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Atmospheric Oxygen Exchange in the Hudson River: Dome Measurements and Comparison With Other Natural Waters

ROXANNE MARINO
ROBERT W. HOWARTH
Section of Ecology and Systematics
309 Corson Hall
Cornell University
Ithaca, New York 14853

ABSTRACT: The measurement of metabolism using diel free-water oxygen techniques requires the estimation of atmospheric oxygen exchanges. We measured such exchange on nine different occasions in the freshwater, tidally-influenced Hudson River estuary using a floating dome technique. We also analyzed previously published data on the exchange of a variety of gases measured in lakes, estuaries, and open ocean waters using a wide variety of techniques. Data were expressed as a "transfer velocity" and normalized to an exchange of oxygen at 20°C. Considered together, these data indicate a significant predictive relationship when the natural log of transfer velocity is regressed with measured wind speed ($r^2 = 0.55$; $p = 0.0001$). The influence of wind was particularly pronounced in estuaries and in lakes. Data from open-ocean waters showed much less influence of wind, probably because surface turbulence in these deeper waters can be temporally and spatially decoupled from wind. Our Hudson data agreed well with data collected in other systems. In general, data from estuaries—including the Hudson—indicated slightly higher transfer velocities at any given wind speed than do data from lakes (although this difference was less pronounced for our Hudson data than for other estuaries). The difference may result from some interaction of wind and tidal currents, or it may reflect a bias in the dome method of measurements; all of the estuarine data were collected using the dome approach, while the majority of the lake data were determined using an added tracer. If the dome method actually gives a biased, high estimate of oxygen flux, this is in contradiction to previous criticisms of this method that domes may underestimate fluxes by blocking wind at the water surface. We have used the regression of the natural log of transfer velocity versus wind speed developed here to estimate respiration in the Hudson estuary from diel changes in dissolved oxygen. To allow for possible biases in technique and for measurement error, we estimated 95% confidence limits around the regression. Estimates of respiration in the Hudson determined using the upper and lower 95% confidence limits are 30% higher and 12% lower than that determined when using the best-fit regression. An independently-constrained carbon budget for the tidally-influenced, freshwater Hudson River estuary indicates that respiration rates cannot be much higher than our mean estimate as calculated using the linear regression of the gas transfer and wind data to correct for air-water oxygen exchange. Gas transfer in natural systems is difficult to measure and is controlled by many interrelated physical factors. In the absence of extensive, system-specific field studies, the regression presented here should be useful in estimating atmospheric oxygen exchange in other estuarine or riverine ecosystems which are relatively deep and wide.

Introduction

In the free-water approach for estimating metabolism rates, decreases in dissolved oxygen overnight and increases in dissolved oxygen during daylight hours are used to estimate whole-ecosystem respiration and gross primary production. This technique is a powerful tool, in part because the measurement of these metabolic processes is integrated over space and time. The free-water approach can be particularly useful in turbulent estuaries and rivers since a variety of "bottle effects"—such as reduced turbulence, altered light fields, or excessive alteration of chemical parameters—can greatly affect metabolism rates in enclosed bottles (Nixon et al. 1979; Kemp and Boynton 1980; Richey et al. 1990, 1991; Howarth et al. 1992).

Although several variations of the free-water method have been used (Odum 1956; Edwards and Owens 1962; Copeland and Duffer 1964; Nixon and Oviatt 1972; Kemp and Boynton 1980; Lehman and Naumoski 1986; Oviatt et al. 1986; Howarth et al. 1992), all of them require an estimate of oxygen exchange between atmosphere and water body. Some workers have assumed that this atmospheric flux is a constant function of the oxygen partial pressure in the water column (Kemp and Boynton 1980; Lehman and Naumoski 1986),

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but this assumption can sometimes result in substantial error in estimating metabolism rates (Howarth et al. 1992).

In natural systems, it is generally accepted that the primary controls on the transfer of oxygen and other low-solubility gases are either current and bottom topography, which generate turbulence due to bottom shear, or wind velocity, which generates turbulence due to surface wind shear and wave formation (Bennett and Rathbun 1972; Jirka and Brutsaert 1984; Liss and Merlivat 1986). In relatively deep waters, surface turbulence is generated largely by wind shear (Dillon et al. 1981; Jirka and Brutsaert 1984; MacKenzie and Leggett 1991), and so it is no surprise that several studies in lakes and open ocean waters have demonstrated that gas exchange with the atmosphere is related to wind velocity (Broecker et al. 1980; Smethie et al. 1985; Wanninkhof et al. 1985, 1987; Frankignoulle 1988; Upstill-Goddard et al. 1990; Wanninkhof 1992). In shallow, flowing waters, turbulence even at the surface can be dominated by the interaction of the current with bottom topography (Roberts 1984), and gas exchange in streams and small rivers is usually modelled as a function of flow-generated turbulence (O'Connor and Dobbins 1958; Bennett and Rathbun 1972; O'Connor 1984; Roberts 1984). Physical controls on gas transfer in estuaries and in large rivers fall somewhere between these two extremes, and both wind- and hydrologically-induced turbulence can be important, depending in part on the depth and width of the system and in part on the velocity of tidal or river flows (Jirka and Brutsaert 1984; O'Connor 1984).

We have used a diel free-water oxygen method for measuring respiration rates in the tidally-influenced, freshwater portion of the Hudson River estuary, a 130-km reach (Howarth et al. 1992). As part of this study, we estimated atmospheric exchanges of oxygen. Studies in both the Narragansett Bay (Roques 1985) and San Francisco Bay (Hartman and Hammond 1984) estuaries concluded that wind is the major determinant of atmospheric oxygen flux in these systems. On the other hand, studies in large rivers have tended to assume that oxygen flux is a result of current or flow shear and is related to parameters such as discharge (Schurr and Ruchti 1977; Hartman and Hammond 1984; Devol et al. 1987; but see also Jirka and Brutsaert 1984). Jirka and Brutsaert (1984) suggested that wind should have a major influence on oxygen exchange in a large river or estuary, but their analysis, as well as that of O'Connor (1984) and the data of Devol et al. (1987) in the Amazon, could not rule out an interaction between wind and current.

We experimentally determined gas transfer velocities in the freshwater portion of the Hudson River by measuring the flux of oxygen into the headspace of a floating dome (Copeland and Duffer 1964; Kemp and Boynton 1980; Hartman and Hammond 1984; Roques 1985; Oviatt et al. 1986; Devol et al. 1987). This approach has been criticized primarily because the dome covers the water surface and may reduce near-surface turbulence generated by wind shear, and therefore gas exchange (Broecker and Peng 1984; Liss and Merlivat 1986). However, in systems such as those with a very large fetch, the near-surface turbulence that is most important in controlling gas transfer may be generated over a fairly large spatial scale through dissipation of stored wind energy as waves (Jähne et al. 1987). If the surface area of the dome is small relative to the scale on which the turbulence is generated, and as long as the dome does not disrupt the surface turbulence beneath it, the gas exchange rates measured should reasonably estimate those of the undisturbed surface (Broecker and Peng 1984). This technique also allows atmospheric flux measurements to be taken on a time scale of hours, providing the most appropriate information for use with the diel free-water method.

A variety of other approaches have been used to estimate air-water gas transfer rates in natural waters, all of which have both advantages and errors associated with their use. As a preface to our data and synthesis, we briefly describe these approaches and discuss their usefulness for understanding O_2 flux in a system such as the Hudson. The applicability of each method is dependent on several factors, including the morphometry and openness of the water body, the desired time scale of gas exchange information, and the resources available to gather field data. For example, modeling fluxes of radon is a good approach for estimating seasonal average gas fluxes in open ocean waters (Broecker and Peng 1984) and has been used by several workers (Broecker et al. 1980; Elsinger and Moore 1983; Hartman and Hammond 1984; Roether and Kromer 1984; Smethie et al. 1985). This approach is not well suited to continentally-influenced systems such as estuaries or rivers because of the difficulty in estimating the radon source terms, and in particular the flux of radon from the sediments (Broecker and Peng 1984). Further, the method is relatively insensitive and requires a major field effort with measurements taken over relatively long time periods (Roether 1986). In order to detect a relationship between wind speed and gas transfer, the wind velocity should be fairly constant for a period equal to several half-lives of radon, or several weeks (Deacon 1981; Liss 1983; Broecker and Peng 1984; Roether and Kromer 1984).

Measurements of both naturally occurring and bomb-produced ^{14}C have been used to estimate atmospheric carbon dioxide exchange in the oceans (Broecker and Peng 1974, 1984) and in lakes (Broecker et al. 1980; Peng and Broecker 1980). This approach yields an estimate which is averaged over very long periods of time (years and longer) and over entire oceans (Broecker and Peng 1984; Liss and Merlivat 1986; Wanninkhof 1992). While this is desirable for understanding the role of the world's oceans as carbon sinks, this averaging provides no information on gas fluxes over short periods of time such as is desirable for estimating metabolism from diel oxygen data.

Several workers have measured air-water gas exchange as the rate of evasion of added tracers such as radon, sulfur hexafluoride, propane, freon, or methyl chloride from the water column (Emerson 1975; Hesslein et al. 1980; Liss 1983; Duran and Hemond 1984; Holley and Yotsukura 1984; Jirka and Brutsaert 1984; Wilcock 1984; Wanninkhof et al. 1985, 1987; Upstill-Goddard et al. 1990). This is a powerful method for estimating atmospheric fluxes in relatively discrete and well-bounded water bodies such as small lakes or small rivers where the tracer can be easily followed, and provides information on a daily time scale. However, it would be difficult and field-intensive to apply this approach in a large and open system such as the tidal Hudson River, and we are unaware of any attempt to use it on any rivers or estuaries having a width greater than 90 m (Holley and Yotsukura 1984). The spatial non-uniformity of the tracer plume requires sophisticated two-dimensional sampling and analysis of both the added tracer gas and a nonvolatile dye (Holley and Yotsukura 1984).

The last commonly used approach to estimating air-water gas exchange—mass balances for carbon dioxide or oxygen—requires independent estimates of all factors other than atmospheric exchange that are affecting the concentrations of these gases. Usually, this requires measuring metabolism rates in bottles (Holley and Yotsukura 1984; Devol et al. 1987). Since our interest in the Hudson was to estimate metabolism from free-water oxygen changes without relying on rate measurements in bottles (Howarth et al. 1992), we wished to avoid this approach. Schurr and Ruchti (1977) avoided this problem in their study of streams and small rivers by modeling primary production as an idealized function of light. Their approach relies on several assumptions, some of which are probably applicable to the Hudson (i.e., light limitation) and others which may not be (uniformity in the river; lack of longitudinal diffusion).

This paper presents our work on the use of the floating dome method for estimating gas transfer rates in the tidally-influenced, freshwater Hudson River estuary. We also summarize a wide variety of flux measurements of several gases made in other estuaries and in lakes and ocean waters and compare these with our oxygen flux data. We have modeled the data in terms of the influence of wind on atmospheric flux since both previous estuarine studies (Hartman and Hammond 1984; Roques 1985) and the analysis of Jirka and Brutsaert (1984) indicated that wind was likely to be the major physical control on air-water gas exchange in the Hudson. We postulated that a strong influence of bottom-induced turbulence on gas flux would show up as a major deviation from the predicted relationship between wind speed and gas transfer rate found in typically wind-driven systems such as lakes.

Methods

Field

We measured oxygen fluxes into a floating dome in the tidally-influenced, freshwater portion of the Hudson River estuary just south of Kingston, New York. This is the midpoint of the 40 km stretch of river in which we have measured respiration by the diel free-water method (Howarth et al. 1992). Tidal amplitude in this section of the river ranges from 0.8 m to 1.4 m and the mean tidal current velocity is 0.38 m s^{-1} (Limburg et al. 1986), although currents of over 2 m s^{-1} regularly occur at peak tidal flows in the main channel (personal observation). This part of the river is typical of the 40 km stretch studied by Howarth et al. (1992), with an average width of approximately 1 km and an average depth of 10 m; it is completely mixed with no vertical stratification. The river is generally oriented in a north-south direction.

For a dome we used a 42-cm diameter stainless steel bowl fitted with two gas tight ports for the introduction and removal of gases, and one gas-tight fitting at the top for an oxygen electrode. The headspace volume was 15.7 l and the surface area of water covered by the dome was 0.139 m^2. A six-inch collar of flexible closed-cell foam attached to the bottom edge of the dome provided flotation and balanced the weight of the dome plus oxygen probe so that the whole apparatus floated well on the surface. The dome was covered with wet cheesecloth to keep it from heating up. Constant temperature inside the dome over the period of measurement is essential in order to accurately calculate gas flux rates using this technique (Holley and Yotsukura 1984; Belanger and Korzun 1991).

For each run, we measured the flux of oxygen into the dome after purging the head space down to an oxygen partial pressure of 0.04 atm or less with nitrogen gas. The oxygen concentration in

the water was within 10% of atmospheric saturation for all of our runs, resulting in a large oxygen gradient from the water to the atmosphere under the dome. Oxygen partial pressure measurements in the dome were usually taken at 2-min intervals for time periods ranging from 30 min to 90 min, depending on the constancy of river conditions. This experimental design allowed us to calculate the oxygen flux rate from a linear increase in oxygen partial pressure in the dome over time since the duration of the experiment was short relative to the turnover time of the dome atmosphere. All oxygen measurements were made with YSI model 58 oxygen meters and polarographic electrodes calibrated with a specially designed chamber to maintain a constant temperature at ambient field levels. We also measured surface water oxygen, temperature, and wind velocity continuously during the flux measurement period. Wind velocity was measured at a height of 2 m off the water surface with a Qualimetrics model F581-B water current meter calibrated in the tilting wind-water tunnel at the DeFrees Hydraulics Laboratory at Cornell University. Temperature was measured both by the YSI probe and with a mercury thermometer. Tidal stage and current were noted but not quantified.

We deployed our dome for a total of nine runs on six different days in late July 1987, May through October 1988, and October 1991. Runs started in the main channel of the river and the boat and dome drifted freely. We generally drifted anywhere from less than 50 m to over 1 km during a run, depending on the wind and current velocities. We felt it was important that the dome drift at the same rate as the boat because prevous workers, using the dome method in a tidal estuary, found that securing a floating chamber to a fixed point resulted in artificially high gas fluxes due to increased turbulence generated by the current (Hartman and Hammond 1984). We deployed a sea anchor from the boat to facilitate matching the drift velocity of the boat and dome. The dome remained floating on the water surface without letting atmospheric oxygen into the headspace during all of our runs (wind gusts up to 8 m s^{-1}).

Data Analysis

Gas transfer across an air-water interface is driven by a partial pressure difference between the air and water, modified by a factor characterizing the rate of transfer due to resistances in the air and water phases (Kanwisher 1963; Liss 1973; Liss and Merlivat 1986). This process can be described by the equation:

$$F = k\,[C_w - (P_a \times K_h)] \qquad \text{Eq. 1}$$

where F is the gas flux in units of mass per surface area of water per time and k is the transfer coefficient (also called the transfer or piston velocity). The term $[C_w - (P_a \times K_h)]$ defines the gas gradient between water and atmosphere driving the flux; within this term, C_w is the molar concentration of gas in the water solution, P_a is the partial pressure of gas in the atmosphere, and k_h is the Henry's Law constant, which relates the partial pressure of a gas in air to its concentration in solution at equilibrium. For sparingly soluble gases, the transfer velocity, k, characterizes the resistance to gas transfer in the water phase and is a function both of the molecular diffusion of the gas and of turbulent mixing processes in the very near-surface water (Liss and Slater 1974; Roether 1986; Jähne et al. 1987). The gas transfer rate that we calculate from field or laboratory measurements of gases of environmental interest, such as O_2 or CO_2 is specific to the molecular diffusivity of the gas (D), the temperature, and the viscosity of the water phase (Smith 1985; Liss and Merlivat 1986; Wanninkhof 1992). In addition, physical parameters such as wind velocity, fetch and morphometry of the water body, and current may influence gas transfer.

In order to compare our data with measurements made in other natural systems, we expressed all the gas transfer velocities in terms of one gas (oxygen) at a common temperature (20°C). There are three predominant models of air-water gas exchange that can be used to do this. The mathematically and conceptually simplest model of gas transfer across an air-water interface describes the transfer rate as being controlled by molecular diffusion through a stagnant film of some thickness (usually 20 μm to 600 μm) above a well-mixed water layer and in contact with a well-mixed atmosphere (Whitman 1923; Broecker and Peng 1974). In this model, k is a function of the molecular diffusivity of the gas to the first power. A second model, the surface renewal model, modifies the stagnant film model by allowing for periodic turnover of the film with water from the well-mixed bulk layer (Danckwerts 1970). In this model, k is proportional to the molecular diffusivity of the gas to the ½ power. Because the surface film turnover rate is extremely difficult to measure in nonlaboratory situations, this model is not often used when considering natural system gas transfer (Liss and Merlivat 1986). Lastly, the boundary layer models described by Deacon (1977) and Ledwell (1984) are derived from considerations of heat and momentum transfer and take into account the effect wind-shear stress has on the size of the interfacial boundary layer, which ultimately controls gas transfer by molecular diffusion (Liss 1973; Liss and Merlivat 1986). In these models, the gas transfer coefficient is related to the

ratio of the water viscosity to the molecular diffusivity (or Schmidt number) to either the $-\frac{2}{3}$ or $-\frac{1}{2}$ power. The Schmidt number to the $-\frac{1}{2}$ power (that is $D^{1/2}$) is considered to be the more accurate for characterizing water surfaces where waves are present but not breaking into bubbles (Jähne et al. 1984, 1987; Liss and Merlivat 1986). Other researchers studying gas transfer and stream reaeration have found exponents for D ranging from ½ to 1 (Dobbins 1956; Tsivoglou 1967; Bennett and Rathbun 1972).

We used both the stagnant film and boundary layer models to normalize literature values of k given for field measurements of various gases to oxygen gas at 20°C. The molecular diffusivities for the different gases used in the literature studies (O_2, CO_2, SF_6, Rn) were calculated as a function of temperature using the modified Wilke-Chang equation as in Hayduk and Laudie (1974). The molecular viscosity of water was determined for fresh waters using the National Bureau of Standards data (Weast 1974) and corrected if necessary for salinity using the relationship in Sverdrup et al. (1942). Although we did not have them available for our calculations, the temperature and salinity corrections to the Schmidt number for most gases of environmental interest are tabulated in Wanninkhof (1992).

In order to look for relationships between wind speed and the gas transfer coefficient, we normalized wind velocities measured in the field to a common height of 10 m assuming a logarithmic wind profile and drag coefficients of 1.5×10^{-3} for oceanic and large estuarine systems (Liss and Merlivat 1986) or 1.3×10^{-3} for lakes (Wanninkhof et al. 1987). We only used literature data sources that included on-site wind data taken over the same time period as the gas transfer measurements.

For our comparative analysis, we used studies in large estuaries (Hartman and Hammond 1984; Roques 1985), lakes (Broecker et al. 1980; Roques 1985; Wanninkhof et al. 1985, 1987; Upstill-Goddard et al. 1990), and open ocean waters (Broecker et al. 1980; Smethie et al. 1985; Frankignoulle 1988). We did not use studies from streams and small rivers where turbulence from bottom shear rather than from wind stress is likely to be the dominant control on gas exchange. Our literature compilation includes data on a variety of gases collected using several different techniques (domes, tracer addition, and radon deficits). We did not use gas transfer estimates obtained with the radiocarbon method because the resulting gas transfer coefficient is an average over years to decades and large (whole ocean) spatial scales. Such data provide constraints on the gas transfer coefficients determined using other methods, but do not provide any information on the relationship between gas transfer rates and wind velocity on the time scale necessary for use with the diel free-water oxygen technique for measuring metabolism (Liss and Merlivat 1986; Roether 1986).

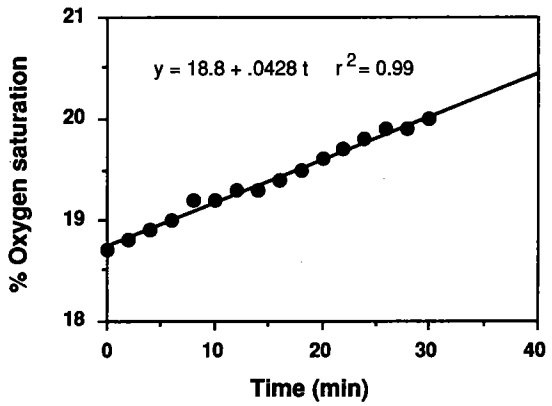

Fig. 1. Change in oxygen concentration over time in the headspace of the floating dome after purging with nitrogen gas. These data are from the October 23, 1991, run on the Hudson River near Kingston, New York. Average wind speed over the measurement period (corrected to 10 m) was 4.2 m s^{-1}.

Results and Discussion

Hudson River Oxygen Diffusion Measurements

Figure 1 shows the increase in oxygen over time in the headspace of the floating dome during one typical deployment on the Hudson River. The oxygen mass flux is calculated from the measured rate of increase of oxygen in the dome atmosphere over time. The diffusion gradient is calculated as the difference between the initial oxygen measurement in the dome and the oxygen concentration measured just below the water surface during the measurement period (Eq. 1). Occasionally, we had problems maintaining constant temperature in the dome, resulting in a nonlinear increase in the oxygen partial pressure in the dome. We only used data from runs when the dome temperature fluctuated by no more than 1.5°C. We also discarded data from runs where the oxygen concentration in the surface water changed considerably over the time of deployment, as sometimes occurred when we drifted into macrophyte beds, or when the wind velocity was highly variable.

We made flux measurements at several different times of the year under different wind and river conditions, with water temperatures ranging from 12.6°C to 26.6°C and average wind speeds ranging from 0.56 m s^{-1} to 6.5 m s^{-1}. The wind speeds given for each flux measurement represent averages of the wind speed measurements taken at 2-min

TABLE 1. Oxygen transfer velocities measured in the Hudson River near Kingston, New York, using the floating dome technique. Measured transfer velocities (k) are converted to oxygen at 20°C and wind speeds are expressed at 10 m as discussed in text.

Date	Temperature (°C)	Wind Speed (m sec^{-1})	k_{O_2}, 20°C (cm h^{-1})
July 31, 1987	26.6	5.9	17.4
	26.5	6.5	24.6
May 20, 1988	16.6	3.4	8.64
July 8, 1988	24.0	1.8	4.67
October 19, 1988	12.6	2.7	6.53
October 22, 1991	13.7	0.56	3.00
	13.7	1.9	5.57
	13.7	4.8	23.4
October 23, 1991	13.7	4.2	13.6

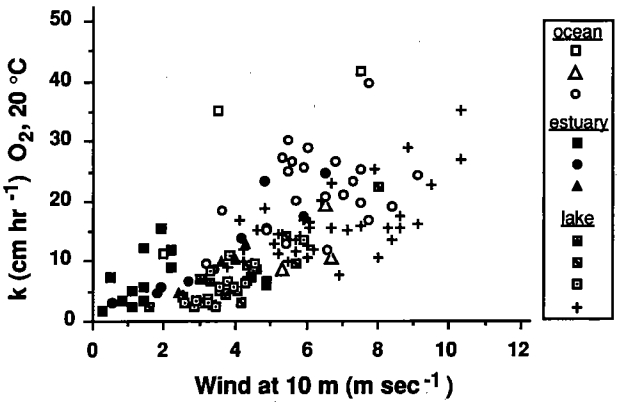

Fig. 2. Plot of our Hudson River estuary gas transfer velocity measurements (solid circles) along with other literature data on gas exchange in natural systems, plotted as a function of wind speed. Other estuarine data (solid symbols) are squares = San Francisco Bay (Hartman and Hammond 1984); triangles = Narragansett Bay (Roques 1985). Ocean data (open symbols) are squares = North Sea (Frankignoulle 1988); triangles = open ocean measurements (Broecker et al. 1980); circles = tropical Atlantic (Smethie et al. 1985). Lake data sources and symbols are squares with cross = Experimental Lakes Area data (Broecker et al. 1980; Roques 1985); squares with diagonal line = Rockland Lake (Wanninkhof et al. 1985); squares with dot = Mono and Crowley Lakes (Wanninkhof et al. 1987); and crosses = Siblyback Lake and Dozmary Pool (Upstill-Goddard et al. 1990). All literature values of k were normalized to oxygen gas at 20°C using assumptions based on the stagnant film model of gas exchange as discussed in the text.

intervals during the time the dome was deployed. Table 1 summarizes our estimates of the transfer velocity for oxygen measured in the Hudson estuary under a variety of wind conditions. The transfer velocities measured (corrected to 20°C) showed a nonlinear dependence on wind, increasing more rapidly than wind speed. The range of values we measured in the Hudson spans approximately an order of magnitude, from 3 cm h^{-1} to 24.6 cm h^{-1}, and encompassed most of the range of values reported for all other systems.

Comparison With Other Published Studies on Air-Water Gas Exchange

Figure 2 illustrates gas transfer velocities for our Hudson data and for a variety of published field studies in other systems plotted as a function of wind velocity. Our data, shown as closed circles, fit well within the range of field measurements of the gas transfer coefficient in other systems. We did not measure wind speeds greater than 10 m s^{-1} during any of our field measurements, and have not included any literature data with wind speeds over 10 m s^{-1} because this regime is usually characterized by breaking waves and bubble formation, which greatly increases gas transfer (Liss and Merlivat 1986). Such conditions were also not encountered during our field measurements of diel oxygen change (Howarth et al. 1992), and so we need not consider oxygen exchange with the atmosphere under high wind conditions when applying a diffusive flux correction to estimate metabolism. While there is a fair amount of noise inherent in field measurements, we can see a trend in these data for k to increase slowly at lower wind speeds and then more quickly at higher ones.

Several laboratory studies using wind tunnels have shown that there is a relationship between gas transfer and wind due to wind-induced surface turbulence and the generation of waves (see reviews by Liss 1983; Smith 1985; Liss and Merlivat 1986; Jähne et al. 1987). Despite the many differences in equipment and experimental design, a general pattern emerges from these studies, with k increasing slowly with wind speed up to 2 m s^{-1} to 5 m s^{-1} and then much more rapidly (Liss 1983; Liss and Merlivat 1986). The exact formulation of this dependence is somewhat specific to the experimental conditions, and several different functional relationships have been suggested for the dependency of the water-side transfer coefficient (k) on wind velocity. For example, several investigators have concluded that k increases as a power of wind velocity, such as wind squared (Downing and Truesdale 1955; Kanwisher 1963; Hoover and Berkshire 1969; Liss 1973; Jähne et al. 1979), while others believed the dependence was best expressed as a series of linear relationships over discrete ranges of wind speed, with break points in slope generally around 2 m s^{-1} to 4 m s^{-1} and again at 10–12 m s^{-1} (Broecker et al. 1978; Liss and Merlivat 1986). In a synthesis of several laboratory studies, Smith (1985) found that the relationship between gas transfer (as indicated by stagnant film thickness) and wind speed normalized to 10 m was best described using an exponential function.

While wind tunnel studies generally try to simulate environmental conditions as closely as pos-

sible, it is problematical to combine studies using different wind tunnels into one predictive model because the wave field developed within a given tunnel when a specific wind velocity is applied is quite dependent on the geometry (circular, linear) and dimensions of that tunnel (Liss 1983; Liss and Merlivat 1986; Jähne et al. 1987). Also, it is difficult to extrapolate laboratory wind tunnel studies to the field because of the large differences in fetch and average water depth, which can have a significant effect on the scale of the near-surface turbulence generated by wind shear (Jirka and Brutsaert 1984; Jähne et al. 1987). We have therefore confined our synthesis to field-collected data in systems where wind-controlled gas transfer might be expected for comparison with our Hudson river diffusive flux data, and to look for a general functional relationship for the oxygen transfer coefficient as a function of wind velocity as suggested by wind tunnel studies.

Synthesis

We modeled the relationship between transfer velocity and wind speed considering both the different theoretical models of gas transfer used to convert k to common units (see METHODS) and the different functional relationships as suggested by the laboratory studies. We started by using the simplest model of air-water gas exchange, the stagnant film model, to convert all of the natural systems data from the literature into common units of oxygen gas at 20°C (Fig. 2). We then tried to fit curves to the transfer velocity-wind speed data set as suggested by the general distribution of the data in Fig. 2 and several of the laboratory wind tunnel studies discussed above. We chose not to model the gas transfer velocity as three linear functions of wind speed as suggested by Liss and Merlivat (1986) because of the difficulty in choosing a discrete break point between the smooth and rough wind regimes. Even under controlled, laboratory conditions the point at which capillary waves are formed and a rough surface regime starts is difficult to define, and wind velocities of 5 ± 3 m s^{-1} have been used (Liss and Merlivat 1986; Jähne et al. 1987).

We next considered using a single function to describe the entire range of natural systems data. Again going back to wind tunnel experiments (Kanwisher 1963; Hoover and Berkshire 1969; Liss 1973; Broecker et al. 1978) and the exponential model suggested by Smith (1985), we found that modeling the natural logarithm of the transfer velocity as a linear function of wind speed explained 91% to 97% of the variability in those data. Figure 3A shows field data from natural systems transformed in this way; the dark circles are our Hudson data and the open circles are literature data. Considering the range of systems included and the different measurement techniques used, this model gives a good fit, with 55% of the variability in the combined data set explained by the relationship, and is highly significant ($p = 0.0001$). Transfer velocity was also modeled as a function of wind speed squared, and a linear regression of the square root of k versus wind speed gave a fit very similar to the log-transformed model ($r^2 = 0.53$ and 0.55, respectively; plot not shown). The actual values predicted for k at a given wind speed differed according to which regression was used, with the ln k versus wind speed function resulting in up to 15% lower predicted gas transfer rates for wind speeds below 7.5 m s^{-1} and 19.5% higher rates at the maximum wind speed of 10 m s^{-1}. As empirical estimates of gas transfer and wind speed in natural systems usually have uncertainties on the order of

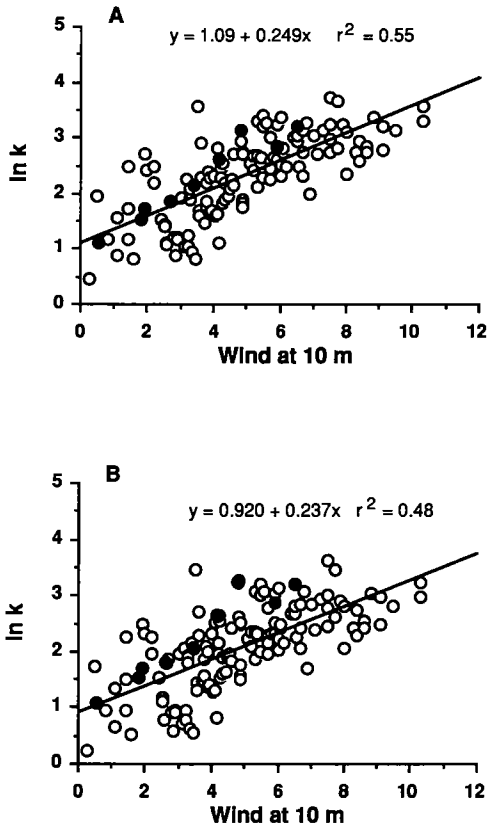

Fig. 3. (A). Plot of the natural logarithm of the gas transfer velocity data shown in Fig. 2 as a function of wind speed at 10 m. Solid circles are our Hudson River data, open circles are all other natural systems data. Units are m s^{-1} for wind speed and cm h^{-1} for k; solid line is the linear regression fit. (B). Similar to (A) except that boundary layer model assumptions with a Schmidt number exponent of $-½$ were used to normalize all literature k values to oxygen gas at 20°C instead of the stagnant film model assumptions used in Figs. 2 and 3A.

±30% associated with them (Broecker and Peng 1984; Wanninkhof et al. 1987; Wanninkhof 1992), and wind tunnel data are difficult to directly extrapolate to the field, it is not possible to infer which functional relationship better characterizes the influence of wind on gas transfer in lake, ocean, and estuarine systems. The natural log transformation allows for a slightly wider range of predicted gas transfer values, and so we chose to use it to develop a predictive model for the dependence of oxygen exchange in the Hudson River on wind speed.

In order to address the related question of which model of gas exchange as a function of molecular diffusivity to apply to both our Hudson field data and the published literature data for natural systems, we repeated the analysis described above using the boundary layer model with a Schmidt number exponent of ½ (Fig. 3B) instead of the stagnant film model. Both regressions are quite similar, with coefficients of determination of 0.55 and 0.48, respectively (Figs. 3A, B), and slopes which are not significantly different ($p = 0.52$). Hence, the choice of a specific formulation for the liquid phase resistance to gas tranfer does not seem to be a dominant factor in describing the dependence of gas transfer on physical parameters such as wind speed. This is not surprising because as Broecker and Peng (1984) point out, the molecular diffusivities of oxygen and all of the other nonreactive gases of environmental interest differ at most by a factor of 2 over the 0°C to 25°C temperature range, which would result in a maximum conversion error of around 40%—an error similar to that associated with field measurements of gas transfer. For our further analyses, we have used the mathematically simpler stagnant film model (Fig. 3A).

Comparison of Gas Transfer Velocities—Effects of Method and System

Figure 4 compares the transfer velocities from the literature studies and from our Hudson data as a function of both the type of system studied and the method used to determine fluxes. In Fig. 4A, we have shown all of the data plotted as in Fig. 3A but with the addition of 95% confidence limits on the regression line (SAS Institute Inc. 1985). The great majority of the data, including all of ours from the Hudson River, fall well within the confidence limits. The regression line and the 95% confidence limits for the combined field and literature data are repeated in Figs. 4B, 4C, and 4D, illustrating the relationship for data from estuaries, open oceans, and lakes, respectively. Note that all of the data in estuaries have been obtained using the floating dome method, a majority of the open ocean data come from radon deficit studies, and a majority of the lake data come from SF_6 tracer studies. Considering the different types of systems studied, the different methods used, and the experimental error inherent in field measurements of both gas exchange and wind speed (Broecker and Peng 1984; Liss and Merlivat 1986; Wanninkhof 1992), we find the amount of variability in the data remarkably low.

The gas transfer data from lakes generated using the SF_6 tracer method should be free of many of the potential measurement or interpretation biases introduced by either the dome or radon deficit methods and thus fairly accurately represent the gas transfer-wind relationship. The lake SF_6 data show a strong relationship with wind, and interestingly, the few lake data generated using the dome method are basically indistinguishable from the SF_6 data (Fig. 4D). The estuarine data can be criticized since they are all based on dome measurements (Broecker and Peng 1984; Liss and Merlivat 1986). Nonetheless, they too show a strong relationship with wind (Fig. 4B). Inspection of the data suggests a slight tendency for the estuarine data to fall above the regression line for the entire data set, particularly at winds speeds above 2 m s^{-1}, while the lake data on average tend to fall slightly below the regression line. Further, the dome data appear to have a steeper slope than do data collected by other methods, although this is less pronounced for our dome data from the Hudson River. That is, for a given wind velocity, the data suggest slightly higher gas transfer velocities—and therefore atmospheric oxygen fluxes—in estuaries than in lakes.

The somewhat greater effect of wind and higher gas fluxes in estuaries as compared to lakes, if real, may simply reflect a bias in the predominant methods used—domes versus SF_6 tracer—although as noted above, the dome data within lakes fit the pattern generated by the SF_6 tracer data quite well. We believe that if there is a methodological bias, the problem is more likely to reside with the dome method than with the SF_6 tracer method. That is, the dome may slightly overestimate fluxes in estuaries. This is exactly the opposite of what the previous criticisms of this method have suggested—that the reduction of the wind-water interaction by the dome leads to artificially reduced surface turbulence beneath it and artificially low rates of gas transfer (Broecker and Peng 1984; Liss and Merlivat 1986). Comparisons of dome measurements made in conjunction with an oxygen-budget approach in the Amazon River (Devol et al. 1987) and with a radon-budget approach in San Francisco Bay (Hartman and Hammond 1984) also found that the dome data showed higher values for the gas transfer velocity, although in both cases

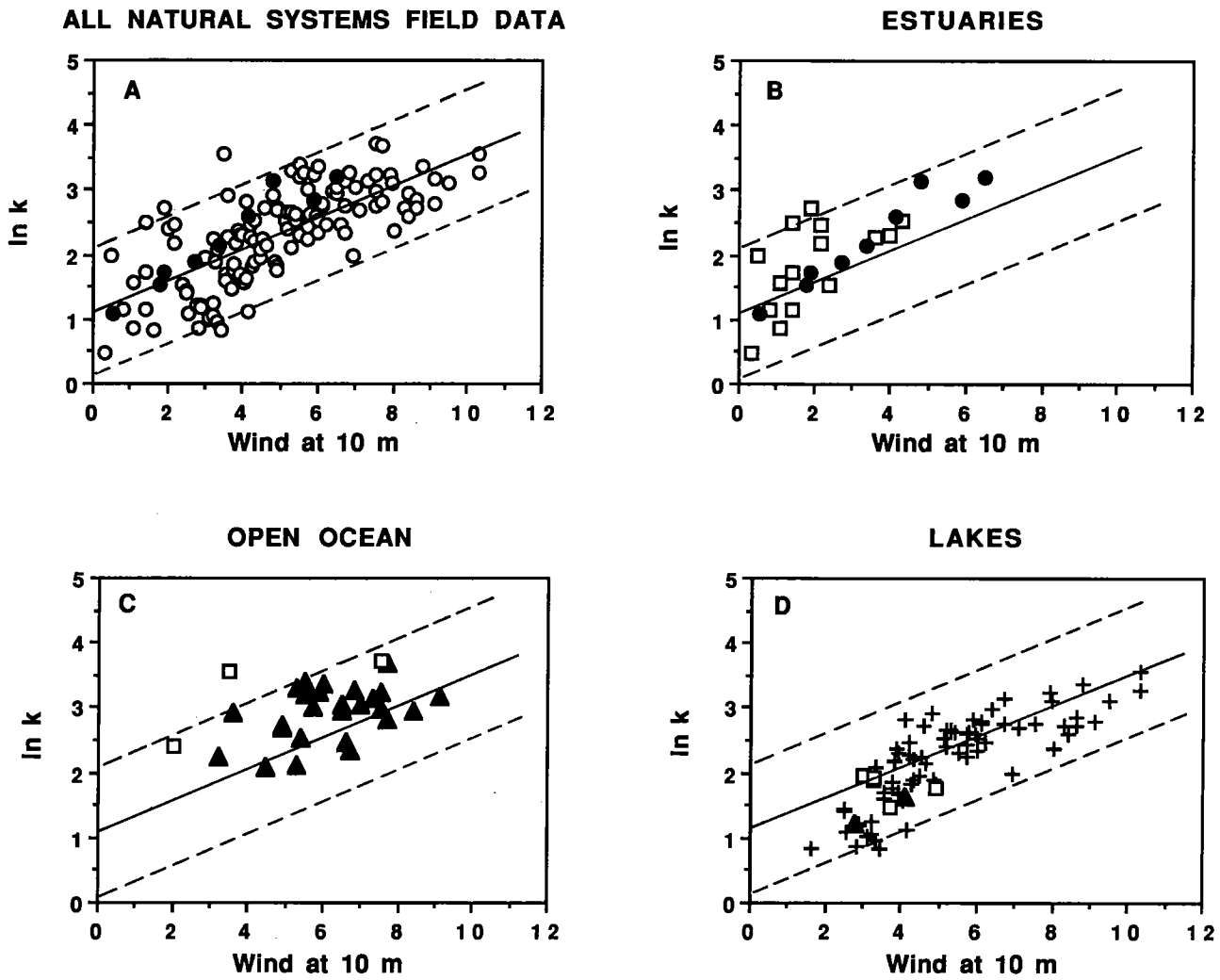

Fig. 4. Solid line is the linear regression line for all of the natural systems ln k versus wind data; dashed lines are 95% confidence intervals for the regression. Solid circles are our Hudson River dome measurements; open squares are all other dome measurements. Solid triangles are measurements made using radon deficit method; and crosses are measurements made using SF_6 as an introduced tracer. All units are the same as in Figure 3. Plot of all natural systems data (A); plot of the subset of all natural systems gas transfer data taken only in estuaries (B); data taken only in oceans (C); and data only in lakes (D).

the differences could be ascribed either to a bias with the dome or to errors in the budgeting approaches. If the dome method does lead to an artificially high estimate of gas flux, it may be a result of the enclosure creating greater surface turbulence beneath it as it moves with the waves. We have watched the behavior of a clear dome (of design similar to that used for our Hudson measurements) in the tilting wind-water tunnel at the DeFrees Hydraulics Laboratory and have observed that larger standing waves are sometimes generated inside the dome when waves are present, perhaps because the edge of the dome extends slightly below the water surface as it moves up and down with the waves.

On the other hand, the dome data may not be biased and the higher gas fluxes in the estuarine systems may reflect some influence of tidal currents interacting with wind to increase surface turbulence in the estuaries (Jirka and Brutsaert 1984). However, Hartman and Hammond (1984) found no influence of tidal current velocity on gas exchange in San Francisco Bay. Also, some of our data in the Hudson were collected at times of high tidal current flow, whereas there was little current at other times; despite this, the majority of our data fall near the regression line relating transfer velocity to wind for the entire data set (Fig. 3A), suggesting little influence of current. We believe either that the floating dome is a reasonable method for measuring oxygen exchange in estuaries such as the Hudson because wind-induced turbu-

lence occurs over a larger scale surface interaction than that of the dome diameter, and thus exclusion of the wind from the water-dome atmosphere is of little consequence in controlling gas fluxes; or that the extent to which a dome blocks wind is counteracted by a tendency for the dome to interact with wind and currents to generate increased turbulence in the surface layers of the water within the dome, perhaps resulting in a slight overestimate of gas exchange.

The gas transfer velocities from studies in open ocean waters (Fig. 4C) tend to show less of a relationship of increasing k with wind speed than do those from either estuaries or lakes. As with the estuarine data, the open ocean data tend to fall slightly above the regression line for the entire data set, suggesting higher gas transfer velocities for a given wind speed relative to the overall pattern. In contrast to the estuarine data, the slope for the ocean data set appears to be much less steep and the modeled k-wind dependence is much weaker. In part, these differences may result from the greater averaging over time and space that is required to use the radon deficit method in the ocean studies (Liss 1983). Wanninkhof et al. (1987) have shown that high variability in wind speed reduces the strength of nonlinear gas transfer-wind relationships derived from field data because the average wind may not be representative of the wind field generating the near-surface turbulence. The oceanic wind measurements used in this analysis were usually averaged over a longer period of time and a greater distance than in the smaller scale, more easily accessible systems. The duration of the wind at the average velocity given and the sea state are also likely to influence the wave fields developed and hence the scale of the wind-wave interaction controlling gas transfer (Jähne et al. 1987; Frankignoulle 1988; Wanninkhof 1992). For example, models developed from wind tunnel experiments and calibrated with oceanic data have demonstrated a much weaker nonlinear dependence of gas transfer on wind speed when the wind is steady as opposed to averaged over long time periods (Wanninkhof 1992). All of these considerations, combined with the very large fetch and great depth of the open ocean, are likely to result in measured gas exchange rates which are more temporally decoupled from the wind velocity than those in lakes or estuaries.

Respiration in the Hudson Estuary—A Constraint on the Estimated Gas Transfer Velocity

We have used the regression between wind velocity and oxygen transfer velocity illustrated in Figs. 3A and 4A, in conjunction with data on wind and diel oxygen changes at ten stations along 40 km of the Hudson, to estimate a respiration rate for the tidally-influenced, freshwater Hudson River estuary of 755 g C m^{-2} yr^{-1} (Howarth et al. 1992). The upper and lower bounds on this estimate, calculated using the upper and lower 95% confidence intervals of our predictive relationship between wind and gas transfer (Fig. 4A), are 984 g C m^{-2} yr^{-1} and 665 g C m^{-2} yr^{-1}, respectively (Howarth et al. 1992). That is, our estimate of whole-ecosystem respiration derived from diel free-water oxygen data is moderately sensitive to the correction for atmospheric oxygen exchange, increasing or decreasing the calculated respiration rate by 30% and 12%, respectively, within the 95% confidence limits of our model relating gas flux data to wind velocity in estuaries, lakes, and oceans.

Our analysis of the available literature data for natural systems, combined with our Hudson field data on gas exchange (Fig. 4) suggests that the SF_6 data for gas transfer in lakes provide a conservative lower limit for estimating atmospheric exchange in estuarine systems. Since all of the lake-SF_6 data fall either on or above the line for the lower 95% confidence interval of the gas transfer relationship we have used, we think it highly unlikely that respiration could be lower than 665 g C m^{-2} yr^{-1}.

An analysis of the carbon budget for the freshwater Hudson estuary indicates it is also highly unlikely that respiration could be greater than our high estimate of 984 g C m^{-2} yr^{-1}. The total known net inputs of organic carbon into the tidally-influenced, freshwater Hudson are less than 1,000–1,100 g C m^{-2} yr^{-1} (Howarth et al. 1991, 1992). Thus, even if there were no net sedimentation or downstream advection of organic carbon, respiration must be less than 1,000–1,100 g C m^{-2} yr^{-1}. Our preliminary estimates are that net sedimentation plus downstream advection of organic carbon equal at least 300–400 g C m^{-2} yr^{-1} (unpublished data). Thus, by difference the carbon budget approach suggests that whole-ecosystem respiration should be at least 600–800 g C m^{-2} yr^{-1}. This is in surprisingly good agreement with our estimate derived from the diel free-water oxygen method. Since the respiration estimate determined from the diel oxygen method is somewhat sensitive to the estimation of atmospheric gas exchange, this analysis adds to our confidence in our approach for estimating atmospheric gas exchange.

Other studies using free-water oxygen methods for measuring metabolism have assumed that atmospheric oxygen exchange is a function only of the air-water gradient and is independent of wind. This is often expressed in terms of a constant boundary layer thickness impeding molecular diffusion of oxygen. For our study in the Hudson

River, the average gas transfer coefficient corresponds roughly to an average boundary layer thickness of just under 200 μm. This is similar to the value used by Lehman and Naumoski (1986) for their study of a lake, but is much thicker (i.e., slower gas transfer) than the boundary layer of 32 μm used by Copeland and Duffer (1964) for a river and by Kemp and Boynton (1980) for Chesapeake Bay. Most river studies have reported boundary layer thickness in the range of 20 μm to 50 μm (Devol et al. 1987), although in the Amazon a range of values from 38 μm to over 200 μm was found depending upon the method used and the time of sampling (Devol et al. 1987). If we assumed a constant boundary layer of 32 μm for the Hudson estuary—which is equivalent to constant wind conditions of approximately 8 m s^{-1} in our model—our estimate of respiration would be increased by 64% to 1,237 g C m^{-2} yr^{-1} (Howarth et al. 1992). Such an estimate seems unreasonably high given the current estimates of organic matter inputs to this ecosystem.

Applicability to Other Ecosystems

We believe the regression of ln k versus wind velocity presented here can be used to estimate oxygen exchange as part of the measurement of metabolism in other relatively deep and wide estuarine and riverine ecosystems. However, the relationship in Figs. 3A and 4A is less applicable to more shallow systems with significant tides or river flows where bottom-induced turbulence may dominate atmospheric gas fluxes (Jirka and Brutsaert 1984; O'Connor 1984; Roberts 1984). In such cases, relating gas fluxes to water flow may be the more desirable approach, or it may be necessary to explicitly consider the effects of both wind and current.

Whether other workers choose to apply the transfer velocity-wind relationship developed here depends in part upon the precision and accuracy desired for estimating metabolism in their studies. One important factor to consider is the depth of the ecosystem; atmospheric fluxes are greater in more shallow systems since a given rate of metabolism will generate steeper water-air oxygen gradients in the smaller volume of water. Hence, the potential errors in estimating atmospheric fluxes pose a greater problem in more shallow systems. Another factor is the extent to which metabolism lowers or raises water column oxygen concentrations relative to saturation. For instance, the atmospheric flux term becomes increasingly important in ecosystems where respiration far exceeds primary production, magnifying water-air oxygen gradients. For context in assessing these potential errors, the reader is reminded that the Hudson River is a relatively deep estuary and has a fairly negative rate of net ecosystem production, with respiration far exceeding primary production (Howarth et al. 1992).

Detailed site-specific measurements made in the estuary of interest may allow increased precision in estimating oxygen exchanges with the atmosphere as a function of some physical parameter such as wind. However, given all of the known and potential errors in making both wind and gas exchange measurements in estuaries and large rivers and in predicting gas transfer from a single parameter such as wind speed (Wanninkhof 1992), we feel more comfortable using the entire data set from the literature with 95% confidence limits to estimate atmospheric oxygen fluxes for our Hudson River estuary study.

Since virtually all of the data we have found on gas fluxes in estuaries come from dome studies, it is not possible at present to determine if the slightly greater tendency for measured gas exchange rates to increase more rapidly with wind speed in estuaries than in lakes is due to a methodological bias in the dome approach or to an influence of tide or other hydrologic characteristics. Further studies should focus on making atmospheric exchange measurements in estuaries using the tracer addition approach, and should include frequent sampling and detailed measurements of system characteristics that may influence turbulence at the air-water interface in order to develop a more tightly constrained predictive model. This approach will require a major effort but should go a long way toward furthering our understanding of the controls on gas exchange in relatively deep and tidal or other flowing water systems.

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