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Technical Notes and Comments

Gas Exchange in Rivers and Estuaries: Choosing a Gas Transfer Velocity

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We are writing this comment to call attention to large uncertainties in the estimates of CO_2 flux from rivers and estuaries, a topic that has been receiving considerable attention recently (Raymond et al. 1997, 2000; Cai and Wang 1998; Frankignoulle et al. 1998). It is our view that there are too few direct measurements of the physical component of gas exchange (e.g., the gas transfer velocity, piston velocity, gas exchange coefficient, or k) for rivers and estuaries. While studies in streams, lakes, and marine systems have progressed to the point where the gas transfer velocity can be partially predicted from physical forcing functions (O'Connor and Dobbins 1958; Cole and Caraco 1998; Wanninkhof and McGillis 1999), this is not yet the case for estuaries and rivers. A comparison of gas transfer velocity measurements in estuaries and rivers reveals a general lack of agreement among studies and physically-based predictive models. Until we have a better understanding of the magnitude and causes of variation in estuarine gas transfer velocity estimates, it will be difficult to use gas exchange in rivers or estuaries to accurately mass-balance gases of interest.

The exchange of CO_2 between an aquatic ecosystem and the overlying atmosphere is an area of intense interest for several reasons: aquatic systems can be significant CO_2 sources or sinks on a global or regional scale (Kling et al. 1991; Quay et al. 1992; Sarmiento and Sundquist 1992; Cole et al. 1994); the magnitude and direction of an ecosystems CO_2 flux can provide important clues about metabolism in a given system (Depetris and Kempe 1993; Gattuso et al. 1993; Hamilton et al. 1995; Raymond et al. 1997; Boehme et al. 1998); and can suggest ways in which the aquatic system is linked to its watershed (Dillon and Molot 1997; Jones and Mulholland 1998; del Giorgio et al. 1999). Estuaries and rivers receive inorganic nutrients and organic C from land and both are important systems where terrestrial nutrients and organic C are processed before entering the ocean. Some estuaries, or parts of estuaries are dominated by autotrophic C inputs while others are clearly net heterotrophic and are considered strong exporters of CO_2 to the atmosphere (Kemp et al. 1997; Smith and Hollibaugh 1997; Cai and Wang 1998; Frankignoulle et al. 1998; Raymond et al. 2000). Developing accurate estimates of the gas transfer velocity in estuaries has become an important research goal in recent years (Marino and Howarth 1993; Clark et al. 1994; Carini et al. 1996).

The flux of CO_2 depends mainly on two factors: the concentration gradient between the surface water and the air and the physical transfer or turbulent energy at this interface (MacIntyre et al. 1995). Thus,

$$\text{Flux} = k\ \alpha\ ((pCO_2 \times K_h) - [CO_2]_{sat})$$

Where $[CO_2]_{sat}$ is the concentration of CO_2 in water at equilibrium with the overlying atmosphere; K_h is Henry's constant for CO_2 at a given temperature and salinity; pCO_2 is the partial pressure of CO_2 in the surface water; k is the gas transfer velocity for CO_2; and α is the coefficient of chemical enhancement, which affects CO_2 flux only at high pH and low values of k (Degrandpre et al. 1995; Wanninkhof and Knox 1996). In the normal range of estuarine pH values, this equation shows that the flux of CO_2 is governed by the concentration gradient between air and water, and k. To make comparisons, k is often reported as k_{600}, which is the k for CO_2 at 20°C in freshwater, that is, k at a Schmidt number of 600. The methodology for measuring CO_2 concentrations in both air and water has progressed to the stage where it is now possible to make continuous, accurate measurements of the concentration gradient by a variety of means in almost any type of aquatic system (Goyet and Snover 1993; Millero 1995; Oudot et al. 1995; Sellers et al. 1995; Carignan 1998; Murphy 1998). While there are a number of measurement options and equations for choosing a value for k_{600}, the estimation of k_{600} is by far the most problematic term in the flux equation.

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Because the number of studies that directly measured k_{600} are few, authors generally rely on predictive equations to constrain k_{600} for their system. Theoretically k_{600} is constrained by turbulent mixing in the surface aqueous boundary layer. Research suggests that in lakes and oceans the dominant source of turbulence in the surface aqueous boundary layer is controlled by wind stress and therefore k_{600} is a function of wind-speed (Broecker and Peng 1974; Liss and Merlivat 1986; Wanninkhof 1992; Cole and Caraco 1998; Wanninkhof and McGillis 1999), although the relationship breaks down at low wind speeds (Clark et al. 1994; MacIntyre et al. 1995; Cole and Caraco 1998). It should be noted that other processes such as rainfall (Ho et al. 1997) and the formation of thin films (Frew 1997) affect the gas transfer velocity. In shallower streams and rivers the source of turbulence in the surface micro-layer is also due to bottom stress (the turbulence created by friction between water passing over the bottom) and k_{600} is a function of the stream depth and flow velocity (O'Connor and Dobbins 1958; Owens et al. 1964; Langbein and Durum 1967). For example, shallow fast running streams generally have higher k_{600}s than slow sluggish streams.

Estuaries represent a unique situation because they may fit in either category. They can be shallow with high tidal velocities, or deep with low tidal velocities. Cerco (1989) concluded, based on theoretical predictive models, that in estuaries the dominant source of turbulence at the surface aqueous boundary layer can originate from both wind and water-shear produced turbulence, and therefore depends on the depth, mean tidal velocity, and wind regime of a given estuary. Recent measurements of k_{600} in estuaries and across systems warrant a new look at the expected magnitude of k_{600} in estuaries. The objective of this comment is to review the predictive equations and measurements of k in rivers and estuaries in an attempt to predict the dominant source of turbulence in estuaries and evaluate if the current models are accurate enough to utilize gas exchange measurements in current inorganic carbon studies.

Figure 1 displays results of predictive equations for k_{600} using wind speed and bottom turbulence. According to Fig. 1, wind stress dominates turbulence in the surface aqueous boundary layer for all systems with depths greater than 10 m, or at windspeeds greater than 8 m s^{-1}; at all other depths and wind speeds either wind stress or bottom stress may dominate. Wind data compiled for 39 coastal cities in the United States shows a mean daily wind speed of 4.6 ± 0.28 m s^{-1} (95% CI) and ranges from 3 to 7.7 m s^{-1} among sites (wind data from www.noaa.gov). The median and modal wind

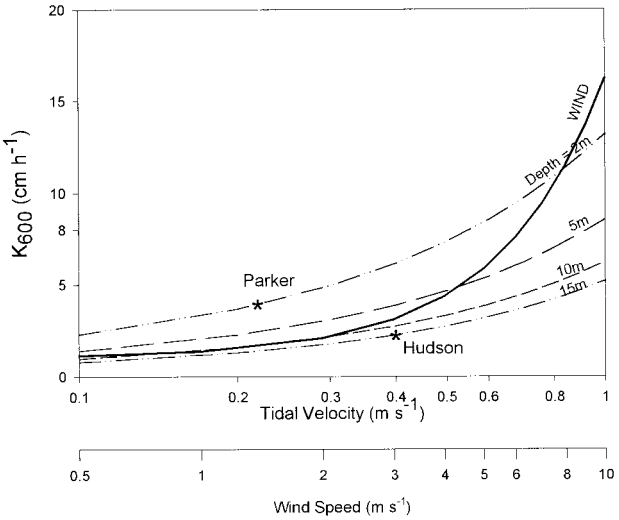

Fig. 1. Values of k_{600} based on predictive equations (after Cerco 1989). The solid line represents values of k_{600} using the average output from equations by Cole and Caraco (1998) and Wanninkhof (1992), which are based on wind-dominated turbulence and were generated through literature review. The dashed lines are the mean output from equations by Langbein and Durum (1967), O'Connor and Dobbins (1958), and Owens et al. (1964), which are based on turbulence generated from bottom stress and were originally developed for stream systems. According to the stream equations, turbulence in the surface aqueous boundary layer is a function of water depth and tidal velocity. For the stream equations, we show the output from systems with a mean depth of 2, 5, 10, and 20 m at varying average tidal velocities. The * locate the Hudson and Parker Rivers on their respective depth and tidal velocity curve.

speeds are 4.7 and 4.74 m s^{-1}, respectively, in this data set. Grouping the Hudson River and Parker River average tidal velocities (0.38 and 0.22 m s^{-1}, respectively) with the tidal velocities reported for 7 estuaries in Officer (1976) produced an average tidal velocity of 0.34 ± 0.18 m s^{-1}. Thus according to Fig. 1, unless an estuary has either above average winds, is exceptionally shallow, or has rapid tidal velocities we would expect k_{600} to be in the range of 3–7 cm h^{-1}.

The predictive equations are in reasonably good agreement with purposeful gas tracer experiments (i.e., SF_6 additions) conducted in two estuaries, the upper-Parker estuary (Carini et al. 1996) and the tidal-freshwater Hudson River (Clark et al. 1994). We believe purposeful gas tracer experiments are the most applicable studies for comparison because they measure average gas transfer velocities over long time scales. The Parker River is a macrotidal estuary with tides of 2.9 m (Vallino and Hopkinson 1998), and the Carini et al. (1996) study was done at depths of ~1.9 m, widths of < 100 m, and tidal velocities of ~0.2 m s^{-1} (Vallino personal communication). The Hudson River study was conducted in the tidal freshwater Hudson at depths of

TABLE 1. Average gas transfer velocities corrected to a Schmidt number of 600 (k_{600}) for rivers and estuaries. We limited our search to systems with depths greater than 1 m. In order to convert reported k for O_2 and radon studies to k_{600} we employed equations offered in Wanninkhof (1992). For the Pee Dee River and South San Francisco Bay natural gas tracer experiments we used the equation in Elsinger and Moore (1983) to estimate the diffusivity of radon at different temperatures.

System and Study	Type of Study	K_{600} (cm h^{-1}) Range	Average
Hudson River, Clark et al. (1994)	Purposeful gas tracer	1.5–9.0	4.8
Parker River, Carini et al. (1996)	Purposeful gas tracer	1.4–6.1	3.8*
South San Francisco Bay, Hammond and Fuller (1979)	Natural gas tracer (^{222}Rn)	1.0–6.7	4.3
South San Francisco Bay, Hartman and Hammond (1984)	Floating Dome	1.1–12.8	5.7
Amazon and Tributaries, Devol et al. (1987)	Floating Dome	2.4–9.9	6.0
Narragansett Bay, Roques (1985)	Floating Dome	4.5–11.0	7.4
Hudson River, Marino and Howarth (1993)	Floating Dome	3.3–26.0	11.6
Pee Dee River, Elsinger and Moore (1983)	Natural gas tracer (^{222}Rn)	10.2–30	12.6
Hudson River, Clark et al. (1992)	Natural gas tracer (CFC)	2.0–4.0	3.0
This study	Predictive Equations	3.0–7.0	

* Data from rain event are excluded.

~10–15 m, widths of ~2 km, and tidal velocities of 0.38 m s^{-1} (Clark et al. 1994). We used the data in Fig. 1c of Carini et al. (1996) which excluded a high rain event during one of the days of the Parker River study. The turbulence created by raindrops increases gas exchange (Ho et al. 1997).

Of the 11 independent estimates of k_{600} offered by Clark et al. (1994) and Carini et al. (1996), only one is above 8 cm h^{-1}, and the average is 4.4 ± 2.4 cm h^{-1}. Clark et al. (1994) and Carini et al. (1996) both reported direct relationships between wind and k_{600}, suggesting that wind is an important source of turbulence at the surface aqueous boundary layer in these two systems.

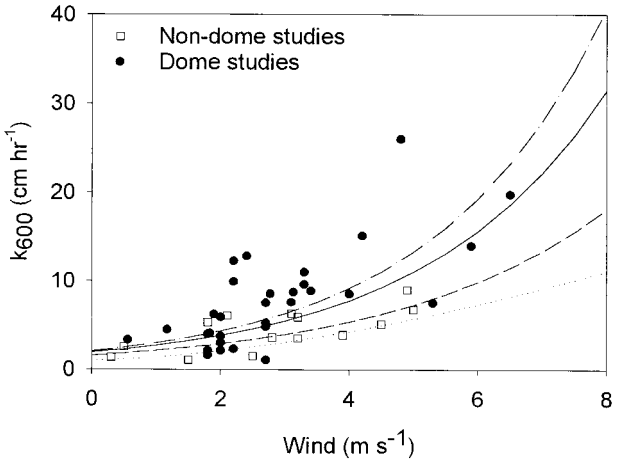

Fig. 2. k_{600} as a function of wind speed for all data that reported wind in Table 1. The circles are for floating dome studies, while the squares are from purposeful tracer additions and natural tracer studies. The lines are regressions for all data (solid line; $y = 1.91e^{0.35x}$; $r^2 = 0.53$; $p < 0.0001$), the dome data (dot to dashed line; $y = 2.06e^{0.37x}$; $r^2 = 0.56$; $p < 0.0001$), non-dome data (dashed line; $y = 1.58e^{0.30x}$; $r^2 = 0.46$; $p < 0.001$), and average output from equations by Cole and Caraco (1998) and Wanninkhof (1992), which were review papers (dotted line).

The two aforementioned purposeful estuarine gas tracer experiments are not the only applicable studies for comparison. There are three approaches that could be used to obtain k_{600}: natural tracers, purposeful tracer additions, and floating domes. Table 1 shows results from the three different methods and reports a range of 1 to 26 cm h^{-1} for k_{600} in riverine/estuarine systems. The purposeful gas tracer studies and predictive equations were on the low end of the reported range (Table 1). Combining all data and methods, we see a significant ($p < 0.001$) relationship between wind and k_{600} (Fig. 2). Splitting the data into dome studies and all other methods reveals that the relationship between dome estimates of k_{600} and wind is different, and slightly higher, than the estimates produced by the other methods (Fig. 2). Interestingly, the resulting estuarine wind-based equations based on the estuarine studies produce larger k_{600} than those produced using the general equations of Cole and Caraco (1998) and Wanninkhof (1992), which were derived largely from lakes and bays (Fig. 2). Therefore, the data indicate that at average wind speeds, estuaries may indeed have higher k_{600} values than average lake and marine systems.

Most of the estuarine measurements have used the floating dome approach (Table 1). The advantages of this method are its ease and simplicity and ability to resolve relatively short-term changes in gas flux. On the other hand, this method has been criticized for theoretical reasons. Mainly that the chamber disturbs the turbulence regime at the boundary layer (Broecker and Peng 1984) and laboratory experiments directly comparing floating dome to other methods have sometimes found little agreement (Belanger and Korzun 1991). Similarly, natural tracers are problematic in estuaries. The largest problem associated with natural tracer studies is that it is extremely difficult to mass bal-

ance any constituent in an estuarine system due to the many possible sources and sinks and complex mixing regimes. Purposeful gas tracer studies are the most difficult to do in field situations, and are rarely performed on estuaries, yet provide the least equivocal answer and are therefore the most promising for estuarine studies. Purposeful gas tracer experiments average exchange over days to weeks and over spatial scales up to several km^2, in contrast to floating domes that provide a snapshot in time and integrate over < 1 m^2. Therefore we believe, the purposeful gas tracers currently provide the best estimates of k_{600} when estimating gas exchange for entire estuaries over long time scales.

Table 1 represents a comprehensive list of studies that have measured k in large rivers and estuaries. The range of reported k_{600} in these systems is a large potential source of error when calculating gas exchange. In the Hudson River, for example, Raymond et al. (1997) obtained about a twofold uncertainty in estimating CO_2 exchange from k_{600} predicted from the Clark et al. (1994) purposeful gas addition study (16 mmol m^{-2} d^{-1}) and the Marino and Howarth's (1993) floating dome study (37 mmol m^{-2} d^{-1}). Had they used a k_{600} of 8 cm h^{-1}, the CO_2 flux estimate would be much larger still (71 mmol m^{-2} d^{-1}), more than 4-fold greater than that based on the purposeful gas tracer study.

Similarly, in order to demonstrate the ramifications of the potential source of error when choosing a k for CO_2 studies, we applied a k_{600} of 4 cm h^{-1} to recent papers that used an average k of 8 cm h^{-1}or greater. We are not stating that a k_{600} of 4 cm h^{-1} is appropriate for the average estuary, however based on the data available it is a plausible alternative. Frankignoulle et al. (1998) used an average k of 8 cm h^{-1} (based on direct measurements using the floating dome method) to estimate CO_2 flux in European estuaries, and the contribution of estuarine CO_2 evasion to anthropogenic CO_2 emissions of Western Europe. Fluxes of 100 to 500 mmol C m^{-2} d^{-1} and an evasion contribution of 5% to 10% were reported. If they had used an average k of 4 cm h^{-1} the flux would drop to 50–250 mmol m^{-2} d^{-1}, and the contribution of estuaries to anthropogenic CO_2 emissions would be 50% less, or 2.5–5%. More importantly, the sources of CO_2 necessary to balance this CO_2 flux would also be 50% less.

Cai et al. (1999) and Cai and Wang (1998) mass balanced carbon and oxygen in the Satilla estuary in order to elucidate the processes that were balancing high CO_2 concentrations and fluxes. For the two studies they used an average k of 12.5 (Cai and Wang 1998) and 8.75 cm h^{-1} (Cai et al. 1999) for CO_2 based on the work of Elsinger and Moore (1983). These articles argue that in the upper reaches (30–35 km from mouth) of the Satilla, atmospheric CO_2 exchange cannot be balanced by pelagic respiration. In the upper reaches using an average k of 8 or 12 cm h^{-1}, they reported atmospheric CO_2 fluxes of ~220 mmol m^{-2} d^{-1} for summer months (Table 4 in Cai and Wang 1998). Summertime pelagic respiratory rates in the Satilla are 24.2 mM m^{-3} d^{-1} (Table 1 in Cai et al. 1999). Assuming a depth of ~4 m (Cai and Wang 1998), pelagic rates of respiration on an areal basis were ~100 mmol m^{-2} d^{-1}, which is 50% of the total atmospheric flux using an average k of 8 cm h^{-1}. If an average k of 4 cm h^{-1} had been used, the atmospheric flux decreases to ~100 mmol m^{-2} d^{-1}, resulting in a system that is much closer to balance.

The bottom line is that there is a lack of direct estuarine k measurements using new accurate gas tracer techniques to predict k with any certainty. However, based on the predictive equations and purposeful gas tracer experiments it appears that at average wind speeds, tidal velocities, and estuary depth, k_{600} should be in the range of 3–7 cm h^{-1}. We believe researchers should bracket gas exchange using k values in this range until further research has been conducted. We hope that this comment will produce discussion and future work that will aid in properly constraining k_{600} in estuarine systems.

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