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Estuary-Specific Variation in the Air-Water Gas Exchange Coefficient for Oxygen

JAMES N. KREMER[1,*], ALYSSA REISCHAUER[2], and CHARLENE D'AVANZO[3]

[1] *Department of Marine Sciences, University of Connecticut at Avery Point, Groton, Connecticut 06340-6097*

[2] *Oregon Department of Fish and Wildlife, NE Region Fish Research and Development, Eastern Oregon University, La Grande, Oregon 97850*

[3] *Department of Natural Sciences, Hampshire College, Amherst, Massachusetts 01002*

ABSTRACT: Oxygen air-water gas exchange was measured using floating chambers in two shallow tidal estuaries of differing bathymetry and local terrain, near Waquoit Bay, Massachusetts (United States). The specific chamber design permitted measurements of gas flux in 15 min, allowing analysis of the relationship with wind speed and tidal stage. Exchange coefficients ranged from 0.5 to 2.5 g $O_2 \cdot m^{-2}$ h^{-1} atm^{-1} (equivalent to piston velocities of 1.5 to 7 cm h^{-1}) for wind speeds of 0.3 to 9 m s^{-1} at 10 m elevation. While the relationships for each estuary appear linear (significant linear regressions with wind speed were shown for each estuary, and the slopes were different at the 99.5% confidence level), the range of speeds differed at the two sites and an exponential function of wind speed was consistent with the combined data from both estuaries. A power function of wind speed was not an acceptable model. The exchange coefficients for our estuaries are from 57% to as low as 9% of that predicted by previously published generic equations. Because the atmospheric correction can be significant in shallow, metabolically active coastal waters, we suggest that empirically determined relationships for gas exchange versus wind for a specific estuary are preferable to the predictions of the general equations. While the floating chamber method should be used cautiously, at low winds speeds (below 8 m s^{-1}) and in slowly flowing waters, it provides a convenient approach for quantifying these site-specific differences. The differences, especially those between shallow sheltered systems and the open waters best fit by some published relationships, are ecologically important and do not appear yet to be measurable by other methods.

Introduction

In studies of watershed-estuary coupling and coastal eutrophication, we have sought to assess and compare ecosystem metabolism in estuaries that have different numbers of houses in their watershed and thus differing nutrient loading rates. Such case studies were part of the Waquoit Bay Land Margin Ecosystem Research project (Cape Cod, Massachusetts, United States). Metabolism measurements based on changes in free-water oxygen were done in two shallow, tidal sites of differing geography and hydrology: Childs River and Sage Lot Pond.

Measurements of ecosystem metabolism based on diel changes in free-water oxygen require a correction for the physical flux of gas between the atmosphere and water (Odum 1956; Odum and Hoskin 1958; Murphy and Kremer 1983). This correction is especially important to evaluate in shallow waters. Our goal was to determine the relationship between the gas exchange coefficient and wind speed, presumably an important independent variable. Since our research seeks a quantitative comparison of ecosystem production and respiration in the estuaries, we sought to determine if oxygen gas-water exchange varied significantly between our estuaries that differ in local topography, basin bathymetry, freshwater stratification, and prevailing winds. We compared our functions for these sheltered, shallow tidal sites with published generic functions suggested for predicting the exchange coefficient versus wind speed.

Gas exchange is an important ecological restoring process that depends on many factors. Fick's law defines a phenomenological transfer coefficient, K, such that the actual flux (J) is in proportion to the saturation deficit (SD), i.e., $J = K \times SD$. Different authors prefer different units and forms of the equation, but most are inter-convertible. We define the permeability coefficient K in g O_2 m^{-2} h^{-1} atm^{-1}, and a saturation deficit for the water in atmospheres as

$$SD = 0.209 \cdot (C_s - C_o) \times C_s^{-1}$$

where C_o is the concentration (g O_2 m^{-3}) observed in the surface water and C_s is the concentration in water that is in equilibrium with the atmosphere, given the partial pressure of oxygen in air of 0.209 atm. Many ecologists use this formulation of gas

* Corresponding author; tele: 860/405-9027; fax: 860/405-9153; e-mail: jkremer@uconn.edu.

exchange (e.g., Roques 1985), perhaps because the permeability coefficient K is more obviously related to fluxes of oxygen per unit volume or surface area. Physicists and geochemists often use a mass transfer coefficient (e.g., Hartman and Hammond 1985). In this form, SD = $(C_s - C_o)$ has units of concentration for the specific gas, and the transfer coefficient K_L has the units length × time^{-1}, thus the name piston velocity. The two forms are related by $K_L = K \times 0.209$ (atm) $\times$ S(g O_2 m^{-3})$^{-1}$. We present our results here both as K and as K_L (cm·h^{-1}). The flux J is in g O_2 m^{-2} h^{-1}. Any change in the flux J at a given value of SD can be related to changes in the value of K, and K may depend on various factors. For example, bottom friction is a dominant factor in flowing streams (O'Connor and Dobbins 1958). At specific field sites, empirical relationships might be expected between K and wind speed, wind direction, current speed, or near-surface velocity shear, and such relationships might differ by location. While data combined from many estuaries may suggest a general trend, site-specific factors certainly contribute to variability. We sought the most defensible functional equation by a comparison of measurements from two estuaries with each other and with two published suggestions for a generic equation.

We measured the air-water flux of oxygen directly using a floating chamber. Concerns have been raised that the presence of the floating device interferes with the processes governing gas exchange resulting in artificially high rates. A number of papers have discussed the issue (Broecker and Peng 1984; Hartman and Hammond 1984, 1985; most recently Raymond and Cole 2001), and the method continues to be widely used. Marino and Howarth (1993) present a good synopsis of the strengths and weaknesses of various methods including the chamber method, plus a favorable comparison of results from domes and other methods. Based on a review of a number of direct comparisons under laboratory and natural conditions, we believe that there is good reason to accept flux estimates using the floating chamber method within certain practical limits: wind speeds up to perhaps 8–10 m s^{-1} with limited fetch and no whitecaps, and care to minimize chamber motion relative to surface water motion. An accompanying technical note addresses the methodological concerns (Kremer et al. 2003).

Methods

Childs River is a narrow tidal river, about 1.5 m deep in the channel, 100 m wide and 2 km in length, surrounded by trees and dense housing development. Sage Lot Pond is a shallow salt marsh lagoon, generally less than 1 m deep, oval in shape,

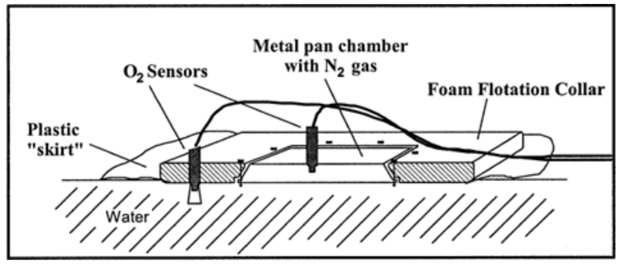

Fig. 1. Schematic diagram of the floating chamber used to measure the oxygen exchange coefficient. Use of a low shallow metal cake pan (19 × 19 × 4.5 cm) minimized wind drag while providing a high surface–to–volume ratio allowing precise measurements in about 15 min.

with a narrow, constricted inlet. The tidal river is often stratified at 20–50 cm by freshwater and temperature, while Sage Lot Pond, which receives little freshwater inflow, is generally well mixed or slightly temperature stratified. Adjacent forest cover restricts winds in Childs River, while the low marsh surrounding Sage Lot and its proximity to Vineyard Sound allow prevailing local winds to blow relatively unimpeded (see more complete site description in D'Avanzo et al. 1996).

Gas exchange was measured 12 times at Childs River and 11 times at Sage Lot Pond during 10 separate days in August–September 1991. Five additional points were added in June 1994 to add low wind conditions at Sage Lot, plus two more to augment the Childs River set. Air-sea gas flux was measured using the floating chamber method (Copeland and Duffer 1964; Roques 1985), in which the influx of oxygen into the head space of a floating chamber initially filled with oxygen-free gas at 1 atm was measured through time. To enhance the response time of our device, permitting frequent short-term measurements of K during changing wind conditions, we chose a shallow metal cake pan (19 × 19 × 4.5 cm) with large surface area-to-head space volume as the chamber (Fig. 1). The pan was painted inside and out with white enamel to minimize solar heating and avoid rusting. Flotation was achieved by a rectangular foam collar 33 × 40 cm, 5 cm thick. The low, wide design reduced wind drag compared to hemispherical domes with taller rectangular floats often used. A skirt of flexible plastic sheet extended 7 cm from the foam collar on all sides to suppress direct aeration by wave-generated bubbles at higher wind speeds.

Two sensors, each measuring oxygen and temperature, were mounted on the floating device, one with a stirrer to monitor ambient water conditions just below the water surface, and another without a stirrer in the head space of the floating pan (Fig. 1). Sensor cables were connected to two meters in a small skiff. Deployments were at anchored stations so the chamber was not drifting freely, with the cables trailing from a boom extending 1 m laterally from the skiff, orientated to minimize interference. Advection of the surface water was slow ($\approx$ 1 cm s^{-1} by visual estimate), so that much less turbulence was introduced by the tethered chamber in this case than if it were allowed to float with the wind.

On deployment, the pan plus flotation was inverted and completely submerged, then righted and gently floated to the surface with the chamber filled with water. Nitrogen gas was let into the pan gently through plastic tubing until bubbles emerging from the underside indicated that all the water had been displaced. To ensure the chamber head space was of known volume and at 1 atm, the tubing was then disconnected from the gas cylinder, held open for 5–10 s to allow pressure to equilibrate at ambient atmospheric pressure (assumed to be 1.0 atm), and then removed. This procedure isolated an oxygen-free atmosphere of known and reproducible volume inside the head space with the bottom of the float and the lip of the pan extending about 1 cm below the water surface.

Oxygen concentration within the head space was monitored continuously over 10–30 min using a digital oxygen meter (YSI Model 58). The rate of increase into the chamber was measured precisely by recording the time to the nearest second whenever the oxygen in the chamber increased 0.01 ppm. Short-term changes (5 min or less) in the influx rate were detectable, apparently related to changes in wind, boat wakes, etc. For this analysis, we specifically selected data from times when wind conditions were steady prior to and during the exchange measurements.

A recording anemometer logged 1 min averages of wind speed and direction before and during all gas flux measurements. These instruments (Digitar #7902 Anemometers with Onset Tattletale 2-B data-logging computers) were calibrated within $\pm$1 m s^{-1} by comparison to a C.M. Young meter on a National Oceanic and Atmospheric Administration (NOAA) buoy. Wind sensors were mounted at our two estuaries, one at 1.5 m and the other at 2.5 m above mean sea level. Measured wind speeds in this paper have been converted to wind at 10 m (U_{10}) using the logarithmic correction $U_{10} = U_z\ (0.097\ \ln(z/10) + 1)^{-1}$ (Pond 1975; Hartman and Hammond 1985).

Dissolved oxygen, temperature, and salinity were recorded in the surface water at the start and end of each run. Water level was recorded before and after each series and used to estimate tidal stage and rate of change in water level.

The specific reaeration coefficient, k_s (h^{-1}) was calculated as the exponential slope of the change in oxygen in the chamber. The coefficient may be determined as the slope of the least squares regression of ln(concentration) versus time (Roques 1985). We used a 2-point approximation of this slope, which is nearly identical for data that fit the exponential model well.

$$k_s = \frac{1}{t}\ln\left[\frac{(C_w - C_i)}{(C_w - C_f)}\right] \qquad (1)$$

where C_w = average concentration of oxygen in the water during the incubation (g O_2 m^{-3}); and C_i, C_f = concentration of oxygen in the chamber at the beginning and the end of the incubation interval, t (h).

The gas exchange coefficient K (g O_2 m^{-2} h^{-1} atm^{-1}) was computed from k_s, the dimensions of the chamber, molar properties of oxygen, and the partial pressure of oxygen in air:

$$K = k_s\ (h^{-1}) \times \frac{V\ (m^3)}{A\ (m^2)} \times \frac{32\ (g\ O_2)}{22.4\ (l\ O_2)} \times \frac{0.209\ (l\ O_2)}{l\ air \times P_\Sigma\ (atm)} \times \frac{1000\ l\ air}{1\ m^3} \qquad (2)$$

where V and A = volume and area of chamber (0.00109 m^3 and 0.0353 m^2); P_Σ = total gas pressure in the chamber (1 atm).

For comparison with the piston velocity (K_L, cm h^{-1}) reported by other authors, the gas exchange, or permeability coefficient K was converted using the oxygen concentration at saturation. For temperatures and salinities of our measurements, K_L = 3.0 K (r^2 = 0.99, n = 35).

Regressions with 95% confidence limits were computed by model I linear assumptions (Sokal and Rohlf 1981) on raw and natural log transformed data. The average accuracy of each statistical model's prediction (P_i) versus observed data (O_i) was calculated as $\epsilon = (\Sigma|P_i - O_i|)/n$ for a sample of n points.

Results

Measurements of oxygen flux and calculations of the exchange coefficients were done 14 times in the Childs River and 16 times in Sage Lot Pond. The oxygen increase into the chamber was readily measurable in all cases (Fig. 2). Temperature change within the chamber was less than 0.5°C during these short incubations.

The ability to make short-term measurements of the oxygen influx permitted a detailed analysis of the relationship with wind. For data used in this analysis, wind speeds were steady ($\pm$0.5 m s^{-1}) prior to and during the gas exchange measurements (Fig. 2), and the oxygen increase was at a nearly

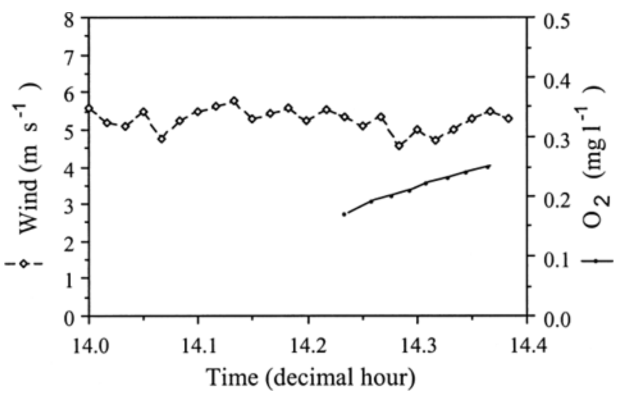

Fig. 2. Sample of data from which atmospheric exchange coefficients were calculated. Wind speeds (open diamonds) are 1-min averages that were automatically logged by a nearby anemometer, while the increase of oxygen was measured within the floating metal chamber (solid dots).

constant rate ($r^2 = 0.996 \pm 0.002$ [standard deviation for all cases of 5 to 20 points]). Cases where a wind change altered the rate of increase were not used unless conditions were steady for long enough to achieve a new constant rate. An average wind speed was calculated from 1-min averages logged during the gas flux incubation and the preceding 15 min. These values were converted to wind at 10 m. The range of converted wind speeds was from 0.3 to 9 m s^{-1}.

The gas transfer coefficient K was positively related to wind speed for both estuaries (Fig. 3). The slopes of the two predictive linear regressions were significantly different at the 99.5% level.

The linear correlation coefficient was quite high ($r^2 = 0.88$) for Sage Lot, where the open terrain allows a consistent wind field leading to a strong relationship. In Childs River, wind speeds were generally lower, due to the narrow geometry of the basin and the shelter of nearby houses and trees. The values of K were correspondingly lower there, with the smaller range resulting in a weaker linear correlation ($r^2 = 0.43$) despite a consistent trend.

When the data from both estuaries were combined, the relationship was no longer linear (Fig. 3). Various functional forms were evaluated. The exponential model provided the best curvilinear fit (linear $r^2 = 0.73$ in log domain). The average accuracy was better for the linear models ($\epsilon = 0.14$ and 0.19 g O_2 m^{-2} h^{-1} atm^{-1} for linear equations at Childs River and Sage Lot Pond, respectively) than the untransformed exponential with the combined data ($\epsilon = 0.22$).

Our attempts to account for more of the observed variability in K have been unsuccessful. Anticipating that advection and shear could influence the air-water boundary layer, changes in water level during each measurement (presumably related to tidal velocity) were included in multiple regressions. In one estuary, the coefficient of determination improved for the multiple linear regression (Childs River, where r^2 increased from 0.43 to 0.67), but this was not the case for the data from Sage Lot Pond. Present data are insufficient to evaluate the possible contribution of wind direction and fetch. Further studies are needed to define a more complete relationship, probably including water velocity in addition to wind, for different tidal ranges and bathymetry.

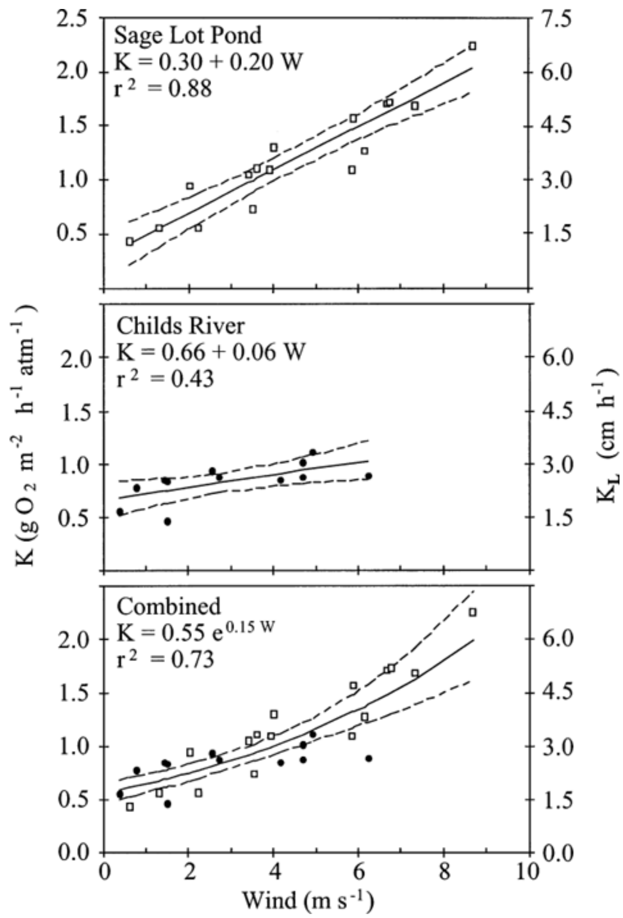

Fig. 3. Relationships between wind speed at 10 m (W) and gas exchange coefficient (K) for two estuaries near Waquoit Bay, Massachusetts. The predictive linear regressions (solid lines) are significantly different at the 99.5% level. The combined data were well fit by an exponential curve. Dashed lines indicate the 95% confidence intervals for the three regressions. The gas exchange coefficients are plotted both as a permeability coefficient (K) and piston velocity (K_L). Equations shown are for the permeability coefficient K. Equivalent equations for K_L are Sage Lot Pond: $K_L = 0.9 + 0.6W$; Childs River: $K_L = 1.98 + 0.18W$; and Combined: $K_L = 1.65e^{(0.15W)}$.

Discussion

Despite the strong dependence of K on wind at both estuaries, the choice of the best descriptive equation is not straightforward. We ultimately chose an exponential equation, but consider briefly two other models suggested in the literature. The key question is whether published generic equations are acceptable for shallow coastal embayments or whether different equations are preferable for different localities? Our answer is that the generic equations are seriously inaccurate for shallow coastal sites such as ours, but it remains unclear whether different functions are appropriate for each of these separate sites.

Considering both estuaries independently, each shows a strong linear trend. Assuming this model, the 95% confidence limits leave little doubt that the regressions differ by estuary (Fig. 3). This model is the simplest and provides the best predictions. Although most authors recognize a curvilinear relationship, Liss and Merlivat (1986) proposed separate straight lines for each of three domains of wind speed. Prevailing winds in Childs River are consistently lower than those in Sage Lot Pond. The lack of high wind speeds ($W < 6$ m s^{-1}) for Childs River is unfortunate, since the difference in slope would make curvature detectable. The y-intercept seems more likely to vary with site-specific hydrodynamics than the wind-dependent slope. Despite their statistical validity, the linear equations are questionable outside of the measured wind speeds at their respective sites.

Hartman and Hammond (1985) review literature that K_L (cm h^{-1}) may be a power function of wind. They suggest a fitted exponent

$$K_L = 34.6R_\nu(Dm_{20})^{0.5}(U_{10})^{1.5} \quad (3)$$

where R_ν is kinematic viscosity ratio of pure water at 20°C to that at the temperature and salinity of interest, Dm_{20} is the molecular diffusivity of the gas at 20°C in cm^2 s^{-1}, and U_{10} is the average wind speed at a height of 10 m in m s^{-1}. A recent study of CO_2 exchange in the North Atlantic (Wanninkhof and McGillis 1999) uses an analogous equation but fixes the exponent and defines the exchange coefficient to be a cubic function of wind.

A conspicuous feature of such a function (Eq. 3) is that it passes through the origin, i.e., K_L must approach zero with no wind. Hartman and Hammond (1985) lacked data below 2.5 m s^{-1}. Away from coastal influences very low fluxes are observed under some circumstances, and Wanninkhof and McGillis (1999) found the higher order curvature was necessary to fit both the high values at high wind speeds and the fluxes at low winds that were quite low attributable to the action of surfactants. For our Waquoit Bay data and in some other cases, a positive intercept is definitely indicated. Whether the power exponent of wind speed is specified as a fitted parameter, or fixed as a cubic relation, this model is incapable of approaching the positive fluxes at low wind speeds in these data.

While a near-zero intercept might be physically meaningful in still water, when a significant intercept is present it suggests that processes other than wind are maintaining turbulent renewal of the surface boundary layer. In estuaries and coastal waters, there are a host of processes that could be responsible, including freshwater flow, tidal advection, or bottom friction, so the appearance of a significant flux at zero wind is not only plausible but likely. For our data set, and probably for any coastal situation, this model is unacceptable.

Marino and Howarth (1993) selected an exponential model to describe gas exchange coefficients from oceans, estuaries, and lakes. They reported the least squares fit on a semi-log transformation of the data to be:

$$K_L = 2.97e^{(0.25U_{10})} \qquad (r^2 = 0.55 \text{ in semi-log domain}) \quad (4)$$

This expression allows positive exchange coefficients at low winds. Applying this model for our combined data (Fig. 3 bottom) yields:

$$K_L = 1.65e^{(0.15U_{10})} \qquad (r^2 = 0.73) \quad (5)$$

Two reviews that consider data from floating chambers and other methods (Hartman and Hammond 1985; Marino and Howarth 1993) offer generic functions to estimate gas exchange coefficients. When data from various sources are combined, the scatter increases so that the choice of the best model becomes less clear. For many of the component data sets the within-site variability is small, an important point noted by Marino and Howarth. Their data from estuaries show a different trend from the regression of all sites. Their data for just the Hudson River are quite well constrained relative to the combined variability of other systems and had a different slope (Fig. 4; see also Fig. 4 in Marino and Howarth 1993). A more recent study in the Hudson using a dual tracer technique (Clark et al. 1994) also found exchange rates that were less varied and well below the published generic trend for the open ocean, and in fact 25% below the coefficients reported for the Hudson River by Marino and Howarth (1993).

The wide scatter of generic regressions is expected, since they are combinations of coefficients measured in different systems by different people with differing methods. A consequence of this is that using generalized functions must introduce substantial errors for a given specific site. While it seems obvious that measurements in a particular estuary are to be preferred over predictions from generic regressions, it is not necessarily so. If the scatter in measurements for one estuary were typ-

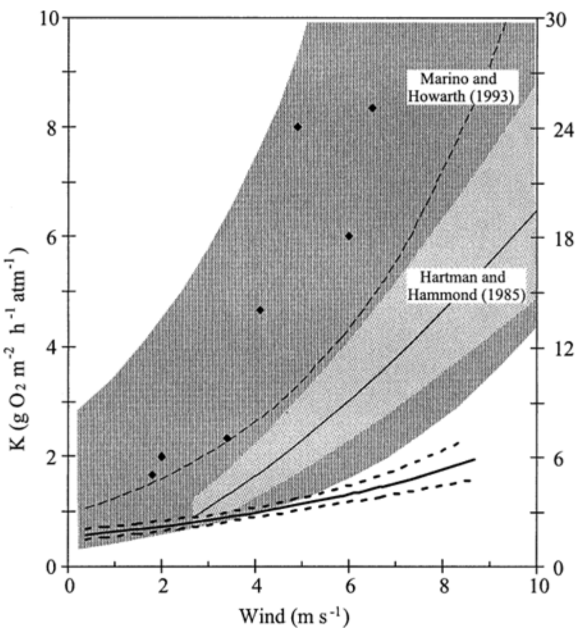

Fig. 4. Comparison of the exponential regression for two estuaries in this study (Solid line with dashed 95% confidence limits; also see Fig. 3, bottom) with general functions suggested by Hartman and Hammond (1985) and Marino and Howarth (1993). Stippled areas are the 95% limits of the two published multi-site regressions, which are asymmetrical when untransformed. Solid diamonds are Marino and Howarth's measurements using floating chambers for the Hudson River only.

ically as large as with combined data for many sites, generalized functions would be acceptable, even preferable. But the fact that this is not the case confirms that differences among water bodies are being obscured by grouping them.

In the exponential model, it seems logical that the intercept represents enhanced exchange at low winds, due most likely to water currents, shear, or bottom friction. If these additional sources of near-surface turbulence act independently of wind, then a logical general form for the equation might be $K_L = K_o + e^{(K_w U_{10})}$. The non-wind effect ($K_o$) might be related to current speed and bottom depth in shallow systems (O'Connor and Dobbins 1958; O'Connor 1984; Roberts 1984), and a more consistent wind effect (exponent) might emerge among estuaries. It does not appear that the wind effect itself (K_w) is uniform and independent of K_o. It is clear from Fig. 4 that the exponential curvature of data from Waquoit Bay, Hudson River, and the two generic equations are not consistent with each other. It appears either that the slope of the wind effect is itself variable from estuary to estuary, or that there is an interaction with non-wind contribution. In situations where fetch is short, it is sensible that the effect of a given wind speed on K is well below what is seen in more open sites, and may even approach values in experimental conditions (Hartman 1983; Smith 1985).

Are site-specific functions justified? We feel that our analysis proves the need for different predictive equations for large open systems (the generic functions) and the shallow tidal systems such as our two sites. The question of whether these two sites also differ from each other is not as clear. Statistically, two straight lines are not sufficiently better than the combined exponential, but the differing geographical constraints on the prevailing winds limit the region of overlap that would allow a difference to be confirmed.

When disparate data from various sites are combined, large confidence limits surround the regressions. Marino and Howarth (1993) show 95% confidence limits of −60% and +250% of the predicted coefficient (the limits are asymmetrical after backtransforming the predicted ln K_L). Compare this with Marino and Howarth's estimated empirical precision of ±30% associated with field measurements of K_L in the Hudson River. This is consistent with our results as well (Fig. 3) in which the standard error of the exponential model was 10–30%.

Despite improved precision, we must also consider the accuracy of the field methods. Marino and Howarth (1993) suggest that uncertain accuracy of the different methods precludes more precise analyses of field data. This is especially true for the floating chamber method. If this method is not accurate, improved precision is no advantage. There are credible reasons to believe that the method works. Marino and Howarth (1993) present detailed theoretical arguments that the surface area affected by the device is small compared to the scales over which surface turbulence are determined. More importantly, simultaneous direct comparisons of floating chamber measurements with non-invasive tracer studies in a diverse range of lab and field conditions have agreed well, and a number of indirect inferences are also favorable (Roques 1985; Kremer et al. 2003). Certainly the floating chamber method has limitations; the verification tests have been at wind speeds below 5 m s^{-1}, with wave action below the threshold for whitecaps and bubble injection. The actual wind cutoff for safe use at a site will depend on local conditions, but within these practical limits, and with careful implementation in appropriate systems, empirical data support its accuracy.

Traditional alternatives simply cannot provide data at appropriate time scales for diel ecological studies. Some new techniques (e.g., deliberate tracers, direct covariance, atmospheric profiles) may eventually prove useful at hourly time scales, but this is by no means clear at this time, and all applications to date have emphasized longer time scales that are not useful for diel ecological studies (Carini et al. 1996; McGillis et al. 2001; Donelan and Wanninkhof 2002). Each new method has associated uncertain assumptions, is more expensive and time-consuming, and the tracer methods involve extensive sampling of water column concentration and basin bathymetry to support mass budget calculations. This potential of these approaches is discussed more fully in an accompanying note (Kremer et al. 2003).

The ecological implications of employing the different relationships discussed here should be considered. In large basins with deep water, the correction for atmospheric exchange is often small, and the issue is moot. In shallow, productive coastal systems correcting for air-water exchanges can be very important. Published generic models are readily available to provide flux estimates, but this study suggests that their use is invalid with significant consequences. For shallow tidal rivers not unlike the Waquoit Bay sites, Cai et al. (1999) used literature estimates of K_L that were about twice the average we measured, unquestionably with consequences for their estimates of metabolic rates. For Childs River, our calculated air-sea flux usually accounted for between 5–20% of the summer daytime apparent production. For Sage Lot Pond, which is shallower and more exposed, the air-sea flux was even more significant, half the time accounting for 20–50% of the summer daytime apparent production. In Sage Lot Pond for one day when winds ranged from 4–6.5 m s^{-1} daytime net production increased from 0.29–0.93 g O_2 m^{-2} h^{-1} when corrected for air-water exchange—a change of 320%. Use of generic equations from the literature would increase the calculated correction an additional 150–230% above the best empirical estimate measured in this study. These are large effects.

Because of diurnal asymmetry in winds, changes in the atmospheric correction can dramatically alter the Production : Respiration ratio. High winds in the late afternoon when oxygen levels are supersaturated predict large effluxes that are added to the measured change to increase the daytime production; calm winds during pre-dawn oxygen minima reduce the influx from the atmosphere used to compute nighttime respiration. For Waquoit Bay, use of the generic regression of Marino and Howarth (1993) shifts the average annual Production : Respiration from 1.05 to 1.3, with a corresponding apparent export of 900 g O_2 m^{-2} y^{-1} ($\approx$ 340 g C) rather than our best estimate of 4.6 ($\approx$ 2 g C). The choice of the gas exchange equation has major implications for attempts to determine whether or not coastal waters are exporting significant organic matter.

The confidence limits of published generic equations are large. These uncertainties are maximized in highly productive coastal systems where dramatic undersaturation and supersaturation occurs in shallow waters. Use of an appropriate gas exchange relationship can significantly alter estimates of ecosystem metabolism, and direct measurements of the exchange function in the local site should be done whenever possible.

Acknowledgments

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