reaeration coefficient of 1.05 d^{-1} was reported for the low-wind-speed region. Because the authors did not report the transfer coefficient of the low-wind-speed region, we estimated its value by subtracting the effect of mechanical motor mixing (i.e., 0.56 d^{-1}) from the apparent reaeration coefficient (i.e., 1.05 d^{-1}) and multiplying the mean depth of the pool: The oxygen transfer coefficient of the low-wind-speed region was estimated to be 5.2×10^{-6} m/s (Eq. 19). The oxygen transfer coefficient of the higher wind-speed regions was estimated based on data with U_{10} ranging from 4.2 to 9.0 m/s.

Careful examination of their raw data (Table IV-5 of Yu et al., 1977) revealed that Eq. 20 predicted values at least one order of magnitude higher than their observed values (Figure 4). Therefore, we performed independent linear regression analysis on their raw data for $U_{10} > 3.2$ m/s. Equation 21 is the resulting linear regression equation.

Overall, these empirical oxygen transfer coefficient formulas developed from reaeration studies are heterogeneous and inconsistent over the range of wind speeds that were validated by the authors. O'Connor (1983) attempted to explain these widely varying oxygen transfer coefficient data based on the scale of the experimental systems. He argued that the experimental system scale affected the characteristic viscous sublayer thickness or/and the roughness height; as a result, the oxygen transfer coefficient varied by a factor greater than 2 for a given friction velocity. For instance, the characteristic viscous sublayer thickness or the roughness height for larger systems typically encountered in field studies would be small. These characteristic

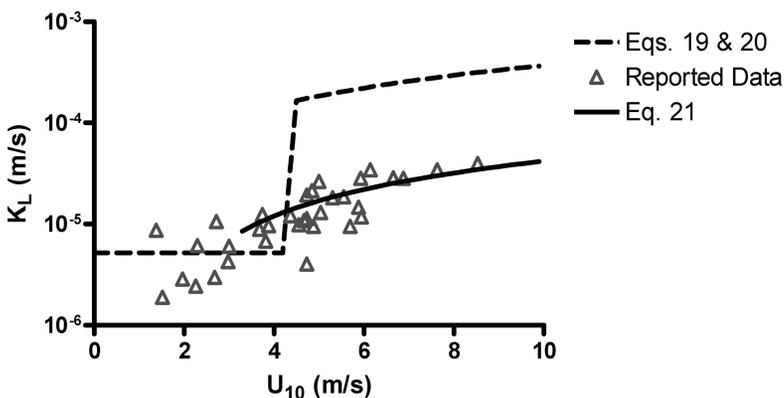


FIGURE 4. Modified equation for the work of Yu et al. (1977). Oxygen transfer coefficient for various scales and wind speeds based on O'Connor's correlations.

lengths were incorporated in dimensionless Reynolds numbers for different flow regimes as:

$$\Gamma_o = \frac{u_{*,a}\delta}{\nu} \quad \text{for smooth flow} \quad (28)$$

$$\frac{1}{\lambda_l} = \frac{u_{*,a}z_o}{\nu} \quad \text{for rough flow.} \quad (29)$$

where δ is the viscous sublayer thickness (m), z_o the height of roughness elements of the water surface (m), and Γ_o or $1/\lambda_l$ the Reynolds numbers for different flow regimes.

He reported that $\lambda_l = 10$ and $\Gamma_o = 10$ for small laboratory systems with limited fetch; $\lambda_l = 3$ and $\Gamma_o = 6.5$ for the intermediate scale of larger laboratory systems and moderate-size lakes; and $\lambda_l = 3$ or 2 and $\Gamma_o = 5$ or 2.5 for the large lakes and oceans with extended fetch. These turbulent boundary layer observations were utilized in developing oxygen transfer coefficient correlations for different flow regimes. A resistance in series model (O'Connor, 1984) was used to correlate the literature transfer coefficients (Eqs. 22–24). It employed the two-film theory for smooth flow, the surface renewal theory for rough flow, and the combination of these two theories for transitional flow.

O'Connor (1983) defined the smooth flow regime as a wind speed of approximately up to 6 m/s and the rough flow regime as winds greater than 20 m/s. The dimensionless roughness height was empirically correlated with the friction velocity as:

$$\frac{1}{z_{o+}} = \frac{1}{z_{e+}} + \lambda_l \exp\left(-\frac{u_{*,a}}{u_{*,t}}\right) \quad (30)$$

where $z_{e+} = \frac{u_{*,a}z_o}{\nu}$

and $u_{*,t}$ is the transitional friction velocity (about 0.1 m/s).

The raw transfer coefficient data in the literature were then plotted against these correlations (Figure 6 of his paper). Although the literature transfer coefficient data appeared to fit these correlations rather well, O'Connor did not provide detail of how he classified these data into small-scale laboratory, intermediate, and large-scale field classes. Furthermore, he did not explain how he defined the different flow regimes. One of his references, Wu (1969), defined aerodynamical regimes differently: smooth flow regime to a wind speed of 3 m/s, and rough flow regime with wind speed higher than 7 m/s. Wu (1969) also reported 8 cm, not 0.25 cm, for the equilibrium surface roughness.

O'Connor's correlations require the knowledge of friction velocity, a rather inconvenient parameter that must be estimated from vertical wind speed profiles. Csanady (1997) recently introduced a convenient

relationship between friction velocity and U_{10} . Csanady improved the existing friction velocity formulation of Amorocho and Devries (1980) with the additional data from Garratt (1977), Large and Pond (1981), and Smith (1980).

$$u_{*,a} = 0.03339U_{10} + 0.0004356U_{10}^2 \quad (31)$$

Using Eq. 31 to estimate the friction velocity, oxygen transfer coefficients for various scales and wind speeds were estimated based on the O'Connor's correlations (Figure 4). The values of Sc and diffusivity of oxygen were estimated using the polynomial equations suggested by Wanninkhof (1992). Other than the friction velocity correlation, we used the same parameter values for λ_l , $u_{*,t}$, $u_{*,a}$, z_e , and Γ_o (Table 2 of O'Connor, 1983) to generate Figure 4. To evaluate O'Connor's correlations with more recent data, the transfer coefficients obtained from small (2.4 m long) to medium (20 m long) size wind tunnels (Lunney, 1983; Chu and Jirka, 2003) and from intermediate size lakes (Crusis and Wanninkhof, 2003; Wanninkhof et al., 1985) were plotted in Figure 4. Although the data were widely scattered, the transfer coefficients determined from laboratory wind tunnels were generally lower than those obtained from intermediate size lakes as predicted by O'Connor's equations. The transfer coefficients obtained from the Rockland Lake with about 100 ha surface area were fitted reasonably well to O'Connor's intermediate-scale equation (Wanninkhof et al., 1985). Yet the transfer coefficients obtained from a smaller Lake 302N having about 12.8 ha surface area were actually higher than those predicted by O'Connor's large-scale equation (Crusis and Wanninkhof, 2003). This inconsistency illustrates that the characteristic viscous sublayer thickness/roughness length alone may not be able to adequately model the scaling effects on transfer coefficients as O'Connor originally envisioned.

EMPIRICAL EQUATIONS FROM OTHER GAS EXCHANGE STUDIES (TABLE 2)

To better understand the oxygen absorption process into lagoons, we expanded our literature search of gas exchange studies involving gases other than oxygen—a methodology commonly employed by oceanographers and meteorologists. These scientists used wind tunnels of varying sizes and/or a tracer gas such as SF₆ (sulfur hexafluoride) in the lakes for studying O₂ and CO₂ exchanges in open water bodies. Because CO₂ and SF₆ have similar transfer characteristics to that of oxygen, the transfer coefficients of these gases were normalized to that for oxygen.

The trend and values of CO₂ transfer coefficients determined by Kanwisher (1963) were very similar to that of Downing and Truesdale's oxygen

TABLE 2. Empirical Equations from Other Gas Exchange Studies

$K_{L,600}(m/s) = (0.17 \cdot U_{10}) \cdot 2.78 \times 10^{-6}$	for $U_{10} \leq 3.6$ m/s	(32)	
$K_{L,600}(m/s) = (2.85 \cdot U_{10} - 9.65) \cdot 2.78$	$\times 10^{-6}$	for 3.6 m/s $< U_{10} \leq 13$ m/s	(33)
$K_{L,600}(m/s) = (5.9 \cdot U_{10} - 49.3) \cdot 2.78 \times 10^{-6}$	for $U_{10} > 13$ m/s	(34)	
$K_{L,600}(m/s) = (1.11U_{10} + 0.35) \cdot 2.78$	$\times 10^{-6}$	for $U_{10} < 9.5 \pm 3$ m/s	(35)
$K_{L,600}(m/s) = (2.53U_{10} - 13.09) \cdot 2.78$	$\times 10^{-6}$	for $U_{10} > 9.5 \pm 3$ m/s	(36)
$K_{L,600}(m/s) = 2.78 \times 10^{-6}$	for $U_{10} < 3.7$ m/s	(37)	
$K_{L,600}(m/s) = (5.14 \cdot U_{10} - 17.9) \cdot 2.78 \times 10^{-6}$	for $U_{10} \geq 3.7$ m/s	(38)	
$K_{L,600}(m/s) = (0.32 \cdot U_{10}^{1.73}) \cdot 2.78 \times 10^{-6}$		(39)	

where $K_{L,600}$ = transfer coefficient of CO_2 (Sc for CO_2 at $20^\circ C = 600$)

$$K_{L,600} (m/s) = \left(0.45 \cdot U_{10}^{1.6}\right) \cdot 2.78 \times 10^{-6} \quad (40)$$

$$K_{L,Sc} (m/s) = \left(0.31 \cdot U_{10}^2 \left(\frac{Sc}{660}\right)^{-0.5}\right) \cdot 2.78 \times 10^{-6} \quad (41)$$

transfer coefficient. In this CO_2 investigation, a laboratory wind tunnel was used to determine the values of CO_2 transfer coefficients; the wind speed ranged from 0 to 10 m/s measured at 10 cm above water surface. The effects of wind on the transfer coefficients of oxygen and CO_2 were very similar, low or no wind influence at lower wind speeds. The CO_2 coefficients were rather stationary at about 2 cm/h for wind speed up to 2.6 m/s, but they increased rapidly when wind speeds exceeded 2.6 m/s. At the higher wind speeds, the increase in gas exchange rate was observed to be proportional to square of wind speed, which was similar to other research (Liss, 1973; Banks, 1975).

The study of CO_2 exchange at low wind speed and high pH may be complicated by the chemical reactivity of CO_2 with water; it would significantly enhance the CO_2 mass transfer rate (Liss, 1973, 1983). The problem of the gas reactivity with water during gas exchange studies was first addressed by Wanninkhof et al. (1985, 1987). To circumvent the gas reactivity problem, they used SF_6 as a tracer gas for noninvasively measuring gas exchange velocities (i.e., transfer coefficients) in lakes. Sulfur hexafluoride is very useful

because of the following characteristics: (1) biochemically inert; (2) present in background concentrations of less than 10^{-13} M in natural waters; (3) similar solubility and diffusivity values to that of O_2 and CO_2 ; (4) no adsorption to sediment; and (5) detected at less than 10^{-16} M. Although this gas is one of the greenhouse gases, the minute quantity required when used as a tracer makes the gas environmentally safe. Because the only important sink is the atmosphere, it is an ideal tracer gas for aquatic environments studying gas exchange processes involving slightly soluble gases such as O_2 and CO_2 . Accordingly, sulfur hexafluoride has become an established tracer for atmospheric transport and oceanic diffusion studies (Brown et al., 1975; Watson and Liddicoat, 1985; Ledwell et al., 1986).

One of the very intriguing insights from the use of SF_6 relative to the question of oxygen diffusion into lagoons came from a lake investigation. Wanninkhof et al. (1985) spiked SF_6 into the Rockland Lake, in New York, which is roughly elliptical in shape with a long axis of 1.4 km, a short axis of 1.0 km, and an average depth of 6 m. The SF_6 was completely mixed in the lake without any horizontal and vertical variations in concentration within a week. The transfer coefficient of SF_6 ($K_{L,SF6}$) was then estimated based on the time-series SF_6 concentrations of the lake water. At low wind speeds (<2.4 m/s), the SF_6 transfer coefficients were small and poorly correlated with wind speed. At wind speed above 2.4 m/s, Wanninkhof et al. (1985) concluded that SF_6 transfer coefficients increased linearly with wind speed.

The simple linearity was further defined by Liss and Merlivat (1986). From the literature of K values and wind data, they derived three separate linear transfer coefficient equations for CO_2 corresponding to three separate wind zones in series (Eqs. 32–34). Other linear K equations in separate wind zones were developed from the SF_6 tracer studies of two small lakes of England (Upstill-Goddard et al., 1990). These SF_6 data were expressed with the two straight lines in two wind zones (Eqs. 35 and 36). Both of the two-wind zone equations predict lower values of transfer coefficients than that predicted from Eqs. 32–34. Upstill-Goddard et al. (1990) cautioned that Eqs. 35 and 36 did not uniquely define the wind speed and gas transfer velocity of their experiments because the data showed greater scatter than would be predicted from the experimental uncertainties. They suggested that the time variation of wind speed and direction should be included in the predictive transfer coefficient model.

Recently Crusius and Wanninkhof (2003) reported yet another linear transfer coefficient equations (Eqs. 37–38) for separated wind zones based on the SF_6 tracer study of a low-wind-speed lake. The experiment was carried out on a small lake in Ontario using SF_6 . The wind speeds were lower than that of previous gas transfer studies. They used a constant 10-m drag coefficient (C_{10}) of 1.3×10^{-3} to estimate the 10-m reference wind speed from their wind speed measurement height of 1 m (Large and Pond, 1981).

Although Large and Pond actually reported a C_{10} value of 1.2×10^{-3} , rather than 1.3×10^{-3} as used by Crusius and Wanninkhof, this small difference would minimally affect the estimated values of U_{10} for low wind speeds.

Additional refinement of the K versus wind speed relationship was made by expressing K as a nonlinear power function of wind speed. One of the interesting trace gas studies that led to nonlinear expression of K was conducted in a large wind-wave tank, (100m long, 8 m wide and 0.7 m deep) in Delft, Netherlands (Wanninkhof and Bliven, 1991). The tracer-gas experimental methods were similar to the Rockland Lake study. Specifically, the rate of decrease in gas concentrations was measured in water that was initially saturated with SF_6 , N_2O , and CH_4 . From these data, the transfer coefficients of each gas were estimated by solving the dispersive-transport equations. They then normalized these K_{SF_6} to K_{CO_2} using the relationship between Schmidt numbers:

$$\frac{K_1}{K_2} = \left(\frac{Sc_1}{Sc_2} \right)^{-0.5} \quad (42)$$

where K_1 and K_2 are the transfer coefficients of gas 1 and gas 2, respectively (m/s).

The transfer coefficients of different gases were related to $Sc^{-1/2}$, which was predicted by the surface renewal theory. The normalized CO_2 gas transfer coefficient was nonlinearly related to the wind speed as a power-law expression (Eq. 39).

Another nonlinear K equation was suggested by Macintyre et al. (1995). They fitted the field data of the five lakes previously investigated by Wanninkhof et al. (1985, 1987) and Upstill-Goddard et al. (1990) into a power-law equation with a power index of 1.6 (Eq. 40).

The variability of the wind-speed dependency in the K equations might also result from the fact that field studies encounter complex environmental factors which are inherently dynamic in nature. For instance, the magnitude of wind speed and its direction continuously change in the field, which would influence the effective fetch lengths and the turbulence. Wanninkhof (1992) questioned the validity of using a mean wind speed as a characteristic wind in correlating the field-determined gas transfer coefficients. Instead of using a mean speed, he proposed to use the Rayleigh probability distribution function (i.e., Weibull distribution with a shape parameter $\beta = 2$) to represent the field wind speed distribution. Based on the ^{14}C gas transfer velocity and long-term average wind speed data (Erickson and Taylor, 1989; Pavia and O'Brien, 1986; Broecker et al., 1985, 1986; Cember, 1989), he developed the quadratic Eq. 41 to estimate the CO_2 transfer coefficient in seawater at $20^\circ C$. The Schmidt number for CO_2 in seawater at $20^\circ C$ is 660, compared to Sc of 600 in fresh water. The power indices of 1.6 and 1.73 in Eqs. 39 and 40 lies

between the linear relationships (Eqs. 32–36) and the quadratic relationship of Eq. 41.

COMPARISON AMONG EMPIRICAL EQUATIONS

To compare these empirical transfer coefficient formulas for different gases, equations that were developed based on wind speeds measured at various heights above the water surface, it is necessary to normalize the wind speed at a reference height and to convert the transfer coefficient formulas for oxygen at a reference temperature.

Normalization of Wind Speed at a Reference Height

The wind speed not measured at 10 m can be normalized to 10-m speed, assuming the seventh-root wind profiles (Arya, 2001). The “seventh-root law” relates the wind speeds at various heights and provides simple and reasonable fits to the observed wind profiles in the atmospheric boundary layer.

$$\frac{U_z}{U_{10}} = \left(\frac{Z}{10} \right)^{1/7} \quad (43)$$

In this article, Eq. 43 was used to normalize wind speeds of various heights to U_{10} .

Normalization of Different Gases to O₂ at 20°C

Based on dimensional analysis, the transfer coefficient can be expressed as a product of Sc^{-n} and the turbulence of water (Cussler, 1984; Deacon, 1977; Jahne et al., 1987; Macintyre et al., 1995). The transfer coefficients of different gases are then related with the ratio of Schmidt numbers of the gases as long as the turbulence does not change significantly over small temperature differences.

$$\frac{K_{L1}}{K_{L2}} = \left(\frac{Sc_1}{Sc_2} \right)^{-n} \quad (44)$$

where n is the power index, $K_{L,1\text{ or }2}$ the transfer coefficient of gas 1 or gas 2, respectively (m/s), and $Sc_{1\text{ or }2}$ the Schmidt number of gas 1 or gas 2, respectively.

The values of n vary from 1 to $1/2$: The two film theory suggests $n = 1$; the penetration/surface renewal theories suggest $n = 1/2$; and both laminar and turbulent boundary-layer theories suggest $n = \frac{2}{3}$ (Crusius and Wanninkhof, 2003; Cussler, 1984; Deacon, 1977; Hsieh et al., 1993; Rainwater and Holley,

1983; Watson et al., 1991; Whitmore and Corsi, 1994). To normalize and compare above empirical formulas developed for different gases, we adapted the surface renewal theory with $n = 1/2$. The Schmidt numbers of the gases at different temperatures were estimated using the third-order polynomial interpolations with temperature (Wanninkhof, 1992).

Comparison of Various Correlations and a New Unified Equation

Figure 5 compares the previous K_L equations normalized to O_2 at $20^\circ C$. These equations predict K_L from 0 to about 9.4×10^{-5} m/s for wind speed from 0 to 10 m/s, the range of wind speed typically encountered in treatment lagoons and surface impoundments. Kadlec and Knight (1996) reported a narrower range of oxygen transfer coefficient (5.6×10^{-7} to 5.8×10^{-5} m/s) for treatment wetlands. This lack of agreement among these formulations creates a great difficulty for end users in selecting proper equations for various applications. Recognizing the need, Ro and Hunt (2006) recently developed a new unified transfer coefficient equation (Eq. 45) based on compiled K_L data reported in the literature for the last 50 years. A total of 297 literature K_L data fit the new equation quite well with the coefficient of determination of 0.92 as shown in Figure 6. Because Eq. 45 is a continuous function of environmentally relevant variables, it will be useful for developing mathematical gas exchange models for surface impoundments and treatment lagoons.

$$K_L(m/s) = \left[170.6 \cdot Sc^{-1/2} U_{10}^{1.81} \left(\frac{\rho_a}{\rho_w} \right)^{1/2} \right] \cdot 2.78 \times 10^{-6} \text{ for } U_{10} > 0 \quad (45)$$

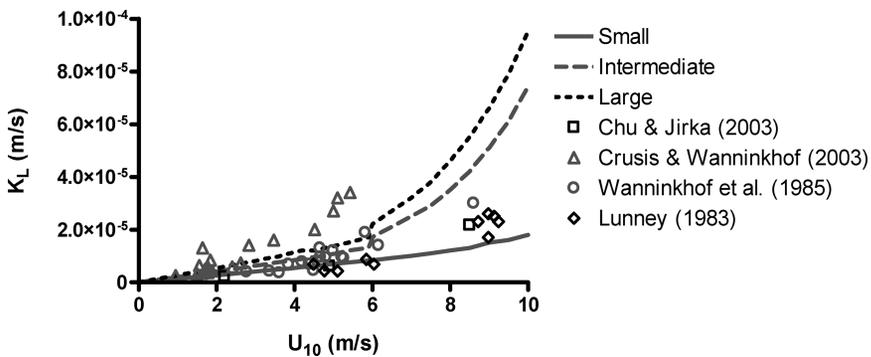


FIGURE 5. Oxygen transfer coefficient for various scales and wind speeds based on O'Connor's correlations.

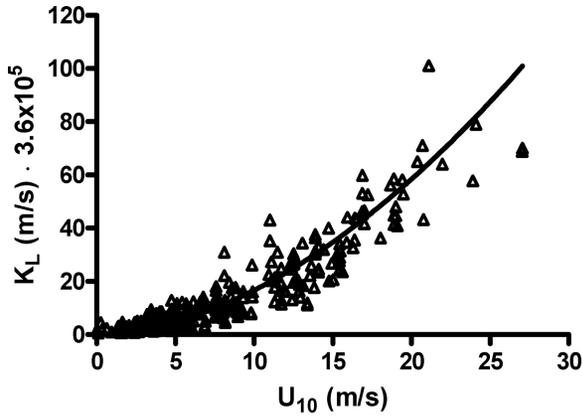


FIGURE 6. Equation 45 with literature K_L (normalized to O_2 at $20^\circ C$).

Other Important Environmental Variables

All formulas including Eq. 45 consider only wind as a single most important variable for gas transfer into stagnant water bodies; however, other environmental factors may also significantly influence surficial oxygen transfer processes. For instance, the impact of wind direction thereby affecting the effective fetch length and the wave field on the measurements of field transfer coefficients was rarely studied nor characterized. Also, many environmentally important water bodies such as treatment lagoons are not pure, but contain rather high levels of suspended solids and other organics. The effects of suspended solids on the oxygen transfer have not been studied adequately. Even among the limited studies done, the reported data were at best conflicting on the effects of suspended solids on the oxygen transfer rate (Holley, 1976). Ro and Singh (1994) observed the reduction of oxygen transfer rate with increase in suspended solids in their air-lift reactor. Similar decrease in oxygen transfer rate due to suspended solids had been observed by van der Kroon (1968) and Eckenfelder et al. (1956), while Poon and Campbell (1967) reported the increase in the transfer rate by suspended solids. Furthermore, rain can significantly influence the oxygen transfer rate especially in the low wind speed regime, where wind influence on the gas transfer is minimal. Rain may generate turbulence, resulting in increase in the gas transfer coefficient (Ho et al., 1997). Cole and Caraco (1998) reported that the gas transfer coefficient of small (15 ha) Mirror Lake, New Hampshire, was better correlated to precipitation events than to the wind speed.

Empirical correlations incorporating the effects of above environmental variables along with wind speed on surficial oxygen transfer will greatly improve predictability and usefulness of the formulation. This may be the challenge for gas exchange researchers in the near future.

SUMMARY

The following statements summarize the important findings of this critical literature review:

- Many equations exist in the literature for predicting liquid-phase controlled surficial transfer coefficients from nonmoving water bodies for oxygen and other gases. Wind was the single most important variable for these equations. Although each of these equations adequately describes limited sets of K_L data, large disagreements exist when all of these are compared.
- The literature transfer coefficients were not strongly influenced by fetch to depth (F/D) ratio, which was used by some empirical correlations as a variable.
- Field transfer coefficients were generally larger than the transfer coefficients determined from laboratory wind tunnels at given wind speed. The empirical correlations with characteristic viscous sublayer thickness/roughness length did not adequately model the scaling effects on transfer coefficients.
- To overcome the difficulty of selecting an equation to predict surficial oxygen transfer among the many existing correlations in the literature, a new unified surficial oxygen transfer coefficient equation was recently developed based on compiled transfer coefficient data published during the last 50 years.
- Although wind is a significant turbulence agent facilitating gas exchange for non-moving water bodies, other environmental variables such as precipitation and solid content may play important roles, especially under low-wind regimes. Consequently, more comprehensive empirical correlations incorporating these variables are needed in the future.

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REFERENCES

- Amoroch, J., and DeVries, J.J. A new evaluation of the wind stress coefficient over water surfaces, *J. Geophys. Res.* 85, 433–442, 1980.
- Arya, S.P. *Introduction to micrometeorology*. Academic Press. New York, 2001.
- Banks, R.B. Some features of wind action on shallow lakes, *ASCE J. Environ. Eng. Div.* 101(E5), 813–827, 1975.

- Banks, R.B., and Chandrasekhara, D.V. The penetration of a high-velocity gas jet through a liquid surface, *J. Fluid Mechanics* 15, 13–34, 1963.
- Bennett, J., and Rathbun, R. Reaeration in open channel flow, *Geological Survey Professional Paper 737*, U.S. Government Printing Office, Washington, DC, 1972.
- Bowie, G.L., Mills, W.B., Porcella, D.B., Campbell, C.L., Pagenkopf, J.R., Rupp, G.L., Johnson, K.M., Chan, P.W.H., Gherini, S.A., and Tetra Tech, *Rates, constants, and kinetic formulations in surface water quality modeling* (second edition). EPA/600/3-85/040, U.S. EPA, Athens, GA, 1985.
- Broecker, H., Petermann, C.J., and Siems, W. 1978. The influence of wind on CO₂ exchange in a wind-wave tunnel, *J. Marine Res.* 36(4), 595–610, 1978.
- Broecker, W.S., Peng, T.-H., Ostlund, G., and Stuiver, M. The distribution of bomb radiocarbon in the ocean, *J. Geophys. Res.* 90, 6953–6970, 1985.
- Brown, R., Dietz, R., and Cote, E. The use of SF₆ in atmospheric transport and diffusion studies, *J. Geophys. Res.* 80, 3393–3398, 1975.
- Brumley, B.H., and Jirka, G.H. Air-water transfer of slightly soluble gases: Turbulence, interfacial processes and conceptual models, *PCH PhysicoChemical Hydrodynamics* 10(3), 295–319, 1988.
- Cember, R. Bomb radiocarbon in the Red Sea: A medium-scale gas exchange experiment, *J. Geophys. Res.* 94, 2111–2123, 1989.
- Chu, C.R., and Jirka, G.H. Wind and stream flow induced reaeration, *J. Environ. Eng.* 129(12), 1129–1136, 2003.
- Clark, J.F., Wanninkhof, R., Simpson, J.H., Schuster, W.S.F., and Ho, D.T. Gas transfer velocities for SF₆ and ³He in a small pond at low wind speeds, *Geophysical Res. Letters* 22(2), 93–96, 1995.
- Coehn, Y., Cocchio, W., and Mackay, D. Laboratory study of liquid-phase controlled volatilization rates in presence of wind waves, *Environ. Sci. Technol.* 12(5), 553–558, 1978.
- Cole, J.J., and N.F. Caraco. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF₆, *Limnol. Oceanogr.* 43, 647–656, 1998.
- Crusius, J., and Wanninkhof, R. Gas transfer velocities measured at low wind speed over a lake, *Limnol. Oceanogr.* 48(3), 1010–1017, 2003.
- Csanady, G.T. The role of breaking waves in air-sea gas transfer, *J. Geophys. Res.* 95, 749–759, 1990.
- Csanady, G.T. The “slip law” of the free surface, *J. Oceanogr.* 53, 67–80, 1997.
- Cussler, E.L. *Diffusion MASS TRANSFER IN FLUID SYSTEMS*. Cambridge University Press, New York, 1984.
- Dankwerts, P.V. Significance of liquid film coefficients in gas absorption, *Ind. Eng. Chem.* 43, 1460–1467, 1951.
- Deacon, E.L. Gas transfer to and across an air-water interface, *Tellus* 29, 363–374, 1977.
- Downing, A.L., and Truesdale, G.A. Some factors affecting the rate of solution of oxygen in water, *J. Appl. Chem.* 5 (October), 570–581, 1955.
- Eckenfelder, W.W., Lawrence, W.R., and Lauria, D.T. Effects of various organic substances on oxygen absorption efficiency, *Sew. Ind. Wastes* 28(11), 1357–1364, 1956.

- Eloubaidy, A.F., and Plate, E.J. Wind shear turbulence and reaeration coefficient, *J. Hydraul. Div. Am. Soc. Civil Eng.* 98(HY1), 153–170, 1972.
- Erickson, D.J. III, and Taylor, J.A. Non-Weibull behavior observed in a model-generated global surface wind field frequency distribution, *J. Geophys. Res.* 94, 12693–12699, 1989.
- Garratt, J.R. Review of drag coefficients over oceans and continents, *Monthly Weather Rev.* 105, 915–929, 1977.
- Harper, L.A., Sharpe, R.R., and Parkin, P.B. Gaseous nitrogen emissions from anaerobic swine lagoons: Ammonia, nitrous oxide, and dinitrogen gas, *J. Environ. Qual.* 29, 1356–1365, 2000.
- Harper, L.A., Sharpe, R.R., Parkin, T.B., Visscher, A.De, van Cleemput, O., and Byers, F.M. Nitrogen cycling through swine production systems: Ammonia, dinitrogen, and nitrous oxide emissions, *J. Environ. Qual.* 33, 1189–1201, 2004.
- Hidy, G.M., and Plate, E.J. Wind action on water standing in a laboratory channel. *J. Fluid Mech.* 26, 651–687, 1966.
- Higbie, R. The rate of absorption of a pure gas into a still liquid during short periods of exposure, *Trans. Am. Inst. Chem. Eng.* 31, 365–388, 1935.
- Hindley, P.D., and Miner, R.M. Evaluating water surface heat exchange coefficients, *ASCE J. Hydraul. Div.* 98(HY8), 1411–1426, 1972.
- Holley, E.R. 1976. Oxygen transfer at the air-water interface. In: *Proceedings of a Symposium on Transport Processes in the Oceans*, 87nd National Meeting of the Am. Inst. of Chemical Engrs, Atlantic City, NJ, August 29–September 1.
- Hsieh, C.C., Ro, K.S., and Stenstrom, M.K. Estimating emissions of 20 VOCs. I: Surface aeration, *ASCE J. Environ. Eng.* 119, 1077–1098, 1993.
- Ho, D.T., Bliven, L.F., Wanninkhof, R., and Schlosser, P. The effects of rain on air-water exchange, *Tellus* 49B, 149–158, 1997.
- Hunt, P.G., Matheny, T.A., and Szogi, A.A. Denitrification in constructed wetlands used for treatment of swine wastewater, *J. Environ. Qual.* 32, 727–735, 2003..
- Jahne, B., Wais, T., Memery, L., Caulliez, G., Merlivat, L., Munnich, K.O., and Coantic, M. He and Rn gas exchange experiments in the large wind-wave facility of IMST, *J. Geophys. Res.* 90, 11989–11997, 1985.
- Jahne, B., Munnich, K.O., Bosinger, R., Dutzi, A., Huber, W., and Libner, P. On the parameters influencing air-water gas exchange, *J. Geophys. Res.* 92, 1937–1950, 1987.
- Jahne, B., Libner, P., Fischer, R., Billen, T., and Plate, E.J. Investigating the transfer processes across the free aqueous viscous boundary layer by the controlled flux method, *Tellus* 41B(2), 177–195, 1989.
- Jones, M.L., Liehr, S.K., Classen, J.J., and Robarge, W. Mechanisms of dinitrogen gas formation in anaerobic lagoons, *Adv. Environ. Res.* 4, 133–139, 2000.
- Kadlec, R.H., and Knight, R.L. *Treatment wetlands*. Lewis, Boca Raton, FL, 1996.
- Kanwisher, J. On the exchange of gases between the atmosphere and the sea, *Deep-Sea Res.* 10, 195–207, 1963.
- Kraft, K. *Der sauerstoffeintrag in eine windinduzierte Kanal-stromung*, Diploma thesis, University of Karlsruhe. 1983.
- Large, W.P., and Pond, S. Open ocean momentum flux measurements in moderate to strong winds, *J. Phys. Oceanogr.* 11, 324–326, 1981.

- Ledwell, J.R., Watson, A.J., and Broecker, W.S. A deliberate tracer experiment in the Santa Monica Basin, *Nature* 323, 322–324, 1986.
- Lewis, W.K., and Whitman, W.G. Principles of gas absorption, *Ind. Eng. Chem.* 16(12), 1215–1220, 1924.
- Liggett, J.A., and Hadjithodorou, C. Circulation in shallow homogenous lakes, *ASCE J. Hydraul. Div.* 95(HY2), 609–620, 1969.
- Liss, P.S. Processes of gas exchange across an air-water interface, *Deep-Sea Res.* 20, 221–238, 1973.
- Liss, P.S. Experiments and geochemical implications. In: *Air-sea exchange of gases and particles*. P.S. Liss and W.G.N. Slinn, eds. Reidel, Boston, 241–298, 1983.
- Liss, P.S., and Merlivat, L. 1986. Air-sea gas exchange rates: Introduction and synthesis. In: *The role of air-sea exchange in geochemical cycling*, ed. P. Buat-Menard, 113–129, D. Reidel, Hingham, MA.
- Lunney, P.D. 1983. *Characterization of wind and depth effects upon liquid phase mass transfer coefficients: Simulation studies*. MS thesis, Department of Chemical Engineering, University of Arkansas.
- Lunney, P.D., Springer, C., and Thibodeaux, L.J. Liquid-phase mass transfer coefficients for surface impoundments, *Environ. Prog.* 4(3), 203–211, 1985.
- Macintyre, S., Wahhninkhof, R., and Chanton, J.P. 1995. Tracer gas exchange across the air–water interface in fresh waters and coastal marine environments. In: *Biogenic trace gases: Measuring emission from soil and water*. Matson, P.A., and R.C. Harris, eds. Blackwell, Malden, MA, 52–97, 1995.
- Mackay, D. Environmental and laboratory rates of volatilization of toxic chemicals from water, *Hazardous Assessment of Chemicals Current Development*, Vol. 1, 303–322, 1981.
- Mackay, D., and Yeun, A.T.K. Mass transfer coefficient correlations for volatilization of organic solutes from water, *Environ. Sci. Technol.* 17(4), 211–217, 1983.
- Mattingly, G.E. Experimental study of wind effects on reaeration, *J. Hydraul. Div. ASCE* 103(HY3), 311–323, 1977.
- Nakayama, T. 2000. *Turbulence and coherent structures across air–water interface and relationship with gas transfer*. PhD dissertation. Kyoto University, Kyoto, Japan.
- Newmann, G., and Pierson, W.L. Jr. 1966. *Principles of physical oceanography*. Prentice Hall, Englewood Cliffs, NJ.
- Ocampo Torres, F.J., and Donelan, M.A. Laboratory measurement of mass transfer of carbon dioxide and water vapor for smooth and rough flow conditions, *Tellus* 46B, 16–32, 1994.
- O'Connor, D.J. Wind effects on gas–liquid transfer coefficients, *ASCE J. Environ. Eng.* 109(3), 731–752, 1983.
- O'Connor, D.J. 1984. Turbulent transfer across smooth and rough surfaces. In: *Gas transfer at water surfaces*, eds. W. Brutsaert and G.H. Jirka. D. Reidel, Hingham, MA, 321–331, 1984.
- Pavia, E.G., and O'Brien, J.J. Weibull statistics of wind speed over the ocean, *J. Clim. Appl. Meteorol.* 25, 1324–1332, 1986.
- Poach, M.E., Hunt, P.G., Sadler, E.J., Matheny, T.A., Johnson, M.H., Stone, K.C., Humenik, F.J., and Rice, J.M. Ammonia volatilization from constructed wetlands that treat swine wastewater, *Trans. ASAE* 45(3), 619–627, 2002.

- Poon, C.P.C., and Campbell, H. Diffused aeration in polluted water, *Water Sew. Works* 114, 461–463, 1967.
- Rainwater, K.A., and Holley, E.R. Laboratory studies on hydrocarbon tracer gases, *ASCE J. Environ. Eng.* 110(1), 27–41, 1983.
- Ro, K.S., and Hunt, P.G. A new unified equation for wind-driven surficial oxygen transfer into stationary water bodies, *Trans. ASAE* 49(5), 1–8, 2006.
- Ro, K.S., and Singh, M.K. Effects of solid concentration and size on gas holdup and oxygen mass transfer coefficient of a three-phase air-lift reactor, *J. Environ. Sci. Health A29*, 2219–2227, 1994.
- Smith, S.D. Wind stress and heat flux over the ocean in gale force winds, *J. Phys. Oceanogr.* 10, 709–726, 1980.
- Tennekes, H., and Lumley, J.L. 1972. *A first course in turbulence*. MIT Press, Cambridge, MA.
- Thames Survey Committee and the Water Pollution Research Laboratory. *Effects of Polluting Discharges on the Thames Estuary*. Water Pollution Research Technical Paper, No. 11, Her Majesty's Stationary Office, London, England, 1964.
- Upstill-Goddard, R.C., Watson, A.J., Liss, P.S., and Liddicoat, M.I. Gas transfer velocities in lakes measured with SF₆, *Tellus* 42B, 364–377, 1990.
- U.S. EPA. 1994. *Air emissions models for water and wastewater*. EPA-453/R-94-080A, Research Triangle Park, NC.
- van der Kroon, G.T.M. The influence of suspended solids on the rate of oxygen transfer in aqueous solutions, *Water Res.* 2, 26–30, 1968.
- Wanninkhof, R. Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.* 97(C5), 7373–7382, 1992.
- Wanninkhof, R., and Bliven, L.F. Relationship between gas exchange, wind speed, and radar backscatter in a large wind-wave tank, *J. Geophys. Res.* 96(2), 2785–2796, 1991.
- Wanninkhof, R., Ledwell, J., and Broecker, W.S. Gas exchange-wind speed relation measured with sulfur hexafluoride on a lake, *Science* 227, 1224–1226, 1985.
- Wanninkhof, R., Ledwell, J., Broecker, W.S., and Hamilton, M. Gas exchange on Mono Lake and Crowley Lake, California, *J. Geophys. Res.* 92, 14567–14580, 1987.
- Watson, A.J., and Liddicoat, M.I. Recent history of atmospheric trace gas concentrations deduced from measurements in the deep sea: Application to sulphur hexafluoride and carbon tetrachloride, *Atmos. Environ.* 19, 1477–1484, 1985.
- Watson, A.J., Upstill-Goddard, R.C., and Liss, P.S. Air-sea gas exchange in rough and stormy seas measured by a dual-tracer technique, *Nature* 349, 145–147, 1991.
- Whitmore, A., and Corsi, R.L. Measurement of gas-liquid film mass transfer coefficients for volatile organic compounds in sewers, *Environ. Prog.* 13(2), 114–123, 1994.
- Wu, J. Laboratory studies of wind-wave interactions, *J. Fluid Mech.* 34, 91–112, 1968.
- Yu, S.L., Hamrick, J.M., and Lee, D.-S. 1983. Wind effects on air-water oxygen transfer in a lake. Presented at the International Symposium on Gas Transfer at Water Surfaces, June 13 to 15, Cornell University, Ithaca, NY.
- Yu, S.L., T.J. Tuffey, and D.-S. Lee. 1977. *Atmospheric reaeration in a lake*. WRRR Report A-041-N.J., Rutgers University, New Brunswick, NJ.