

DETERMINATION OF GAS EXCHANGE VELOCITIES BASED ON MEASUREMENTS OF
AIR-SEA CO₂ PARTIAL PRESSURE GRADIENTS AND DIRECT CHAMBER FLUXES IN
THE DUPLIN RIVER, SAPELO ISLAND, GA.

by

JUSTIN HARTMANN

(Under the Direction of Wei-Jun Cai)

ABSTRACT

CO₂ fluxes were determined directly, using a floating chamber for ten to fifteen minute intervals over the winter between 2006 and 2007 from Marsh Landing Dock on Sapelo Island, Georgia. Air-Sea pCO₂ differences were measured alongside the fluxes using a coupled equilibrator and infrared gas detector whereby gas transfer velocities (k) were calculated. In addition, current speeds were measured using an acoustic doppler current profiler and correlated with gas transfer velocities along side wind speeds. In the Duplin River, with the exception of spring tides, wind is an important variable controlling k in agreement with prior empirical measurement of estuarine k values. However, bottom generated turbulence was responsible for more than half of the magnitude of measured gas transfer velocities for 17 out of 100 of the deployments. In addition, gas transfer velocities during spring tides may be able to substantially increase k , however independent verification with an un-tethered floating chamber is needed to verify this in the Duplin River.

INDEX WORDS: CO₂ exchange. Interfacial transport, gas transfer velocities, inorganic carbon system, estuaries

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DEDICATION

This thesis is dedicated to my mother and father. To my mother, Louise Hartmann, who gave me everything and asked for nothing, except for me to finish this #!@^% thesis. And to my father, Thom Hartmann, who is a constant source of inspiration to me. His achievements and support have given me the confidence to pursue the highest of my ambitions.

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CHAPTER 1

INTRODUCTION

Understanding the role of air-sea exchange of carbon dioxide (CO₂) is of principal importance in understanding the ocean's role in regulating the atmospheric CO₂ concentration. At present, models and empirical data suggest that the global oceans represent a net sink of CO₂ of about 2 Pg Carbon (C) annually (Watson et al. 1995; Takahashi et al. 2002). In contrast, near-shore and estuarine areas have long been established as a source of CO₂ to the atmosphere (Frankignoulle et al. 1998; Cai et al. 1999; Cai et al. 2000; Raymond and Cole 2001). The near-shore zone source of CO₂ is estimated globally to contribute as much as 0.5 Pg C yr⁻¹ in terms of gas evasion (Borges et al. 2005). Thus, while the coastal oceans and estuarine environments represent a small area (0.4%) of the entire ocean surface (Woodwell et al. 1972), they play a disproportionately important role in oceanic carbon cycling and therefore require particular attention and accuracy in estimating the net air-sea transport of dissolved gases. Existing estimates of air-sea CO₂ fluxes over the global oceans and coastal regions, however, are highly uncertain due to the present inadequate knowledge of gas transfer velocities (Upstill-Goddard 2006).

Gas transfer velocities are a function of turbulent surface processes in ocean and lake environments and they depend primarily on wind friction where there is a large wind fetch and a deep depth. Thus, in the open ocean and many aquatic environments, including estuaries, the gas transfer velocity coefficient (k) is commonly modeled as a function of wind speed alone

(Frankignoulle et al. 1996a; Frankignoulle et al. 1998; Borges et al. 2004b; Wang and Cai 2004).

The two gas transfer models most often used in the literature are the models developed by Liss and Merlivat (1986) and Wanninkhof (1992). Both relationships utilize empirical functions of U_{10} (wind speed at ten meters above the water surface) and vary substantially from one another at higher wind speeds (Fig. 1). Specifically, in a recent paper by Ho et al.(2006), 13 wind speed - gas transfer models were compared and showed large differences in calculated k , particularly at wind speeds over 10 m s^{-1} .

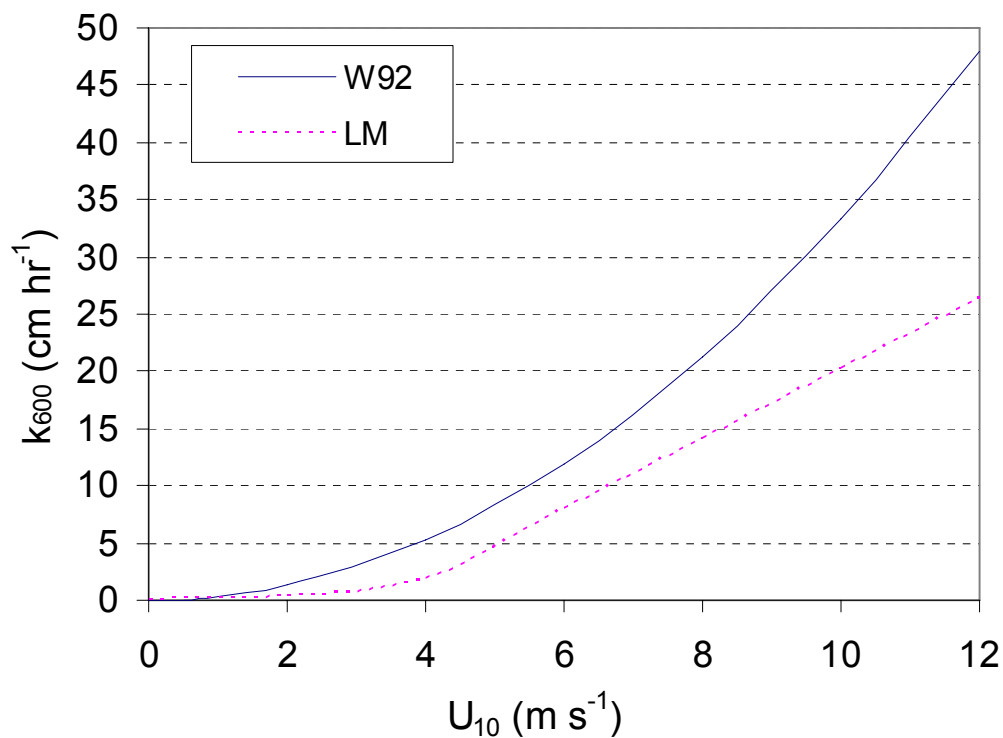


Fig. 1. Comparison of the two most popular models for gas transfer velocities as a function of wind speed in aquatic gas exchange studies. Liss and Merlivat (1986) (LM) and Wanninkhof (1992) (W92).

Because surface mixing is primarily generated by wind friction (Wanninkhof 1992) these relationships may represent an adequate estimation of gas transfer velocities for low to moderate wind speeds in the open ocean and lakes. However, in the coastal zone and particularly in macro-tidal estuaries, tidal action generates strong currents where turbulence and hence gas transfer may be strongly affected by stream bed bottom friction in addition to wind (Carini et al. 1996; Frankignoulle et al. 1998; Borges et al. 2004b). For example, Borges et al. (2004b) demonstrated in the Scheldt and the Thames River estuaries that bottom friction generated turbulence can have a noticeable effect on gas transfer velocities in macro-tidal systems. Their study yielded gas transfer coefficients highly correlated to tidal speed that were measurably altered by water current speeds varying from a low of 4 cm hr^{-1} to a maximum of 12 cm hr^{-1} over low wind days ($U_{10} < 4 \text{ m s}^{-1}$). These gas transfer velocities caused by bottom generated turbulence are analogous to gas transfer velocities generated by wind speeds of $6\text{-}8 \text{ m s}^{-1}$ (see Fig. 1). Another study by Zappa et al. (2003), which compared k determined by the controlled flux technique and measured renewal rates using infrared imagery, similarly showed that at lower wind-speeds ($< 2 \text{ m s}^{-1}$) surface agitation from bottom-generated turbulence can be a substantial variable in gas transfer in the Parker River estuary, generating gas transfer velocities up to 12 cm hr^{-1} . Again these values of k are analogous to gas transfer velocities generated by wind speeds of $6\text{-}8 \text{ m s}^{-1}$. In addition, Hahm et al. (2006) demonstrated that water current speeds of 0.5 m s^{-1} could produce gas transfer velocities of over 42 cm hr^{-1} in the coastal zone of the Southern Sea of Korea, significantly impacting the total air-sea gas flux there. They demonstrated that tidal currents account for more than half of the energy required to exchange dissolved gases such as CH_4 and CO_2 .

In spite of the number of coastal studies suggesting that bottom generated turbulence plays a role in controlling k , there is still little consistency in empirical and theoretical models (O'Connor and Dobbins 1956; Borges et al. 2004b; Hahm et al. 2006). Defining a generalized gas transfer velocity in estuarine zones may be impossible at this stage due to inadequate knowledge of regional estuarine shapes, flow regime, geochemistry and wind characteristics. Nonetheless, increasing data on the relationship between wind shear, hydrodynamic variables and gas transfer velocities in a variety of estuarine zones will increase the overall accuracy in calculating total estuarine degassing. Therefore the aims of this study are:

- 1. To measure gas transfer velocities in an important southeastern U.S. coastal research site: the Duplin River, Sapelo Island, GA*
- 2. Examine potential relationships of gas transfer velocities with estuarine hydrodynamic properties such as current speeds and wind shear.*

Models for gas transfer

Behind most gas transfer calculations exist two main conceptual and physical models: the stagnant layer model and the surface renewal model. The former is a simplified view of gas transfer where k varies linearly with the diffusive layer thickness (δ) (Lewis 1924). Grouping the hydrodynamic variables controlling near-surface transport into one, which represents the boundary layer thickness, is convenient and lends itself to quick calculations in terms of interfacial fluxes. The latter model is often used in riverine cases and is derived in terms of

surface renewal; wherein k varies proportionally to the square root of gas diffusion and a renewal term based on estimations of the turbulent fluid properties.

Interfacial transport can be written in terms of the gradient between the respective interfacial concentrations of the constituents over some distance.

$$flux = -D_{gas} \left(\frac{\partial C}{\partial z} \right) \quad (1)$$

where D_{gas} is the diffusion coefficient and $\frac{\partial C}{\partial z}$ represents the concentration gradient from the sea surface to the well mixed liquid layer. In the stagnant layer model, equation (1) is discretized over some laminar layer thickness (δ) in which transport is assumed to be diffusive only.

$$flux = \frac{D_{gas}}{\delta} (C_b - C_a) \quad (2a)$$

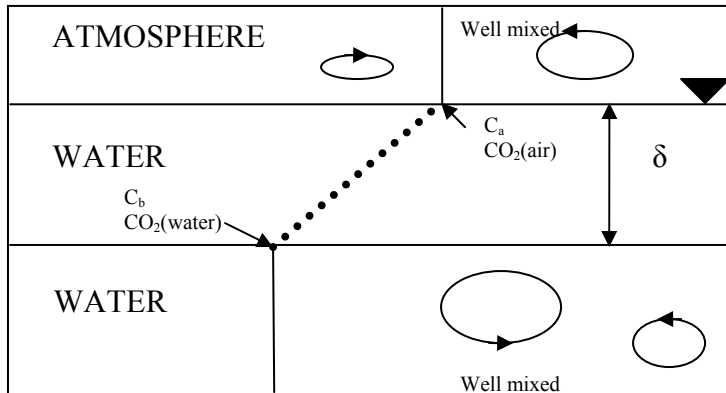


Fig. 2. Stagnant layer model representing a laminar diffusive layer of gas transport into or from the atmosphere and estuary. C_a represents concentration of the top layer equilibrated with the atmosphere and C_b represents the concentration of the bottom layer in equilibrium with the liquid layer. Above and below the atmospheric and water boundaries are assumed to be well mixed.

A schematic for the stagnant layer model is illustrated in Fig. 2. In terms of dissolved CO₂ it is assumed that $C_a = [CO_{2(air)}]$ and $C_b = [CO_{2(water)}]$. In this study, however, dissolved gases were investigated and partial pressures were measured rather than concentrations. Partial pressures are converted into concentrations where K_o represents the solubility coefficient (Weiss 1974) and x may represent the air or liquid side concentration:

$$[CO_{2(x)}] = K_o pCO_{2(x)} \quad (2b)$$

Equation (2c) is derived from equation (2a) where a sole gas transfer term, known partial pressures and the solubility coefficient are used to calculate gas fluxes.

$$flux = kK_o (pCO_{2(water)} - pCO_{2(air)}) \quad (2c)$$

Here $k = D_{gas}/\delta$, and δ 's parameterization affects D_{gas} in such a way as to allow k to increase or decrease based on the size of some theoretical surface microlayer usually assumed to be between 20 and 200 μm thick (Jähne and Hauecker 1998). Since the gas transfer coefficient is proportional to the reciprocal of the diffusive layer ($k \propto \frac{1}{\delta}$) k becomes very large as the microlayer becomes very small.

In addition to a liquid side diffusive layer there is also an air side diffusive layer. However in most gas transfer calculations the diffusive layer on the air side is neglected. The Schmidt number (Sc) relates the strength of diffusion (D) to that of kinematic viscosity (ν) as in equation (3) (Jähne and Hauecker 1998).

$$Sc = \frac{\nu}{D} \quad (3)$$

Using Sc , molecular diffusion and the diffusion of momentum in the fluid can directly be compared. The air side boundary Sc for CO₂ is roughly 0.83 (viscous resistance to mass transport and diffusive resistance are roughly equal), while the liquid side commonly has a Sc

value of 600-1000 (Jähne and Hauecker 1998). The liquid side molecular diffusion is roughly 600-1000 times weaker than the diffusion of momentum. Thus, with sparingly soluble gases like CO₂, the liquid boundary supplies a greater resistance than the air boundary (i.e. the rate limiting step) to gas transfer over the air-sea interface. Therefore, resistance to gas transfer from the liquid phase dominates transport across the interfacial layer.

The second model, the surface renewal model (Dankwerts 1970), defines the gas transfer speed as a function of the residence time of a parcel of water at the surface layer, controlled by stream turbulence and the diffusion rate of gas (equation 4 & Fig. 3),

$$flux = \sqrt{D_{gas}} r K_o (pCO_{2(water)} - pCO_{2(air)}) \quad (4)$$

where D_{gas} is the diffusion coefficient of CO₂ and r is a renewal rate based on turbulent properties of the fluid. Herein the theoretical development of the surface renewal model is discussed.

The surface renewal model assumes a fractional surface age distribution where exposure time is controlled by turbulent properties of the fluid. Here the fractional surface area at any given time of exposure is defined as $S(r, t) = re^{-rt}$. Thus, the flux for one fractional surface area at a given age is:

$$flux = D \frac{\partial C}{\partial z} re^{-rt} \quad (5)$$

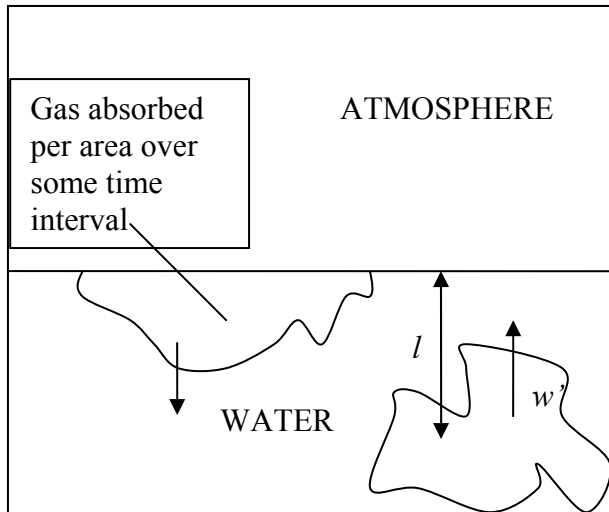


Fig. 3. Drawing of the surface renewal model. The arrow signifies vertical movement of a water parcel at the velocity w' over some mixing length l . Water is then equilibrated with the atmosphere and returned again to depth. The renewal model assumes mixing is over the entire water column (top to bottom).

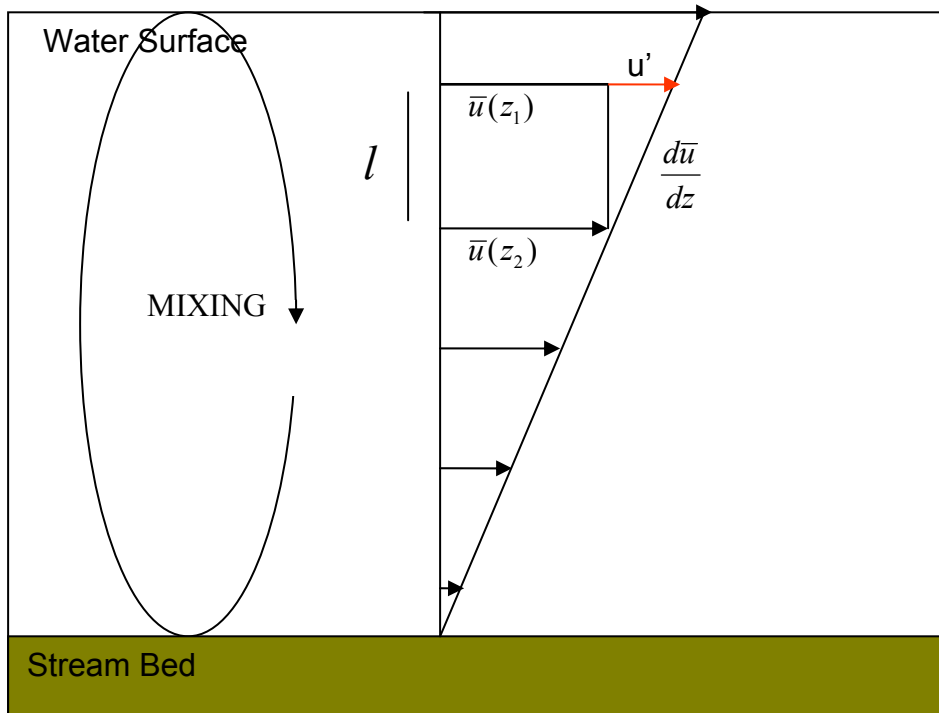


Fig. 4. Schematic for relationship between current shear and surface renewal (Granger 1995). The red arrow represents turbulent fluctuations around the mean velocities (u') and the mixing length (l) can be related back to the velocity gradient in the water column.

A geometrical argument is made in Fig. 4 to relate renewal rates to measurable estuarine velocity gradients and derived in equations (6a-6c). Fluctuations in velocity responsible for mixing are equal to the difference in mean velocities at particular depths z_1 and z_2 (Granger 1995).

$$u' = \bar{u}_{z_1} - \bar{u}_{z_2} = (z_1 - z_2) \frac{d\bar{u}}{dz} \quad (6a)$$

Additionally, the scale of mixing is the distance between the two points of known average velocities at z_1 and z_2 ; so a vertical mixing length (l) can be estimated where $l = z_1 - z_2$. This leads to a new equation that relates turbulent velocity fluctuations and the mixing length to the estuarine vertical velocity gradient:

$$\frac{u'}{l} \approx \frac{d\bar{u}}{dz} \quad (6b)$$

Along with the assumption that the absolute values of the turbulent velocity fluctuations are on the same scale in all directions ($|u'| \sim |w'|$), a fluid parcels speed over its mixing length leads to a surface renewal rate:

$$r \approx \frac{|u'|}{l} \approx \frac{|w'|}{l} \approx \frac{d\bar{u}}{dz} \approx \frac{u}{h} \quad (6c)$$

Current speeds are assumed to decrease linearly with depth to 0 at the stream bed (Fig. 4) therefore the renewal rate can be calculated from the velocity gradient in terms of the whole water column (equation 6c). This leads to a rough time scale for surface renewal based on measurable current velocities eliminating the need for measuring the fine scale turbulent processes directly (O'Connor and Dobbins 1956).

Given the flux over the fractional surface area as a function of the exposure time and the renewal rate from individual exposure times (equation 5), the total flux can be calculated by integrating surface areas over all the times of exposure (t) ranging from 0 to ∞ .

$$flux = -D_{gas} r \int_0^{\infty} e^{-rt} \left(\frac{\partial C}{\partial z} \right)_{z=0} dt \quad (7)$$

Often times when deriving the surface renewal model a renewed laminar surface layer is assumed (Dankwerts 1970), however, laminar flow rarely exists in nature therefore O'Connor and Dobbins (1956) developed a model (equations 8 & 9) whereby water is periodically mixed totally and instantly from top to bottom. Thus, equation (7) can be solved (Appendix 1) and evaluated at the surface ($z = 0$) yielding equation (8).

$$flux = (C_a - C_w)(D_{gas} r)^{1/2} \tanh\left(\frac{rh^2}{D_{gas}}\right)^{1/2} \quad (8)$$

In terms of gas transfer velocities, k is now a function of the diffusion coefficient of a dissolved gas and surface renewal to the half power, multiplied by the hyperbolic tangent of renewal rates, diffusion and the stream or estuary depth (h).

$$k = \frac{flux}{(C_a - C_w)} = (D_{gas} r)^{1/2} \tanh\left(\frac{rh^2}{D_{gas}}\right)^{1/2} \quad (9)$$

Given ordinary renewal rates of 1 s^{-1} and 0.1 s^{-1} and with a diffusion coefficient for CO_2 in water of about $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ the $\tanh\left(\frac{rh^2}{D_{gas}}\right)^{1/2}$ term tends to 1 at depths of just a few micrometers.

Therefore for estuarine and riverine cases, the $\tanh\left(\frac{rh^2}{D_{gas}}\right)^{1/2}$ term goes to 1:

$$k = \sqrt{D_{gas} r} \quad (10)$$

As stated in equation 6, current shear is a good proxy for surface renewal rates ($r \sim u/h$) which can be incorporated into equation (10) to yield equation (11).

$$k = \sqrt{D_{gas} \frac{u}{h}} \quad (11)$$

Taking the square root of the diffusion coefficient of CO₂ in freshwater at 20 °C, (1.6545 X10⁻⁹ m² s⁻¹ in terms of a Sc of 600) a simple model can be derived for k_{600} based on equation (11), where k_{600} is in units of cm hr⁻¹ and u and h are in units of m s⁻¹ and m respectively.

$$k_{600} = 14.6 \sqrt{\frac{u}{h}} \quad (12)$$

By comparison, the stagnant layer model calculates interfacial transport in terms of a stagnant diffusive layer where $k = \frac{D}{\delta}$, while the surface renewal model calculates interfacial transport in terms of a dynamic surface constantly renewed as $k = \sqrt{Dr}$. These two conceptual models provide the framework for most gas transfer studies.

Chamber Fluxes

Fluxes determined from floating chambers have long been a subject of contention, with critics on one hand (Liss and Merlivat 1986; Belanger and Korzum 1991; Raymond and Cole 2001; Matthews et al. 2003) and determined proponents on the other (Marino and Howarth 1993; Borges et al. 2004b; Guerin et al. 2007; Tokoro et al. 2007). The primary critical contention is that the chamber wall blocks wind and therefore blocks one of the dominant processes in gas transfer. However, as stated above, for sparingly soluble gases like CO₂, gas

transfer is controlled by the liquid phase. Therefore as long as the turbulent properties of the fluid are preserved, adequate flux and hence gas transfer velocity values should be obtainable.

Two studies have discounted floating chamber derived fluxes altogether. Belanger and Korzum (1991) determined that temperature and pressure changes within the floating chamber are able to bias results. However, that study demonstrated that hours were required to bias results due to temperature and pressure variations, while most flux measurements with floating chambers are measured over the order of minutes. Moreover, another study by Matthews et al. (2003) reports discrepancies between fluxes determined with a floating chamber and SF₆ evasion rates, although their floating chamber was deployed in stagnant water where uncertainty with chamber fluxes are already known (Kremer et al. 2003).

In contrast to the studies that dismiss floating chamber flux measurements, there are a number of studies that have demonstrated the viability of this method. For example, four deployments where floating chambers with adjustable speed internal fans were compared with un-fanned ‘control’ chambers released at the same time in an enclosed windless bay in an effort to gauge the potential effects of wind blockage on k (Kremer et al. 2003). Under moderate wind conditions simulated by the enclosed fan, agreement was found between two deployments within 1-12% demonstrating that wind blockage from the chamber incurs a nominal error. That same study also compared a number of mass balance studies (O₂, ²²²Rn, ³He) with chamber experiments and found agreement within 10-30% for measured gas transfer velocities between the different methods, further providing evidence for the reliability of floating chamber studies. In addition, Frankignoulle et al. (1996b) compared floating chamber studies with commonly accepted results for k_{600} by Wanninkhof (1992) and Liss and Merlivat (1986) measured over a coral reef. Their results demonstrate that chamber studies do not over-predict gas transfer

velocities due to chamber wall generated turbulence but, instead, agreed with commonly cited geochemical tracer studies relating U_{10} to k . Most recently, Guerin et al. (2007) measured gas transfer velocities in a tropical reservoir in French Guiana and its downstream portion. They were able to relate floating chamber derived fluxes to those determined by the eddy covariance method and found agreement between the two methods within 30%. In addition, there is also great variation among other methods of measuring k . For example, based on the controlled flux technique, Zappa et al. (2003) determined gas transfer velocities that are as much as 8 cm hr^{-1} higher than those determined by Carini et al. (1996), who used the geochemical tracer SF_6 in the Parker River estuary.

Based on the high temporal resolution of measurement times (10 – 15 min.) and the demonstrated viability in the estuarine zone, floating chambers were chosen to measure CO_2 fluxes in this Duplin River study. Here a floating chamber was deployed from Marsh Landing dock at the mouth of the Duplin River and gas transfer velocities were determined over the winter of 2006-2007.

CHAPTER 2

MATERIALS AND METHODS

Site location and description

The Duplin River is a 13 km long tidal creek located on the west side of Sapelo Island near the mouth of the Doboy Sound. It is a marsh-dominated estuarine system with little fresh water input (Chalmers 1985). Fresh water that is brought in is delivered only through rain on its upland and the adjacent marshes, and via discharge from the Altamaha River to the south. This discharge varies throughout the year and during high discharge seasons (winter and spring) the Duplin may receive more fresh water from the Altamaha River. Water circulation within the Duplin River is driven almost totally by tidal action over a 2-3 m range. Gas transfer velocities were measured based on fluxes measured with a floating chamber at the Marsh Landing Dock (Fig. 5) near the mouth of the Duplin River, roughly 36 meters from the top of the marsh bank.



Fig. 5. Sapelo Island, Georgia with Marsh Landing Dock circled in red.

Field measurements

Seven experiments were carried out over the winter of 2006-2007 throughout half tidal cycles: on December 7, 2006; February 7 and 8, 2007; March 3 and 4, 2007; and March 26 and 27, 2007. Over these sampling dates 100 deployments were carried out at night and recorded over 10-15 minute durations. Ten to fifteen minutes was chosen as the floating chamber deployment time length to ensure no leaks or contamination of the CO₂ signal was incurred.

Deployments at night were chosen to avoid artificial increases in temperatures and pressure within the chamber due to solar heating. After each deployment, the chamber was lifted and allowed to return to atmospheric levels prior to redeployment. To ensure the integrity of CO₂ fluxes into the chamber, the $dpCO_2/dt$ term in all chamber deployments had coefficients of determination (r^2) of values 0.90 or higher, with the exception of two deployments on February 7th which correspond to the lowest interfacial pCO₂ levels seen in the study. On the night of February 7, pCO₂ in the water oscillated between above and below atmospheric levels. Large errors are known to be associated with low interfacial pCO₂ gradients in gas transfer velocity measurements (Borges et al. 2004b) and therefore transfer velocities where the $\Delta pCO_2 < 35$ μatm , corresponding to uncertainties in the flux term of greater than 30%, were excluded; on all other experimental nights the interfacial pCO₂ gradient was sufficiently high to keep the error below 3% (Borges et al. 2004a).

Due to the ebbing and flooding of the tides, the current direction oscillated between up and down-river. The chamber was always deployed on the dock side going into the current to minimize the impact of dock pylons on water turbulence and the subsequent gas transfer velocities (Fig. 6). On most deployments the chamber was allowed to drift free with only minor restraint from the top. However, at high current speeds ($u > \sim 0.4 m s^{-1}$) the chamber was tied off from the front to prevent its movement underneath the Marsh Landing dock (Fig. 10).

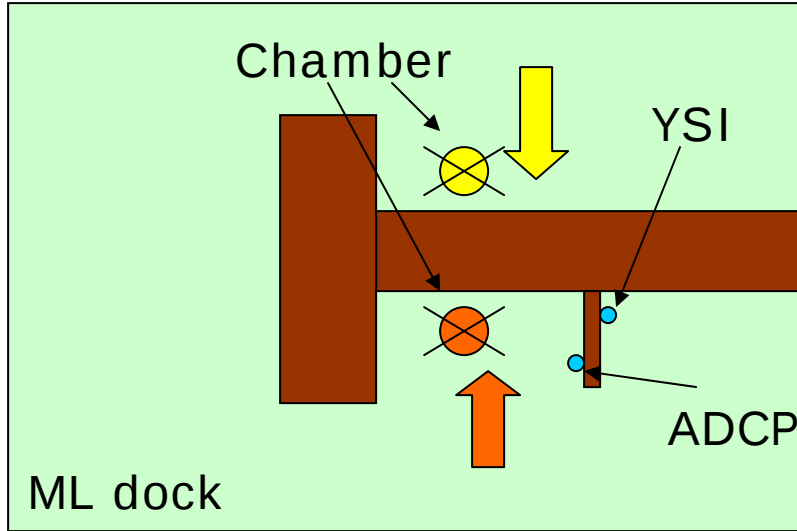


Fig. 6. Map of Marsh Landing Dock. The brown area represents Marsh Landing dock while the colored arrows signify the direction of the current; the circles with crosses signify the chamber deployment side. Therefore, if the current is from above the dock the chamber was deployed above the dock. The two blue dots represent the acoustic doppler current profiler and YSI conductivity and temperature sensor placement.

CO₂ flux calculation from chamber pCO₂ measurements

Based on the change in partial pressure of CO₂ with time measured directly by the floating chamber, gas fluxes were determined using equation 13 where V is the volume (m³) of the chamber and system hoses, $R = 8.2 \times 10^{-5} \text{ atm m}^{-3} \text{ mol}^{-1} \text{ K}^{-1}$ is the ideal gas constant, T is the outside air temperature (K), and S is the water surface area (m²) in the chamber (Frankignoulle 1988).

$$flux = \left(\frac{d(pCO_2)}{dt} \right) \left(\frac{V}{RTS} \right) \quad (13)$$

Interfacial CO₂ gradient measurement

Surface water was continually pumped to the dock via a peristaltic pump (Cole-Palmer instrument Co. model: 7591-50) from roughly 0.3 m below sea surface (Fig. 7). Water was then sprayed into a large equilibrator in which air in the equilibrator headspace comes into equilibrium with the water pCO₂. The headspace volume was then circulated through a separate system, dried with magnesium perchlorate and pumped to a Li-Cor 7000 Infrared gas detector for pCO₂ measurement. After the pCO₂ determination, air was then returned to the equilibrator (Fig. 7). All pCO₂ calculations were corrected for vapor pressure and calculated at 1 atm assuming 100% saturation of water vapor at the *in-situ* temperature. Concentrations of CO₂ in the water and air were then calculated using solubility relationships determined by Weiss (1974).

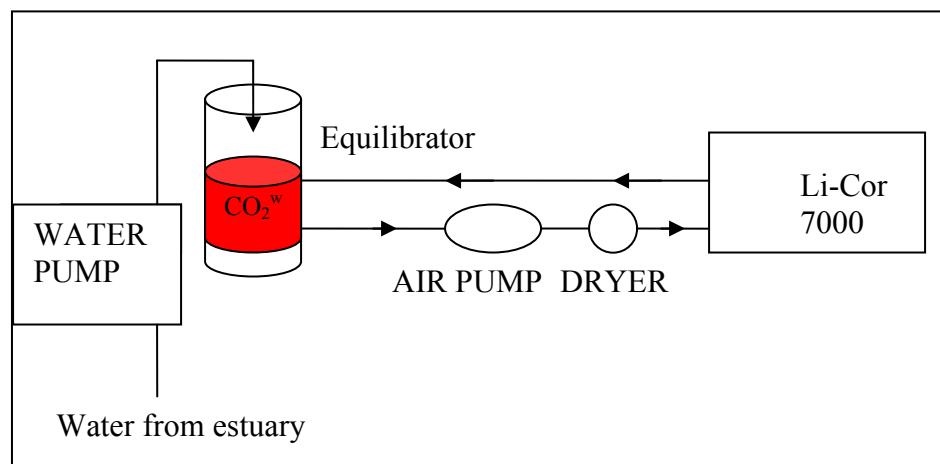


Fig. 7. Schematic depicting system used to measure water pCO₂. Water is pumped up from depth and equilibrated with an enclosed chamber. Equilibrated air is then pumped out and dried with magnesium perchlorate before being analyzed with a Li-Cor infrared gas detector and returned to the equilibrator.

Chamber deployment

Direct CO₂ fluxes were measured with the floating chamber concurrently with measurements of gas partial pressure gradients of CO₂ over the interfacial boundary. This enabled the calculation of gas transfer velocities over a variety of wind and current speeds in an effort to determine dominant factors in coastal CO₂ gas transfer.

The chamber was roughly based on that of Frankignoulle and Disteche (1984) and is essentially an overturned bowl with semi-rigid walls designed to trap gas flux across the air-sea interface (Figs. 8 a and b).

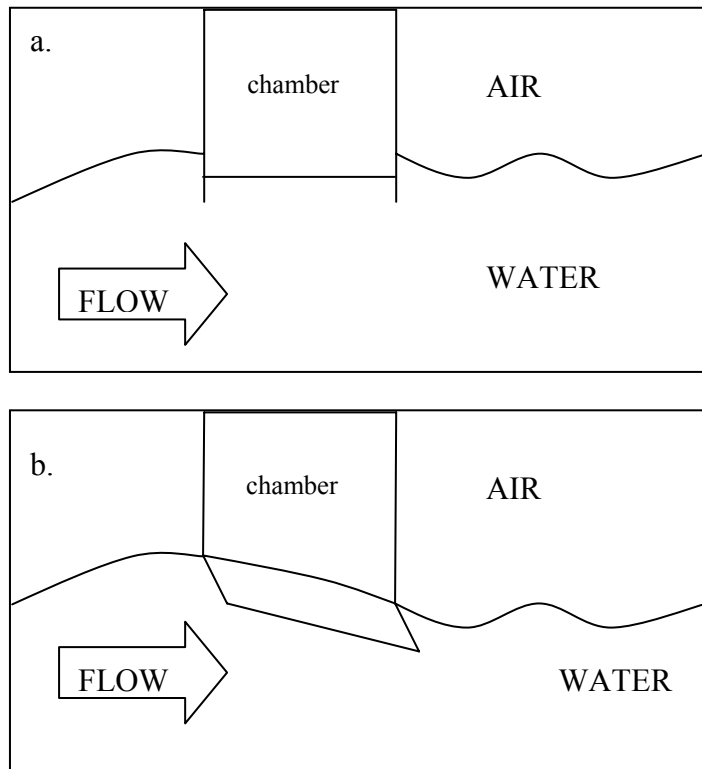


Fig. 8. (a) Schematic showing prior designs for flux chamber with rigid walls. (b) Schematic showing augmented design for the flux chamber where the wall is allowed freer movement.

The floating chamber has a volume (with hoses and dome) of roughly 37 liters of air, a surface area of 0.07 m^2 and a height of 40.8 cm. The bottom lip of the chamber is a sunken buoyant ‘soft wall’ at roughly 2-3 cm depth which moved slightly with wave motion minimizing its impact on fluid movement(Figs. 8 a and b). The soft wall (skirt) was constructed from a gas impermeable plastic sheet, with weighted (approx. 100 2.5 g pellets) floats sewn into the bottom lip of the skirt.

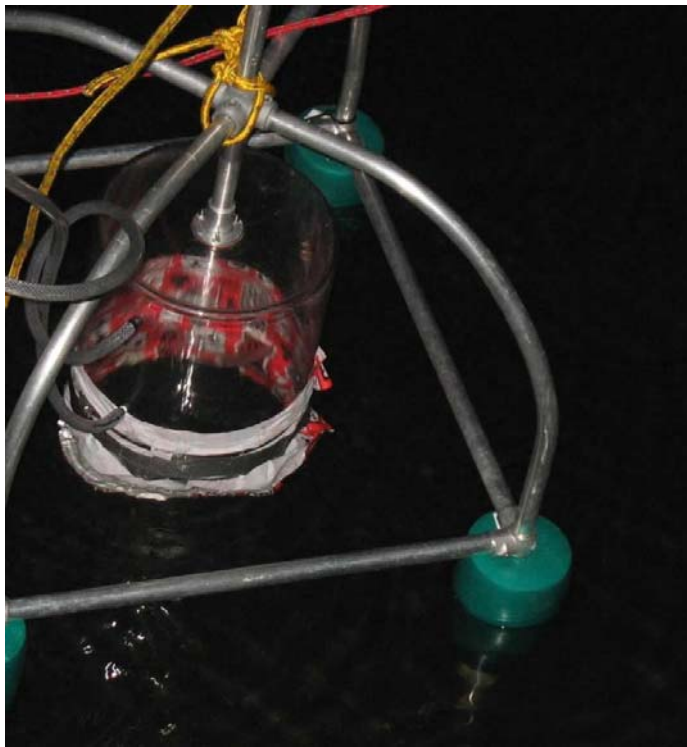


Fig. 9. Floating chamber with 2-3cm sunken skirt.



Fig. 10. Floating chamber tethered from front to prevent movement under dock. This is an example of a high current speed deployment.

The skirt and stitching were sealed with silicon glue to ensure gas and water impermeability. While this design will not completely eliminate the ‘chamber wall’ effect on measured gas transfer velocities, it is designed to reduce effects of the chamber movement on the sea surface integrity. The chamber was housed in a spider-like apparatus comprised of a cross at the top connected to four legs with floats that sit in the water. Using this analogy, the measurement chamber is ‘hung’ from the belly of the spider. Air was continuously pumped through the chamber on one large loop whereby a small amount is pulled out in a separate loop and run through a Li-Cor 840 infrared CO₂ gas detector (Fig. 11).

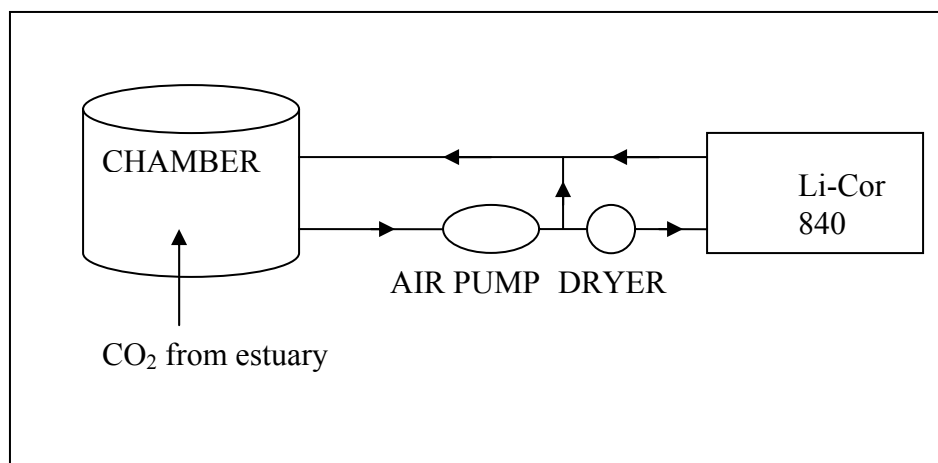


Fig. 11. Schematic of analytical setup for chamber flux measurements. CO_2 is gained to or lost from the floating chamber and while air is circulated through the tubing by a large diaphragm pump a small amount of air is split off dried with magnesium perchlorate and sent to a Li-Cor infrared gas detector for constant CO_2 measurement.

Both Li-Cor infrared gas detectors were calibrated for 0, 502.1, and 1000 μatm CO_2 gas standards before the start of the ~ 6 hr experiments and then checked again at the end of each experiment date with consistent agreement within 4 μatm of the original calibration. The two Li-Cor infrared gas detectors were also checked against each other by deploying the floating chamber with both Li-Cors attached in tandem on two separate occasions, February 7 and March 26, and agreed within 2 μatm .

Calculation of k measured (k_m)

Given the fluxes and interfacial concentration gradients, gas transfer velocities can then be calculated:

$$k_m = \frac{flux}{K_o \left(\overline{pCO_2^{water}} - p(CO_2^{air}) \right)} \quad (14)$$

The $\overline{pCO_2^{water}}$ term represents the average water pCO₂ for any particular chamber deployment. pCO₂^{air} is the initial value in the pCO₂ chamber prior to any particular deployment after the chamber has equilibrated with the atmosphere. For comparison, all measured gas transfer velocities are converted to a Sc of 600 (CO₂ at 20 °C). Because this is a turbulent system with a smooth surface, gas transfer velocities are assumed to be proportional to Sc^{-0.5} (Jähne and Hauecker 1998).

$$k_{600} = k_m (600 / Sc_m)^{-0.5} \quad (15)$$

Schmidt numbers calculated in this study (Sc_m) were taken from empirical measurements reported in Wanninkhof (1992) based on Sc values for seawater; where dissolved gas diffusivities and viscosity have been determined empirically over a variety of temperatures for freshwater and seawater.

Estuary tidal and wind currents

Wind speeds averaged over 15 minutes were collected from the Georgia Coastal Ecosystem SINEER-LTER meteorological station, located 10 m above the ground at Marsh Landing dock. Average wind speeds were then linearly interpolated over the time of deployment. In conjunction with wind speed measurements, current velocity profiles were determined with a Broadband 1228.8 kHz Sentinel RDI Acoustic Doppler Current Profiler, and time averaged over 100 pings or 131 seconds and bin sizes of 10 cm. The ADCP was also

tethered to the dock (Fig. 6) on a rigid platform where only the sensors were submerged (Fig. 12). Current speeds were calculated at a one meter depth. The currents speeds reported for comparison with gas transfer velocities represent an average value over the duration of the chamber deployment (~15min).



Fig. 12. Tethered ADCP on floating dock.

Temperature and Salinity

Temperature and salinity were measured every 30 seconds with a YSI 6000 conductivity and temperature sensor. The sensor was submerged to a depth of 10 cm roughly 8 meters from the chamber deployment on a separate side of the floating dock (Fig. 6). All temperature values

used in gas transfer velocity determination were also averaged over the duration of chamber deployment. Air temperature was taken in 15 minutes averages from the Georgia SINEER-LTER weather station.

CHAPTER 3

RESULTS

Background hydrography

Listed below is information about the changing hydrography with tidal height on all experiment dates. In addition, the relevant quantities for the flux calculations and Sc conversions per deployment are reported in Tables (1 – 7), this includes $dpCO_2/dt$ term (Figs. 13 a and b) as measured from the floating chamber, the interfacial CO_2 gradient (ΔpCO_2), air and water temperatures, salinity and k measured (k_m) along side k_{600} . The error associated with the gas transfer velocity measurements related to a change in volume of the floating chamber from waves is assumed to be less than 4.92% based on a chamber height change of less than 2 cm due to waves and/or rocking of the chamber.

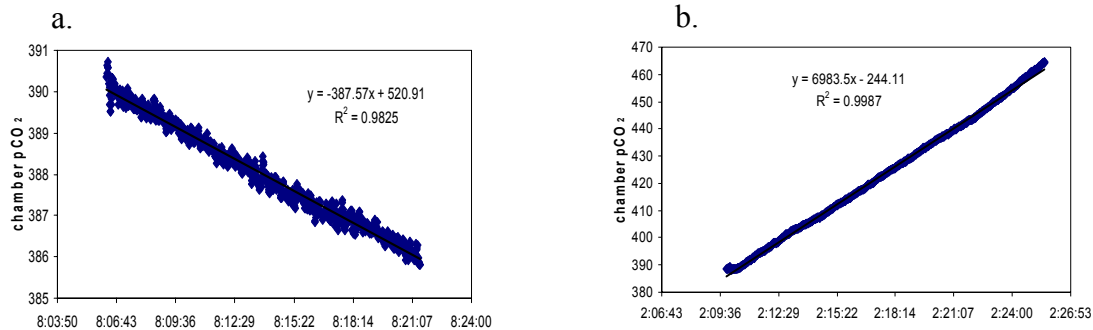


Fig. 13. (a) The $dpCO_2/dt$ term within the chamber, where the CO_2 flux is into the Duplin River. (b) The $dpCO_2/dt$ term within the chamber, where the CO_2 flux is into the atmosphere from the Duplin River.

December 7

On December 7 (Fig. 14a), sampling started at 19:49 before the slack high tide (21:51 12/7/2006) and ended around 03:06 on 12/8/2006 near slack low water (04:01 12/8/2006). The temperature and salinity increased as ocean water entered into the Duplin River and subsequently decreased as water was again exported back to the ocean. The $p\text{CO}_2$ started at 990 μatm and increased to a high of 1016 μatm before decreasing to a value of 850 μatm shortly after the high tide maximum depth and then again increased back up to 1049 μatm . Over the sampling period, the temperature increased from 14.7°C to a maximum of 14.8°C then decreased back to 14.1°C reflecting the lower temperature of the Duplin River over the ebbing tide. The salinity at the beginning of the experiment started at 29.2 and increased to a maximum of 30.6 with the incoming tides and then to a low of 29.5 with the ebbing tide. Current speeds show an initial decrease due to the flooding tide and a subsequent increase after slack tide when the ebb tide begins to a maximum of 0.33 m s^{-1} . There is then a lull in current speeds before the return to speeds of 0.35 m s^{-1} . A discontinuity (~ 0.5 m) is seen in the tidal height around 1:00 on 12/8/2006 (Fig. 14a) corresponding to the lull in the current speeds (Fig. 14c). Since the physical mechanisms causing both these phenomena (the lull in the current speeds and the tidal height discontinuity) are unclear, gas transfer velocities cannot be compared to current speeds over this period and are excluded from comparisons of k_m or k_{600} with u or U_{10} .

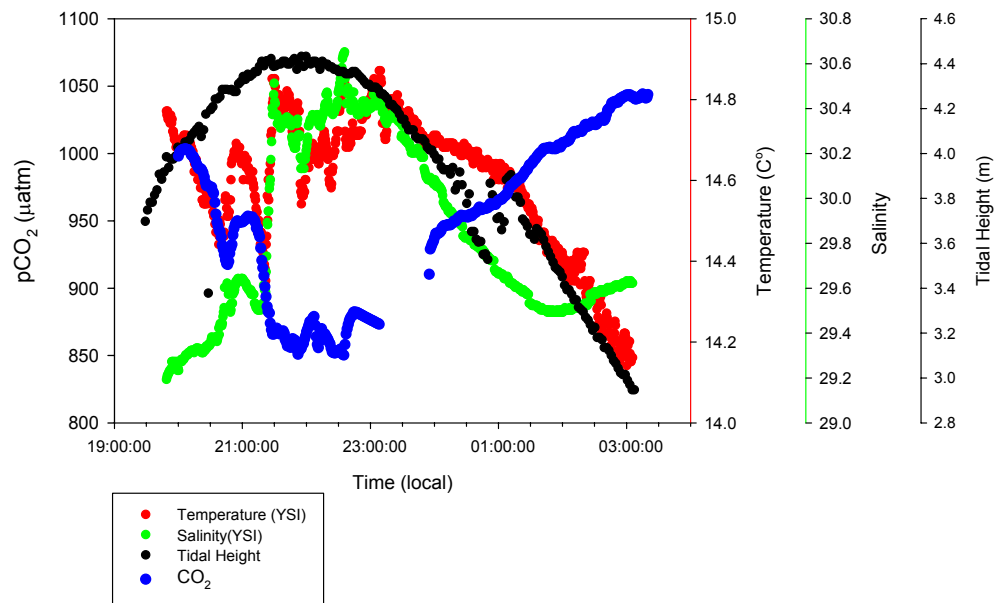


Fig. 14a. Background hydrography for December 7; the blue line is the $p\text{CO}_2$, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

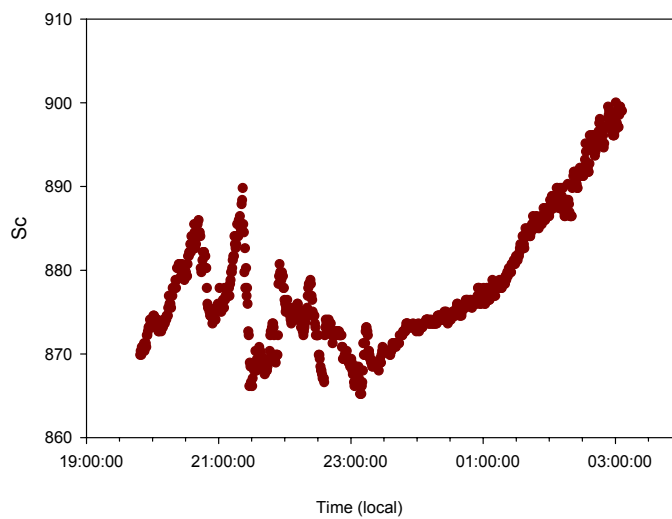


Fig. 14b. Schmidt number (Sc) vs. time for December 7, 2006.

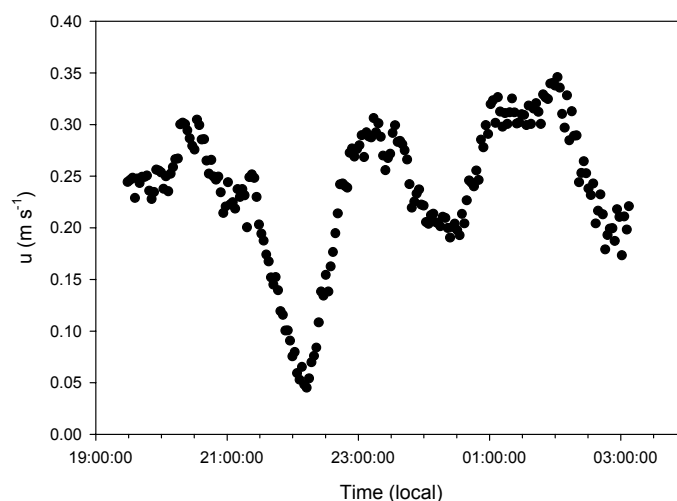


Fig. 14c. Current speed in the Duplin River over December 7.

As can be seen in Fig. 14a., $p\text{CO}_2$ was not recorded over the period of 23:08 – 23:55 due to ice formation within the air hose connecting the equilibrator and infrared gas detector; therefore the chamber was not deployed during this period. All the relevant parameters in calculating k_m and k_{600} are listed in Table 1 and discussed herein. The $dp\text{CO}_2/dt$ was inconsistent over the December 7 half tidal cycle ranging from 3.02×10^{-2} to $1.5 \times 10^{-1} \mu\text{mol CO}_2 \text{ s}^{-1}$. The interfacial ΔCO_2 was always greater than 444 μatm with a maximum at high tide around 651.7 μatm , reflecting the increased Duplin River $p\text{CO}_2$ due to a high marshland $p\text{CO}_2$ signal. In terms of gas transfer rates, both measured and normalized, k_m were in the range of 10.17 to 38 cm hr^{-1} and k_{600} were in the range of 12.37 to 46.21 cm hr^{-1} . Sc values are slightly higher than the value of 600 to which k_m was normalized; the initial Sc was at 870 and increased to a maximum of 890 near the end of the experiment. This led to maximum differences in the measured and calculated k 's of 21.7% (Fig. 14b).

Table. 1 Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for December 7.

Date/time (local)	$dpCO_2/dt$ $\mu atm CO_2 s^{-1}$	r^2	Temperature $^{\circ}C$		Salinity	ΔpCO_2 μatm	k_m $cm hr^{-1}$	k_{600} $cm hr^{-1}$
7-Dec-2007			(air)	(water)				
20:04	5.75×10^{-2}	0.9989	12.2	14.6	29.3	598.7	15.97	19.42
20:35	3.72×10^{-2}	0.9983	11.7	14.5	29.5	544.9	11.21	13.64
20:52	4.24×10^{-2}	0.9994	11.5	14.7	29.6	559.2	12.37	15.04
21:14	4.15×10^{-2}	0.9931	11.0	14.5	29.8	512.7	13.05	15.87
21:34	5.18×10^{-2}	0.9956	10.9	14.6	30.3	474.2	17.59	21.40
21:52	3.55×10^{-2}	0.9988	10.7	14.8	30.3	489.1	11.62	14.13
22:11	3.08×10^{-2}	0.9902	10.5	14.6	30.4	444.3	11.04	13.43
22:29	3.02×10^{-2}	0.9908	10.3	14.7	30.5	498.6	12.13	14.75
22:50	4.38×10^{-2}	0.9970	10.1	14.7	30.4	522.0	13.21	16.07
23:56	4.37×10^{-2}	0.9993	9.7	14.8	30.2	549.0	12.36	15.03
1:31	9.28×10^{-2}	0.9987	6.4	14.5	29.5	595.3	21.80	26.51
1:50	6.85×10^{-2}	0.9986	5.7	14.4	29.5	610.4	15.32	18.63
2:10	8.08×10^{-2}	0.9987	5.4	14.4	29.5	628.8	17.40	21.15
2:30	5.70×10^{-2}	0.9989	4.8	14.3	29.6	637.2	11.84	14.40
2:49	5.07×10^{-2}	0.9988	4.3	14.2	29.6	651.7	10.17	12.37

February 7

Sampling began around 19:49 on 2/7/2007 roughly an hour after low tide (Fig. 15a), continued through the subsequent high tide (23:43 2/7/2007), and terminated around 05:45 on 2/8/2007 at low tide (05:55 2/8/2007). The objective for this experiment date was to gather gas transfer velocity measurements over as much of the entire tidal cycle as possible given the time constraints imposed by the ferry schedule from Marsh Landing dock. The initial pCO_2 was 381 μatm and decreased below atmospheric pCO_2 ($\sim 370 \mu atm$) at 19:50 on 2/7/2007 to a minimum of 323 μatm . The pCO_2 then increased back above atmospheric levels to 450 μatm at 6:00 on 2/8/2007. This is the first time pCO_2 levels in the Duplin River were found to be below atmospheric levels. The salinity was 21.1 around the beginning of the experiment, increased to 24.6 at high tide and fell back to 23.0 at the subsequent low tide. The temperature started out at

10.9°C and increased to 11.4 °C around mid flood tide and then stabilized at 10.9°C. The beginning of current speed measurements corresponded to the flooding tide with speeds of 0.27 m s⁻¹ towards the slack tide lowest speed. Then there is a sharp increase in current speeds at the beginning of the ebbing tide and a slow decrease in current speeds until slack low tide (Fig. 15c).

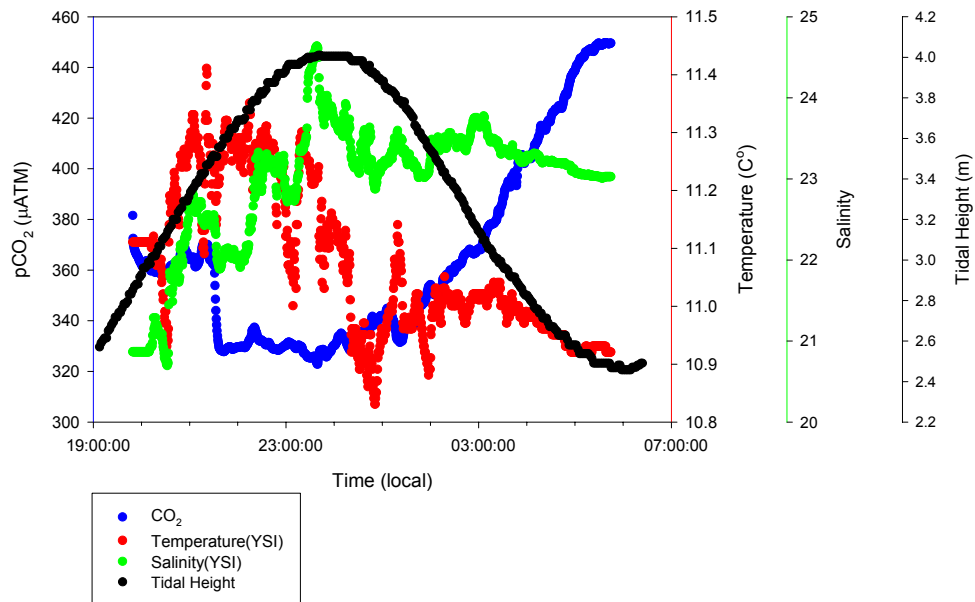


Fig. 15a. Background hydrography for February 7; the blue line is the pCO₂, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

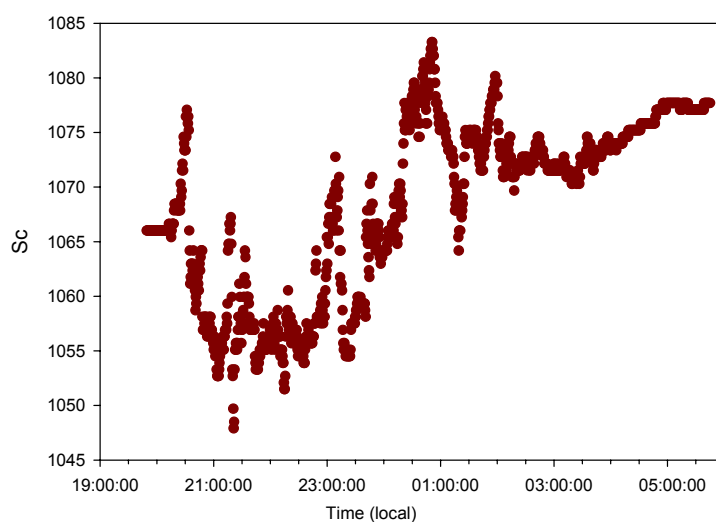


Fig. 15b. Schmidt number (Sc) vs. time for February 7, 2007.

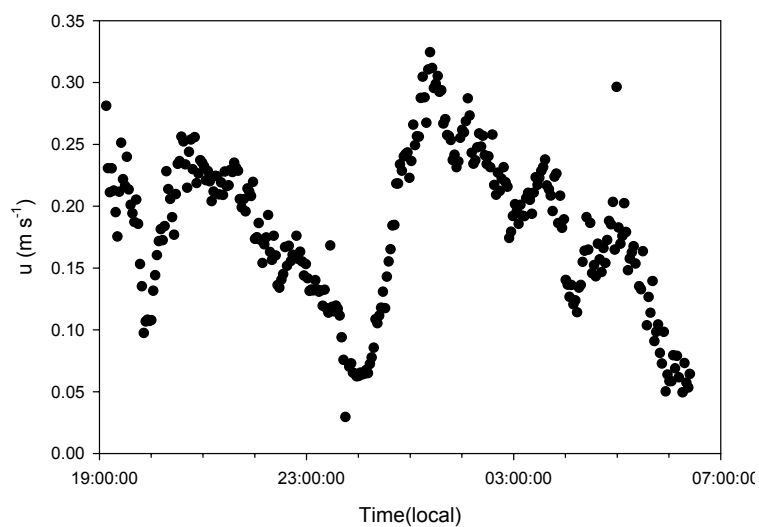


Fig. 15c. Current speed in the Duplin River over February 7.

All the relevant parameters in calculating k_m and k_{600} are listed in Table 2 and discussed herein. On all deployments CO_2 partial pressures are below the atmospheric partial pressures of roughly $390 \mu\text{atm}$ and during these times fluxes were into the estuary with the exception of the

last two deployments at times 4:35 and 5:14 on 2/8/2007. This deployment date exhibits the lowest r^2 values in the $dpCO_2/dt$ term due to scattering resulting from the interfacial pCO_2 differences of almost zero. The $dpCO_2/dt$ was in the range from -2.08×10^{-3} to $1.04 \times 10^{-3} \mu\text{mol CO}_2 \text{ s}^{-1}$. Initial interfacial ΔpCO_2 levels were -70.4 at the beginning of the half tidal cycle and increased to a final value of 51.5 μatm . In terms of gas transfer rates both measured and normalized, k_m range from 2.65 to 5.35 cm hr^{-1} and k_{600} values ranged from 3.54 to 8.49 cm hr^{-1} . Sc values measured are higher than the value of 600 to which k_m was normalized; therefore, Sc began at 1066 and increased toward 1075 at the end of the experiment suggesting that viscous transport on CO_2 was much stronger than diffusive transport due to the low temperature. The colder water temperatures led to differences between k and k_{600} of up to 33.8% (Fig. 15b).

Table 2. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for February 7.

Date/time (local)	$dpCO_2/dt$ $\mu\text{atm CO}_2 \text{ s}^{-1}$	r^2	Temperature $^{\circ}\text{C}$		Salinity	ΔpCO_2 μatm	k_m cm hr^{-1}	k_{600} cm hr^{-1}
7-Feb-2007			(air)	(water)				
22:44	-1.77×10^{-3}	0.9387	10.8	11.2	23.1	-70.4	3.89	5.21
23:06	-1.84×10^{-3}	0.8495	11.1	11.2	23.1	-72.3	3.96	5.30
23:28	-1.20×10^{-3}	0.9501	11.4	11.2	24.1	-71.9	2.65	3.54
0:07	-1.79×10^{-3}	0.9826	12.6	11.0	23.4	-56.8	5.13	6.86
0:56	-2.08×10^{-3}	0.9823	11.8	11.0	23.3	-52.3	6.35	8.49
4:35	7.69×10^{-4}	0.8971	10.4	10.9	23.1	37.0	3.18	4.25
5:14	1.04×10^{-3}	0.9434	9.8	10.9	23.0	51.5	3.02	4.04

February 8

Sampling began following the low tide (17:56 2/8/2007) around 19:22 on 2/8/2007 (Fig. 16a) and continued until 00:15 on 2/9/2007 after high tide (23:56 2/8/2007). The $p\text{CO}_2$ started at 360 μatm and decreased to 308 μatm leading up to high tide. Temperature increased over the half tidal cycle from 11.5°C to 11.8°C suggesting that the ocean water was warmer than the upper tidal creek water. The salinity increased from 22.7 at low tide to 26.7 around the high tide mark. Current speeds were captured over the flooding tide with a sharp initial increase in current speeds to a maximum speed of 0.36 m s^{-1} and subsequent reduction to roughly 0 m s^{-1} toward slack high tide at the end of the experiment (Fig. 16a).

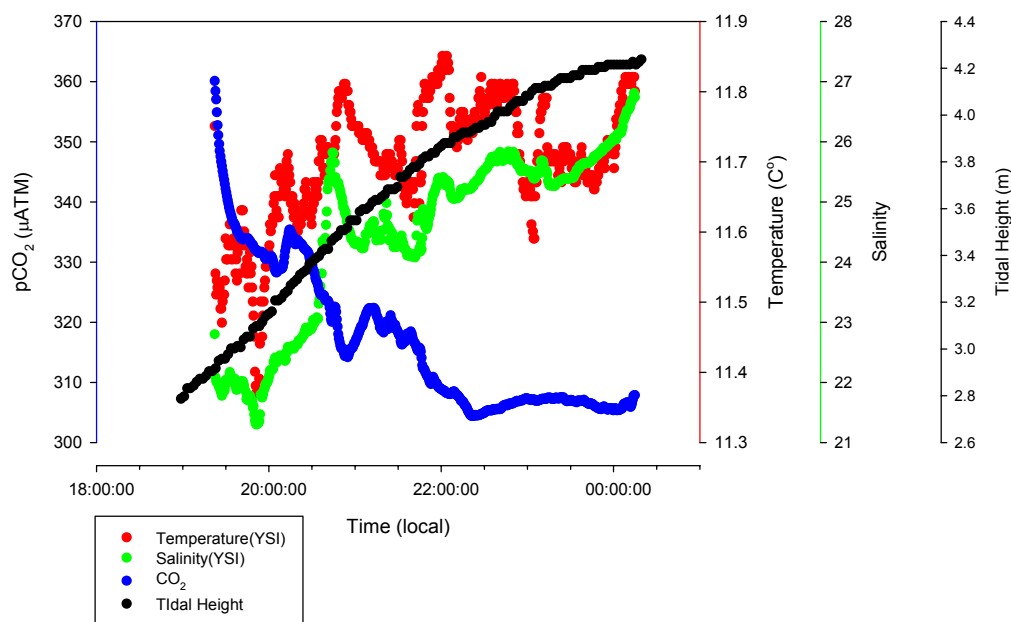


Fig. 16a. Background hydrography for February 8; the blue line is the $p\text{CO}_2$, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

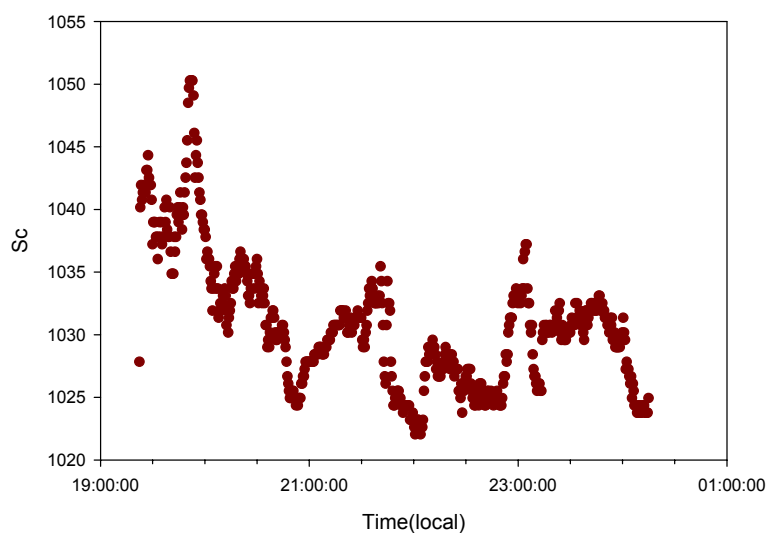


Fig. 16b. Schmidt number (Sc) vs. time for February 8, 2007.

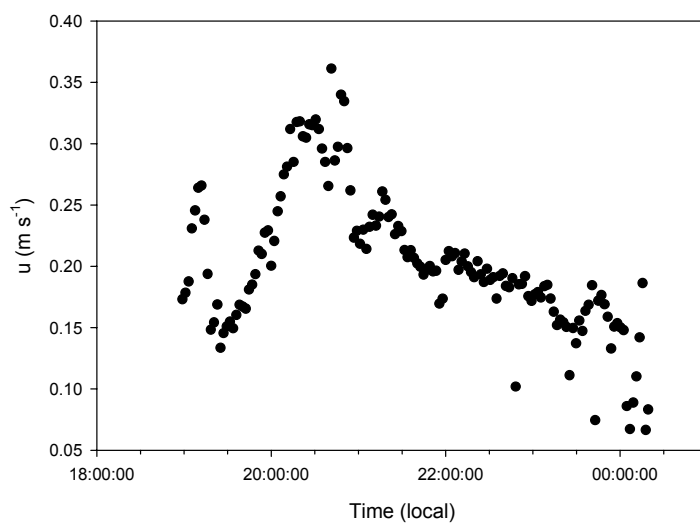


Fig. 16c. Current speed in the Duplin River over February 8.

CO_2 flux was into estuary over the entire experiment date of February 8. The dpCO_2/dt ranged from -6.74×10^{-3} to $-1.83 \times 10^{-3} \mu\text{mol CO}_2 \text{ s}^{-1}$. All the relevant parameters in calculating k_m and k_{600} are listed in Table 3 and discussed herein. The ΔpCO_2 levels were low for the entire experiment and went from -51.0 to $-86.9 \mu\text{atm}$ as water was advected into the Doboy Sound. In

terms of gas transfer velocities both measured and normalized, k_m ranged from 3.40 to 15.52 cm hr⁻¹ and k_{600} ranged from 4.45 to 20.31 cm hr⁻¹. Again the Sc was considerably higher than 600 ranging from 1040 to 1023 resulting in differences between k and k_{600} up to 31.6% (Fig. 16b).

Table 3. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for February 8.

Date/time (local)	$dpCO_2/dt$ $\mu atm CO_2 s^{-1}$	r^2	Temperature °C		Salinity	ΔpCO_2 μatm	k_m cm hr ⁻¹	k_{600} cm hr ⁻¹
8-Feb-2007			(air)	(water)				
19:26	-2.38X10 ⁻³	0.9594	13.4	11.6	22.0	-51.0	8.24	10.85
19:48	-4.32X10 ⁻³	0.9787	13.4	11.5	21.7	-55.2	12.95	17.08
20:06	-4.49X10 ⁻³	0.9825	13.0	11.7	22.5	-55.6	13.28	17.43
20:25	-5.08X10 ⁻³	0.9882	12.8	11.7	23.5	-61.6	13.52	17.73
20:45	-6.74X10 ⁻³	0.9881	12.6	11.8	24.9	-71.5	15.52	20.31
21:08	-2.77X10 ⁻³	0.9786	12.5	11.7	24.5	-68.1	6.68	8.75
21:32	-2.40X10 ⁻³	0.9811	12.4	11.7	24.5	-75.4	5.21	6.82
22:03	-2.41X10 ⁻³	0.9685	12.4	11.8	25.2	-82.8	4.76	6.23
22:33	-2.28X10 ⁻³	0.9809	12.3	11.8	25.7	-83.3	4.47	5.84
23:03	-2.36X10 ⁻³	0.9523	12.0	11.7	25.4	-83.7	4.57	5.99
23:24	-2.35X10 ⁻³	0.9809	11.8	11.7	25.5	-84.9	4.47	5.86
23:57	-1.83X10 ⁻³	0.9284	11.7	11.8	26.2	-86.9	3.40	4.45

March 3

Sampling began shortly after high tide (3/5/2007 20:02) at 3/5/2007 on 21:46 and continued to the subsequent low tide (3/6/2007 2:19) until 02:06 on 3/6/2007 (Fig. 17a). The pCO_2 started at 448 μatm and continued toward low tide levels of 860 μatm . The temperature started at 15.4°C, reflecting cooler ocean water, and increased to 16.1°C. The salinity began at 24.6 and dropped to 22.1 around the end of the half tidal cycle. After the slack high tide which had current speeds of almost 0 m s⁻¹, current speeds increase to 0.59 m s⁻¹ at max ebb then

decrease back to almost 0 m s^{-1} towards slack low tide. Current speeds were captured over the ebbing tide with a sharp initial increase to a maximum speed of 0.36 m s^{-1} and subsequent reduction to roughly 0 m s^{-1} toward slack low tide at the end of the experiment (Fig. 17a).

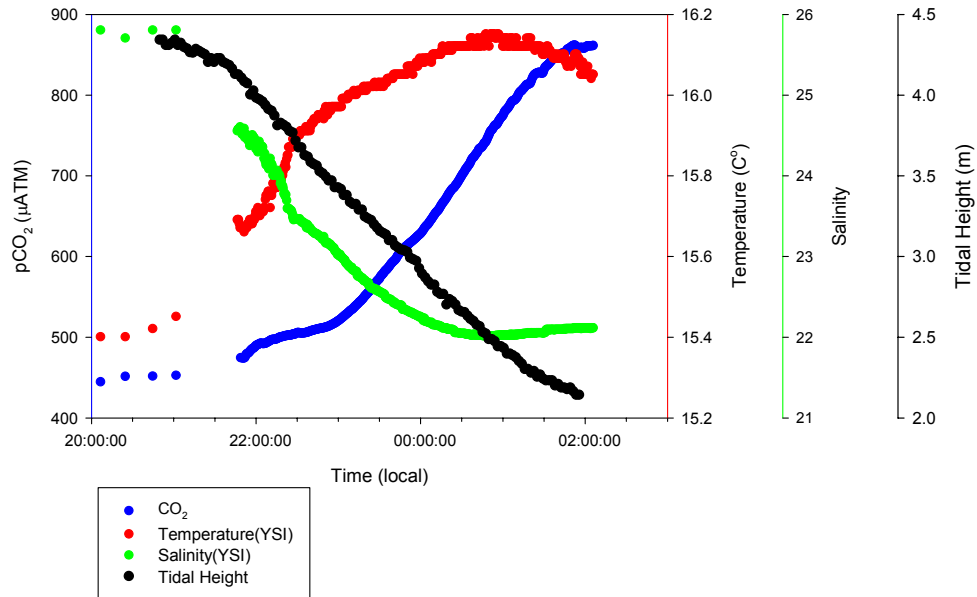


Fig. 17a. Background hydrography for March 3; the blue line is the $p\text{CO}_2$, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

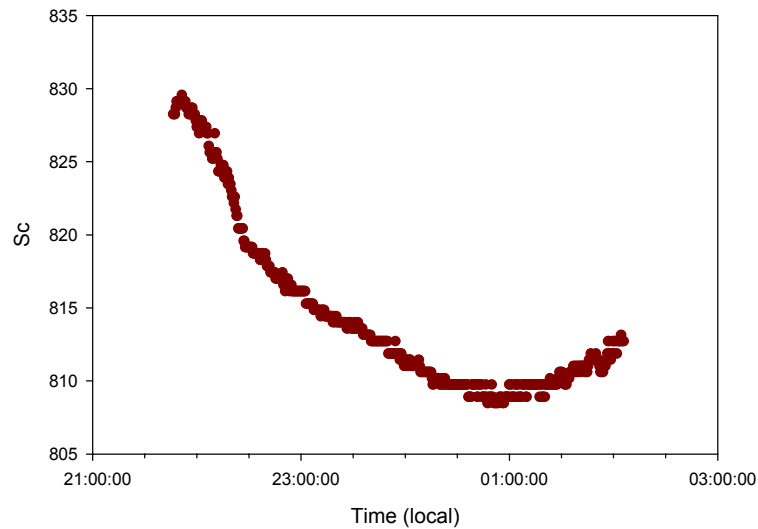


Fig. 17b. Schmidt number (Sc) vs. time for March 3, 2007. .

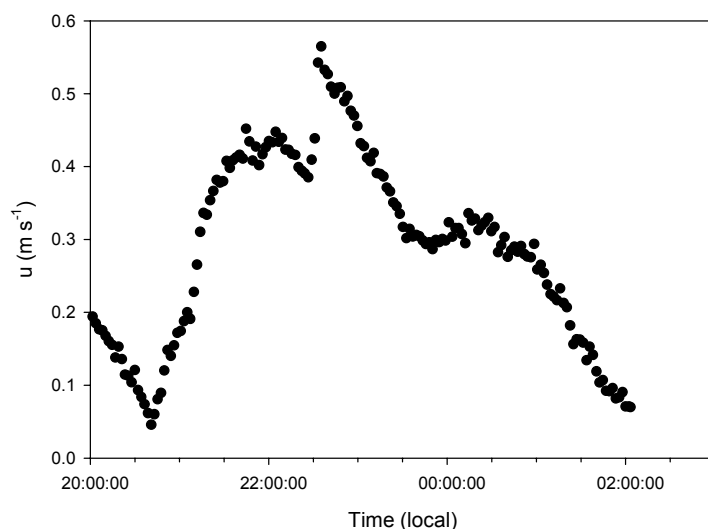


Fig. 17c. Current speed in the Duplin River over March 3.

All the relevant parameters in calculating k_m and k_{600} are listed in Table 4 and discussed herein. The interfacial pCO_2 difference levels were low towards high tide and increased as estuarine water was brought down from the upper Duplin River. The first four deployments are taken from written records because there is no electronic record of pCO_2 levels. The dpCO_2/dt ranged from 2.39×10^{-3} to $3.78 \times 10^{-2} \mu\text{mol CO}_2 \text{ s}^{-1}$ over the March 3 half tidal cycle. The interfacial ΔCO_2 was $50.9 \mu\text{mol}$ at high tide to $465.4 \mu\text{atm}$ at the end of the experiment. In terms of gas transfer rates both measured and normalized, k_m ranged from 5.41 to 58.19 cm hr^{-1} and k_{600} ranged from 5.68 to 61.16 cm hr^{-1} . Sc ranged from 830 at the beginning of the experiment to 810 towards the end; leading to differences between k_m and k_{600} of 17.6% (Fig. 17b).

Table 4. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for March 3.

Date/time (local)	$dpCO_2/dt$ $\mu atm CO_2 s^{-1}$	r^2	Temperature $^{\circ}C$		Salinity	ΔpCO_2 μatm	k_m $cm hr^{-1}$	k_{600} $cm hr^{-1}$
3-Mar-2007			(air)	(water)				
20:07	2.39×10^{-3}	0.9434	15.0	15.4	25.8	50.9	7.43	7.81
20:25	2.89×10^{-3}	0.9681	14.9	15.4	25.7	57.1	9.06	9.53
20:45	2.60×10^{-3}	0.9579	14.9	15.4	25.8	59.6	7.84	8.24
21:02	5.43×10^{-3}	0.9303	14.9	15.4	25.8	61.9	15.99	16.81
21:20	2.58×10^{-2}	0.9974	14.9	15.7	25.8	86.2	52.68	55.37
21:50	3.01×10^{-2}	0.9960	15.2	15.7	25.8	91.9	58.19	61.16
22:04	2.99×10^{-2}	0.9964	15.1	15.8	25.8	104.7	50.62	53.20
22:25	2.54×10^{-2}	0.9934	14.7	15.9	25.8	109.9	40.51	42.57
22:45	3.19×10^{-2}	0.9885	14.4	16.0	25.8	120.5	45.94	48.29
23:03	3.63×10^{-2}	0.9984	14.3	16.0	25.8	142.7	44.14	46.39
23:22	2.62×10^{-2}	0.9960	14.1	16.0	25.8	177.8	25.40	26.69
23:42	1.99×10^{-2}	0.9800	14.0	16.1	25.8	212.4	16.09	16.91
0:21	3.78×10^{-2}	0.9977	14.5	16.0	25.8	302.9	21.74	22.85
0:42	4.04×10^{-2}	0.9980	14.5	16.1	25.7	354.3	19.88	20.89
1:04	3.21×10^{-2}	0.9954	14.1	16.1	25.7	398.5	13.89	14.59
1:24	2.13×10^{-2}	0.9983	14.1	16.1	25.7	434.3	8.47	8.90
1:45	1.44×10^{-2}	0.9940	13.9	16.1	25.7	456.4	5.41	5.68

March 4

Sampling began at 21:20 on 3/4/2006 (Fig. 18a) around slack high tide (3/4/2006 20:38) and ended at roughly 2:00 on 3/5/2006 around slack low tide (3/5/2006 2:58). The pCO_2 increased over the half tidal cycle from roughly 425 to 628 μatm . The temperature increased sharply at the beginning of data collection and stabilized at 15.4°C. The salinity dropped from the high tide levels of 23.3 to 21.8 at low tide. Current speeds were captured over the ebbing tide with a sharp initial increase in current speeds to a maximum speed of 0.45 $m s^{-1}$ and subsequent reduction to roughly 0.19 $m s^{-1}$ toward low tide at the end of the experiment (Fig. 18a).

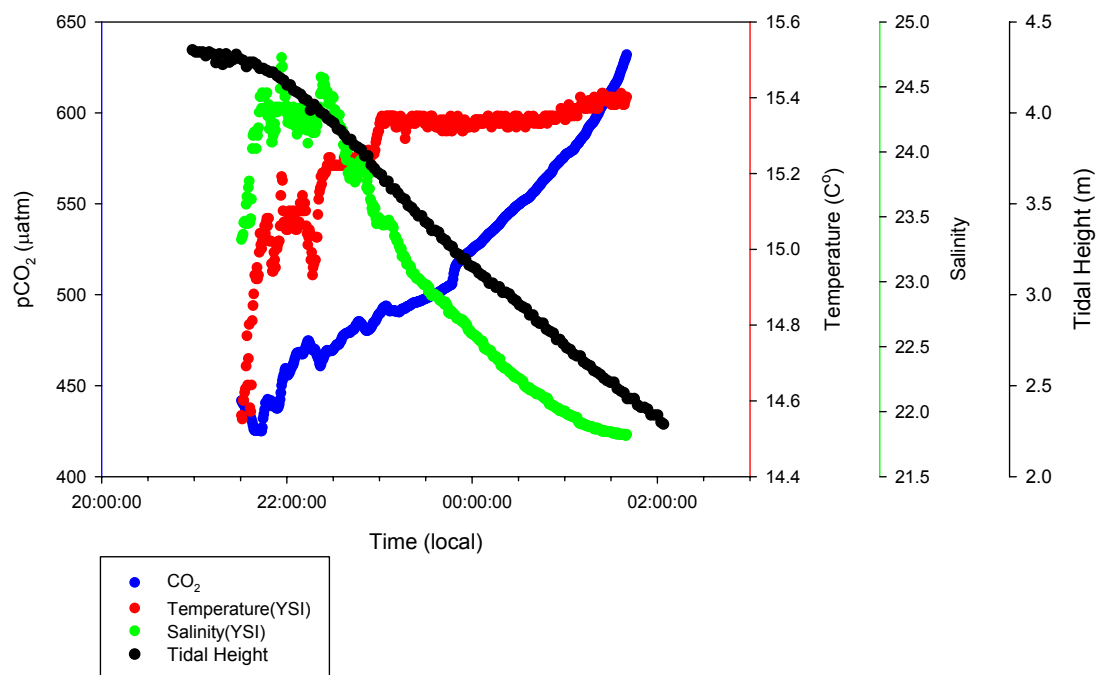


Fig. 18a. Background hydrography for March 4; the blue line is the $p\text{CO}_2$, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

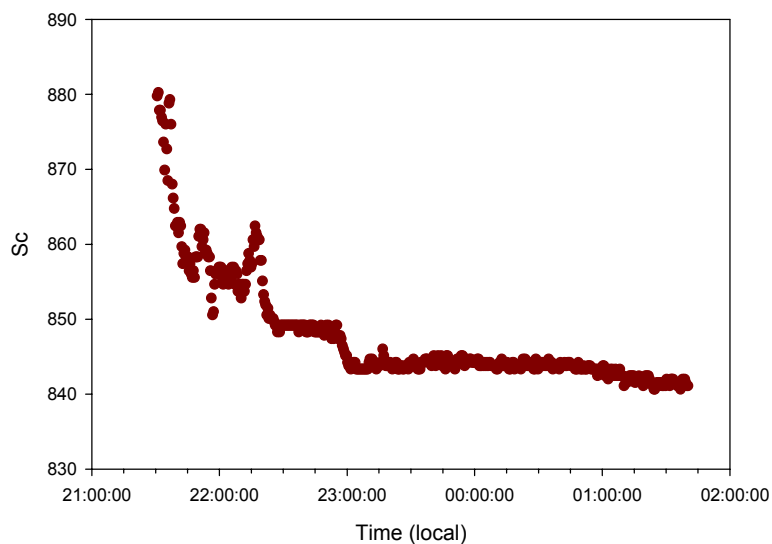


Fig. 18b. Schmidt number (Sc) vs. time for March 4, 2007.

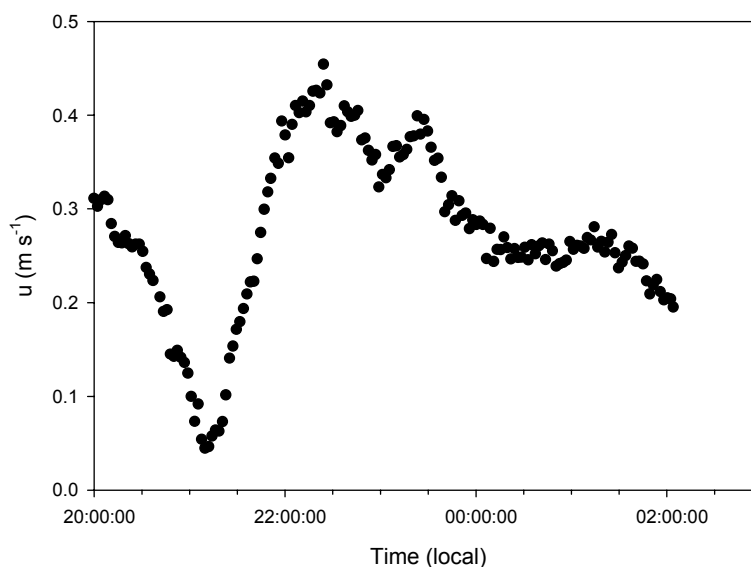


Fig. 18c. Current speed in the Duplin River over March 4.

All the relevant parameters in calculating k_m and k_{600} are listed in Table 5 and discussed herein. Low interfacial $p\text{CO}_2$ differences at high tide which increased from 60.3 to 220.2 μatm on the last deployment near low tide are similar to what was seen on March 3. The dpCO_2/dt ranged from 2.91×10^{-2} at the beginning of the half tidal cycle to $3.43 \times 10^{-3} \mu\text{mol CO}_2 \text{ s}^{-1}$ toward the end of the tidal cycle. In terms of gas transfer rates both measured and normalized, k_m range from 9.16 to 70.73 cm hr^{-1} and k_{600} ranges from 10.88 to 83.97 cm hr^{-1} . With respect to Sc , again March 4th was very similar to March 3rd where the Sc started around 880 and dropped to 842 towards the end of the experiment, this led to differences between k_m and k_{600} of 21.1% (Fig. 18b).

Table 5. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for March 4.

Date/time (local)	$dpCO_2/dt$ $\mu atm CO_2 s^{-1}$	r^2	Temperature $^{\circ}C$		Salinity	ΔpCO_2 μatm	k_m $cm hr^{-1}$	k_{600} $cm hr^{-1}$
4-Mar-2007			(air)	(water)				
21:11	3.43×10^{-3}	0.9778	12.2	14.7	22.9	60.3	9.16	10.88
21:29	5.37×10^{-3}	0.9858	12.1	14.8	22.9	46.1	18.72	22.22
21:52	2.39×10^{-2}	0.9976	12.6	15.0	22.9	55.2	70.73	83.97
22:11	2.91×10^{-2}	0.9981	13.0	15.1	13.0	81.1	59.29	70.38
22:30	2.87×10^{-2}	0.9983	13.3	15.2	23.0	88.9	53.58	63.60
22:50	2.16×10^{-2}	0.9975	13.7	15.3	23.0	96.7	37.60	44.64
23:08	2.51×10^{-2}	0.9952	14.0	15.3	23.0	103.5	41.18	48.88
23:28	1.51×10^{-2}	0.9820	14.5	15.3	23.0	109.0	23.85	28.31
23:48	1.20×10^{-2}	0.9732	14.9	15.3	23.1	129.6	16.10	19.11
0:07	1.02×10^{-2}	0.9968	15.4	15.3	23.1	147.3	12.25	14.54
0:31	1.36×10^{-2}	0.9934	15.4	15.3	23.1	166.4	14.39	17.08
0:58	1.48×10^{-2}	0.9972	15.4	15.4	23.1	192.3	13.54	16.08
1:21	1.53×10^{-2}	0.9979	15.7	15.4	23.1	220.2	12.40	14.72

March 26

Sampling began just before slack low tide (3/26/2007 21:34) at 21:18 on 3/26/2007 and lasted until high tide (3/27/2007 3:59) at 04:09 on 3/27/2007 (Fig. 19a). The temperature started at 19.8°C and at max ebb tidal speed dropped to 19.4°C; it then increased to 20.2°C around 2:10 3/27/2007 and then fell slightly again toward high tide to 20°C. At slack low tide after the lowest current speed of 0.07 m s⁻¹, the maximum flood current speeds (0.35 m s⁻¹) appear at the end of the half tidal cycle of then decrease quickly towards slack high tide (Fig. 19c).

All the relevant parameters in calculating k_m and k_{600} are listed in Table 6 and discussed herein. Interfacial pCO_2 difference was highest (706.1 μatm) at low tide and became lower towards high tide reflecting an estuarine signal with a value of 357.9 μatm . The $dpCO_2/dt$ low was 1.09×10^{-2} to a high of 3.49×10^{-2} $\mu mol CO_2 s^{-1}$. In terms of gas transfer rates both

measured and normalized, k_m ranges from 3.51 to 12.15 cm hr⁻¹ and k_{600} ranges from 3.68 to 12.73 cm hr⁻¹. The Sc is similar to that of the normalized value of 600, this lead to differences between k_m and k_{600} of only 7.2% (Fig. 19b).

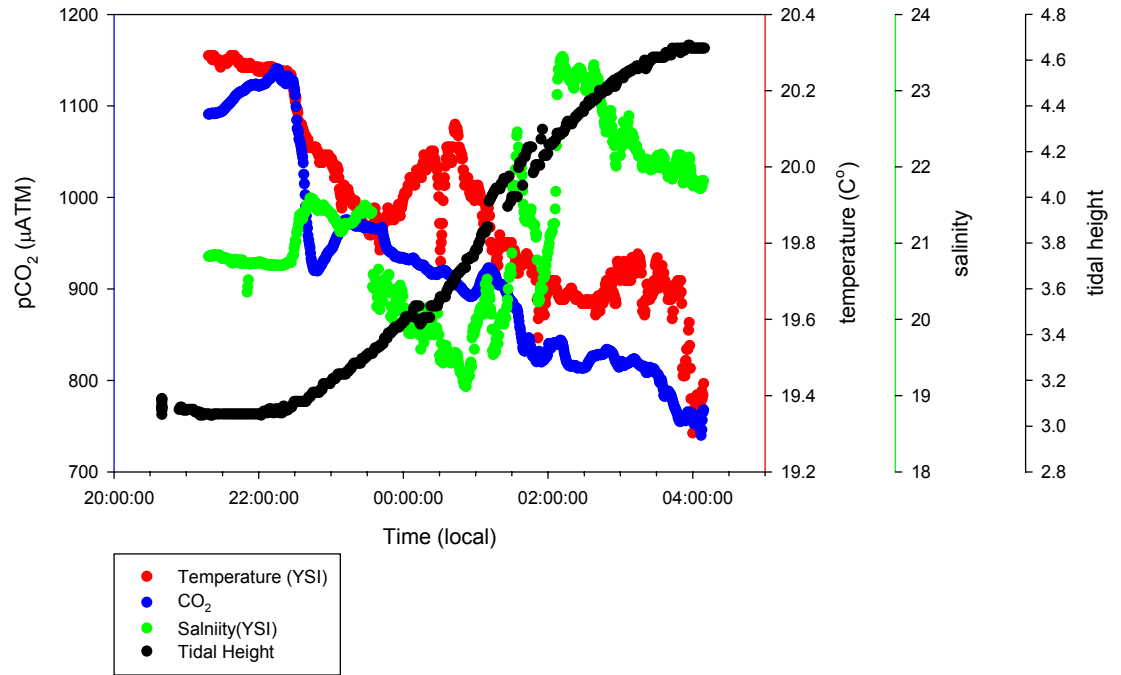


Fig. 19a. Background hydrography for March 26; the blue line is the pCO₂, the red line is the Temperature, the green line is Salinity and the black line is tidal height all with respect to local time.

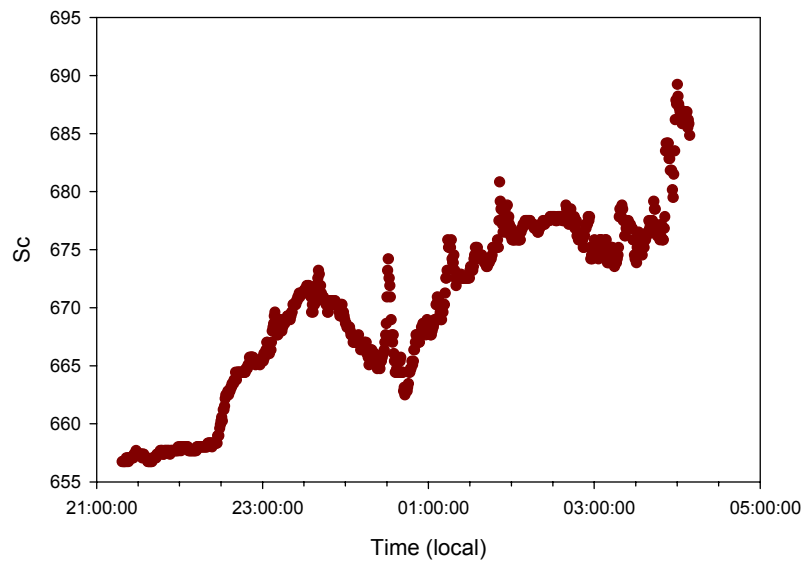


Fig. 19b. Schmidt number (Sc) vs. time for March 26, 2007.

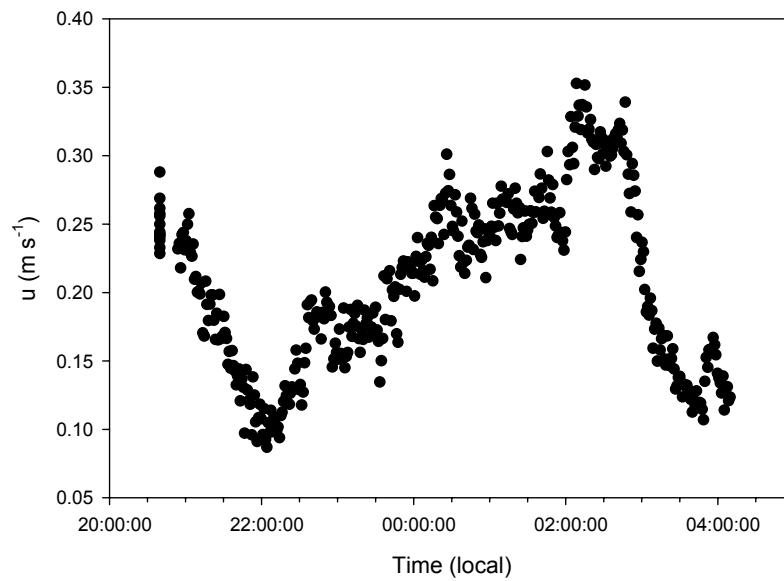


Fig. 19c. Current speed in the Duplin River over March 26.

Table 6. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for March 26.

Date/time (local)	$dpCO_2/dt$ $\mu atm CO_2 s^{-1}$	r^2	Temperature $^{\circ}C$		Salinity	ΔpCO_2 μatm	k_m $cm hr^{-1}$	k_{600} $cm hr^{-1}$
26-Mar-2007			(air)	(water)				
21:19	2.26×10^{-2}	0.9983	18.4	20.3	20.8	706.1	6.04	6.33
21:42	1.97×10^{-2}	0.9986	18.1	20.3	20.3	730.0	5.06	5.30
22:09	1.39×10^{-2}	0.998	18.1	20.3	20.8	742.3	3.51	3.68
22:28	1.54×10^{-2}	0.9977	17.5	20.3	20.8	611.5	4.64	4.86
22:53	1.90×10^{-2}	0.9985	17.6	20.3	20.8	556.6	6.30	6.60
23:14	1.83×10^{-2}	0.9988	17.8	20.3	20.8	576.7	5.92	6.21
23:34	2.63×10^{-2}	0.9985	18.1	20.3	20.8	559.9	8.80	9.23
23:58	3.49×10^{-2}	0.9987	18.0	20.3	20.8	536.5	12.15	12.73
0:20	2.57×10^{-2}	0.9880	18.2	20.3	20.8	523.3	9.21	9.66
0:49	2.31×10^{-2}	0.9977	18.2	20.3	20.8	507.8	8.53	8.94
1:12	1.79×10^{-2}	0.9906	18.1	20.3	20.8	511.4	6.55	6.86
1:34	2.31×10^{-2}	0.9972	17.9	20.3	20.8	444.8	9.67	10.14
1:54	2.17×10^{-2}	0.9879	17.3	20.3	20.8	439.2	9.05	9.49
2:16	2.44×10^{-2}	0.9951	17.1	20.3	20.8	418.5	10.64	11.16
2:39	2.36×10^{-2}	0.9814	17.3	20.3	20.8	424.9	10.19	10.69
3:06	1.64×10^{-2}	0.9873	17.4	20.3	20.9	406.8	6.04	6.33
3:27	1.40×10^{-2}	0.9979	17.9	20.3	20.8	416.2	7.41	7.77
3:48	1.09×10^{-2}	0.9910	18.0	20.3	20.8	357.9	6.26	6.56

March 27

Sampling began before low tide (22:51 3/27/2007) at 21:36 on 3/27/2007 and proceeded until 04:27 on 3/28/2007 (Fig. 20a) before high tide (5:00 3/28/2007). The pCO_2 ranged from 928 to 1061 μatm and then fell evenly until high tide to 667 μatm . The temperature started at 20.7°C and fell to 19.9°C over the half tidal cycle reflecting the cooler ocean signal. The salinity started at 22.7 and fell to 16.7 at the beginning of the ebbing tide and then increased again to 22.3. After the lowest current speeds of 0.07 $m s^{-1}$ at slack low tide, the maximum flood current speeds correspond to the end of the half tidal cycle of 0.35 $m s^{-1}$ then decrease quickly at slack high tide (Fig. 20c) back to almost 0 $m s^{-1}$.

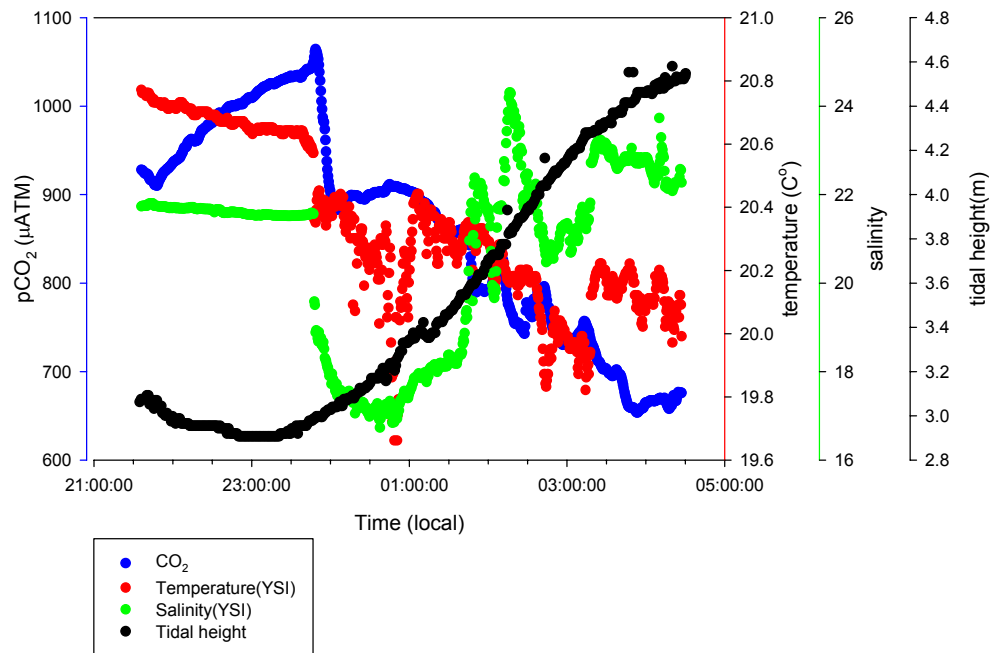


Fig. 20a. Background hydrography for March 27; the blue line is the $p\text{CO}_2$, the red line is the temperature, the green line is salinity and the black line is tidal height all with respect to local time.

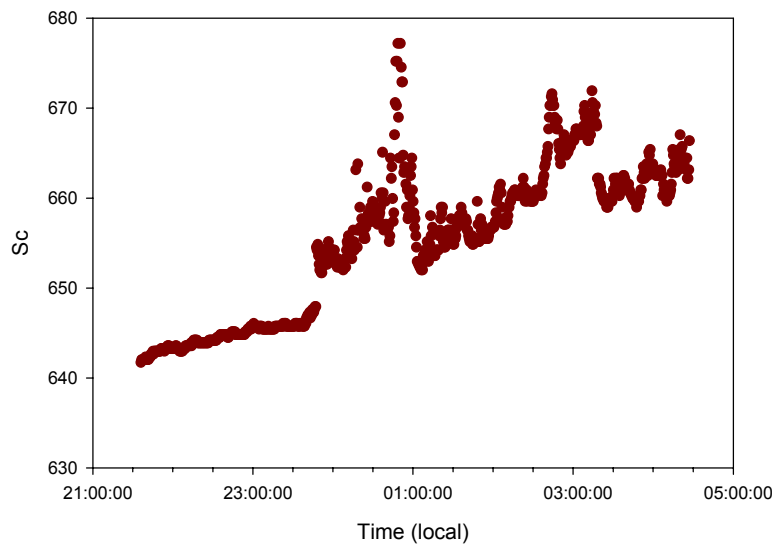


Fig. 20b. Schmidt number (Sc) vs. time for March 27, 2007.

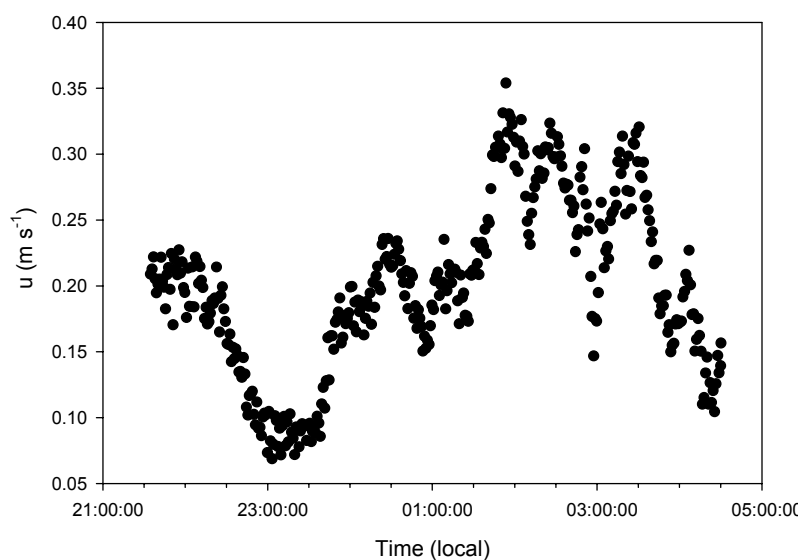


Fig. 20c. Current speed in the Duplin River over March 27.

All the relevant parameters in calculating k_m and k_{600} are listed in Table 7 and discussed herein. The $dpCO_2/dt$ ranged from a high tide low of 6.06×10^{-3} to $4.56 \times 10^{-2} \mu\text{mol CO}_2 \text{ s}^{-1}$ after low tide. The interfacial ΔCO_2 was $549.4 \mu\text{mol}$ at high tide and the beginning of the half tidal cycle to $227.5 \mu\text{atm}$ at low tide. In terms of gas transfer rates both measured and normalized, k_m ranges from 3.52 to 17.63 cm hr^{-1} and k_{600} ranges from 3.65 to 18.26 cm hr^{-1} . Again, the Sc is similar to that of the normalized value of 600 , this lead to maximum differences between k_m and k_{600} of 7.2% (Fig. 20b).

Table 7. Data used in gas transfer velocity calculations and Schmidt number conversions to k_{600} with r^2 values for the dCO_2/dt term in individual chamber deployments for March 27.

Date/time	$dpCO_2/dt$	r^2	Temperature		Salinity	ΔpCO_2	k_m	k_{600}
(local)	$\mu atm CO_2 s^{-1}$		$^{\circ}C$			μatm	$cm hr^{-1}$	$cm hr^{-1}$
26-Mar-2007			(air)	(water)				
21:56	1.77×10^{-2}	0.9986	19.4	20.7	21.7	549.4	6.27	6.50
22:14	1.79×10^{-2}	0.9984	19.1	20.7	21.7	579.4	5.95	6.17
22:32	1.79×10^{-2}	0.9991	18.5	20.7	21.7	603.9	5.63	5.83
22:52	1.48×10^{-2}	0.9988	18.1	20.7	21.7	619.9	4.49	4.66
23:13	1.28×10^{-2}	0.9968	17.8	20.7	21.7	635.6	3.76	3.89
23:35	1.21×10^{-2}	0.9835	17.6	20.7	21.7	638.7	3.52	3.65
0:17	4.56×10^{-2}	0.9908	17.4	20.7	21.7	477.9	17.63	18.26
0:38	2.93×10^{-2}	0.9400	17.2	20.7	21.7	492.2	10.94	11.33
0:58	2.14×10^{-2}	0.9956	17.1	20.7	21.7	496.3	7.91	8.20
1:18	1.97×10^{-2}	0.9928	16.2	20.7	21.7	451.7	7.81	8.09
1:43	1.42×10^{-2}	0.9957	15.8	20.7	21.7	373.2	6.72	6.96
2:03	1.83×10^{-2}	0.9623	15.1	20.7	21.7	364.6	8.71	9.03
2:27	1.69×10^{-2}	0.9946	15.2	20.7	21.7	310.6	9.47	9.81
2:48	1.65×10^{-2}	0.9843	15.1	20.7	21.7	278.7	10.30	10.67
3:08	1.51×10^{-2}	0.9856	15.4	20.7	21.7	303.1	8.73	9.04
3:29	1.51×10^{-2}	0.9939	14.8	20.7	21.7	247.6	10.49	10.87
3:50	8.03×10^{-3}	0.9902	14.0	20.7	21.7	226.0	5.99	6.21
4:11	6.06×10^{-3}	0.9836	14.3	20.7	21.7	227.5	4.53	4.69

k_{600} vs. current speeds (u) and wind speeds (U_{10})

Current and wind speeds were well correlated with gas transfer velocities (Figs. 21a, 21b, 22a, 22b). Normalized gas transfer velocities increase to a maximum of $30 cm hr^{-1}$ with current speeds up to $0.35 m s^{-1}$. Above current speeds of $0.35 m s^{-1}$, k_{600} values increase sharply to a maximum of $84 cm hr^{-1}$; this same signal is reflected in the attenuated k_m values. In addition, gas transfer velocities increase with increasing wind speeds, with the exception of k measured at wind speeds around $4 m s^{-1}$.

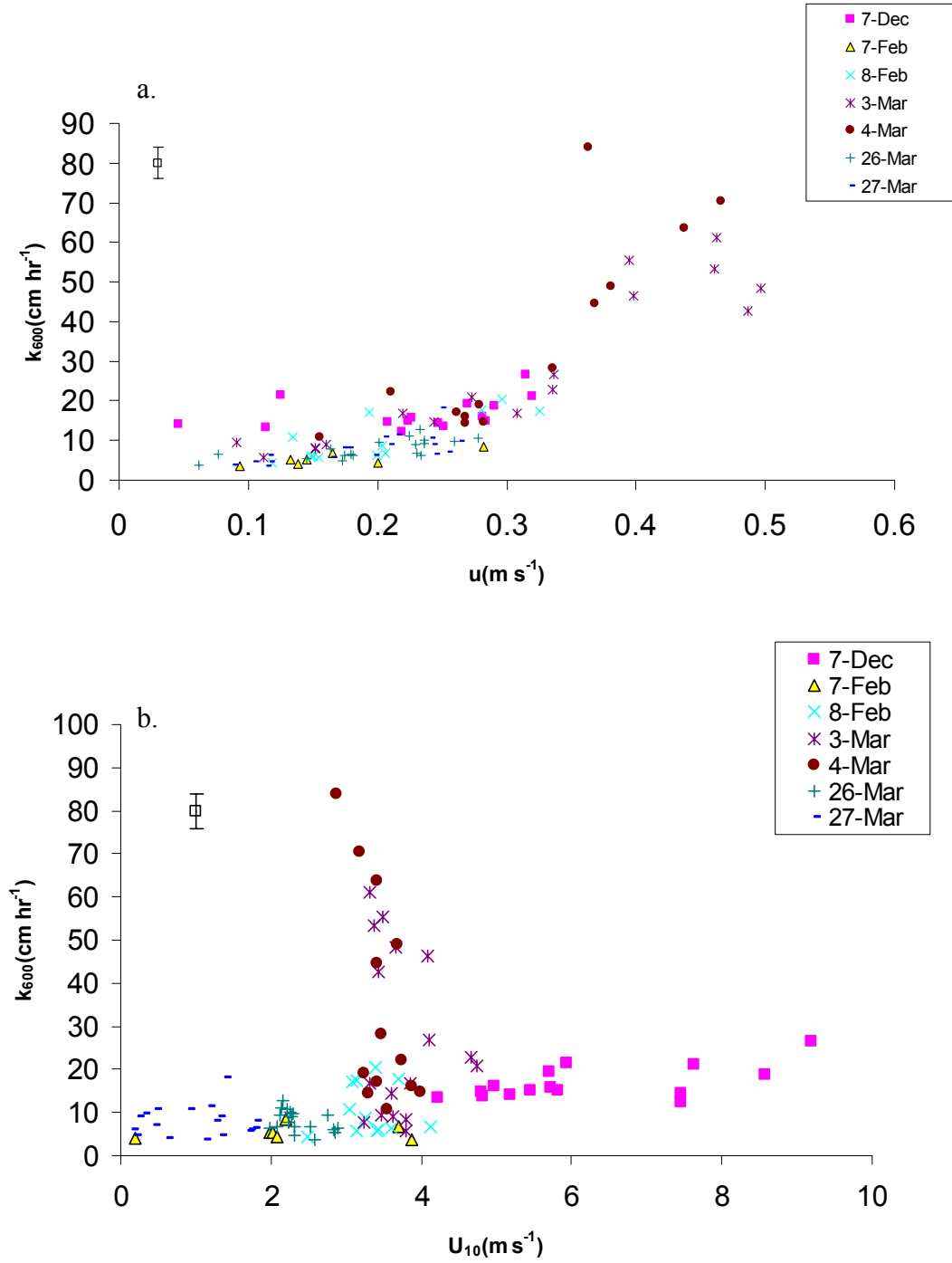


Fig. 21. (a) Total gas transfer velocities normalized to a Sc of 600 with current speed. (b) Total gas transfer velocities normalized to a Sc of 600 with wind speeds at a ten meter height by date. The error reported are ± 4 cm hr⁻¹ (open square) which is commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007).

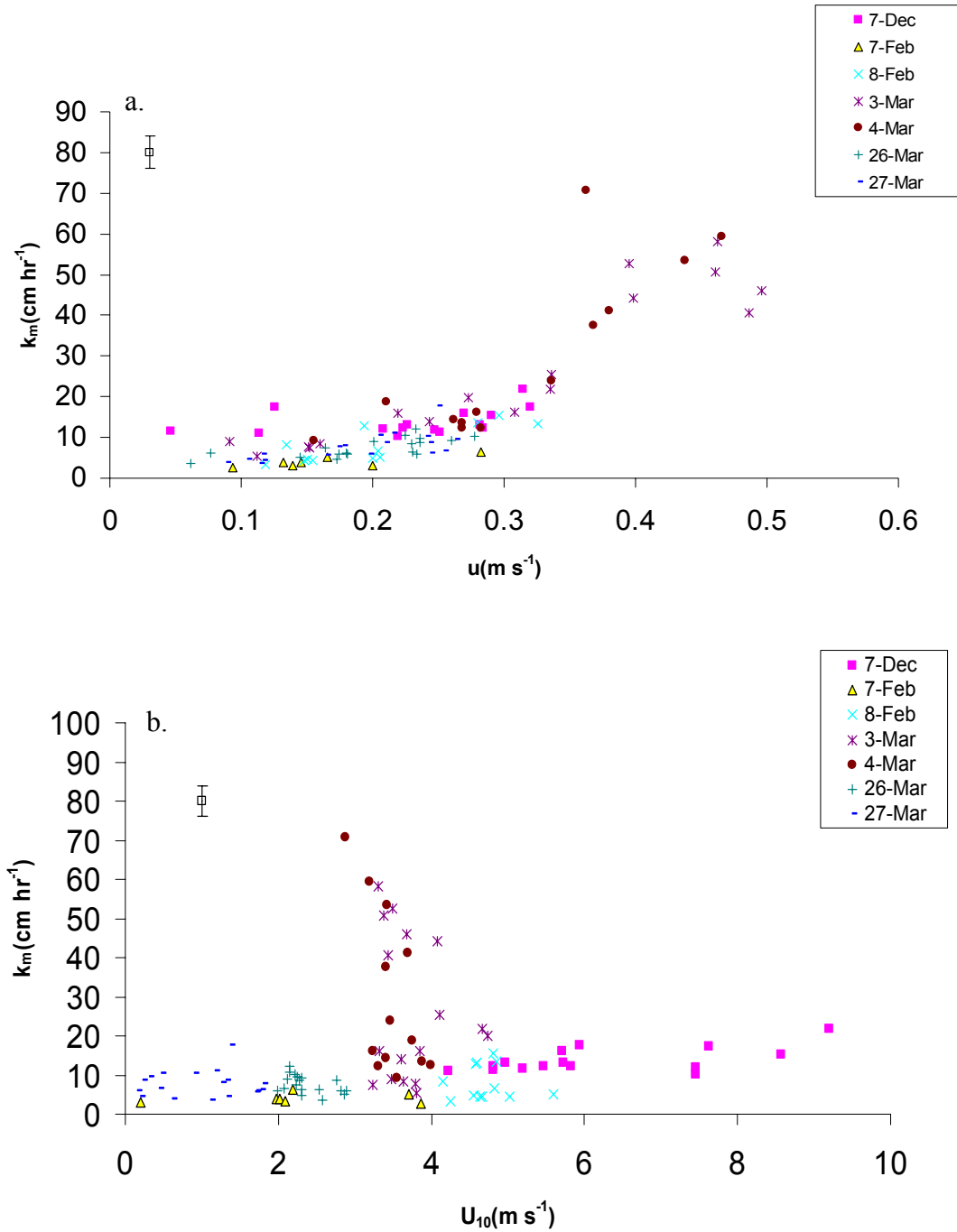


Fig. 22. (a) Total gas transfer velocities measured with current speed uncorrected for Sc of 600. (b) Total gas transfer velocities measured with wind speeds at a ten meter height uncorrected for Sc of 600 by date. The error reported is $\pm 4 \text{ cm hr}^{-1}$ commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007).

The increased values of k_m and k_{600} around wind speeds of 4 m s^{-1} correspond to the highest current speeds measured over the experiment, March 3rd and 4th (Figs. 21b, 22b). In addition, the increased values of k_m and k_{600} over all current speeds (December 7, Figs. 21a, 22a) correspond to the highest wind speeds in which k was measured.

Effect of the chamber wall on k

To evaluate potential artifacts from the chamber wall, current speeds in terms of the surface renewal theory are compared with k_{600} measured under different wind and current speeds (Fig. 23). It is assumed that k should vary approximately linearly with the square root of u/h according to surface renewal theory given the absence of chamber wall effects. Gas transfer velocities measured in category one are consistent with the square root dependence of u/h with k outlined by surface renewal theory. While this is not a total verification that the chamber wall is not contributing to k at these current and wind speeds, it suggests the effects from the chamber wall on k are minimal. Given that the wind speeds are increased in category 2 and k is only slightly higher also suggests the minimal role of chamber wall generated turbulence for this category as well. In contrast, within category 3, gas transfer velocities are as much as four times the values measured in categories one and two. This indicates that in category 3 chamber wall derived turbulence may be a factor and hide any natural processes responsible in controlling the magnitude of k . Therefore, for categories 1 and 2, wall generated turbulence may be considered minimal while transfer velocities measured under category 3 are less certain.

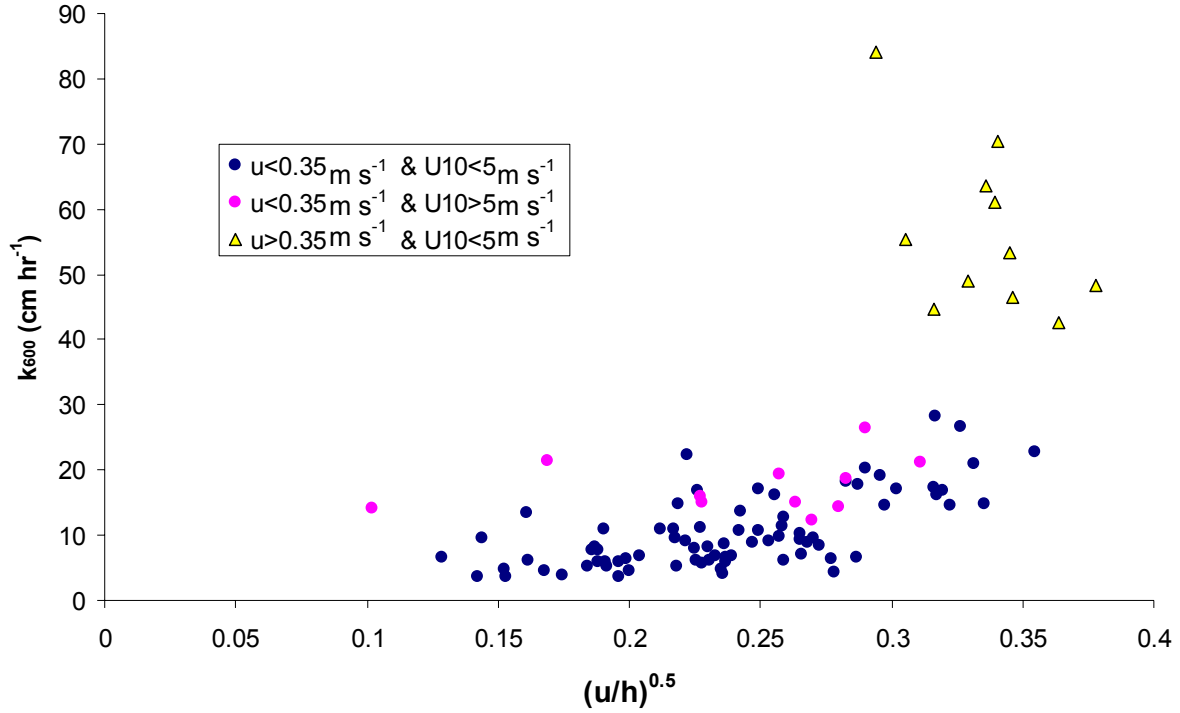


Fig. 23. Total gas transfer velocities with $(u/h)^{0.5}$ broken into 3 categories based on wind and current speeds. (category 1) the blue circles represent gas transfer velocities measured in currents less than 0.35 m s^{-1} and wind speeds less than 5 m s^{-1} ; (category 2) the pink dots represent k_{600} determined under current speeds less than 0.35 m s^{-1} and wind speeds over 5 m s^{-1} ; and (category 3) yellow triangles represent k_{600} collected for current speeds greater than 0.35 m s^{-1} and wind speeds less than 5 m s^{-1} .

Regression of wind speeds (U_{10}) to k_{600}

An exponential fit curve for measured gas transfer velocities in the Duplin River as a function of wind speed is given in equations (16 and 17, Fig. 24). These two models are calculated for both all gas transfer velocities measured and those filtered for current speeds less than 0.35 m s^{-1} . The model in terms of all gas transfer velocities measured is:

$$k_{600} = 11.82e^{0.0965U_{10}} \quad (16)$$

And the second model for the filtered gas transfer velocities ($u < 0.35 \text{ m s}^{-1}$) is given as:

$$k_{600} = 6.77e^{0.142U_{10}} \quad (17)$$

The fit for every k_{600} measurement, equation (16), has a standard error of $\pm 14.5 \text{ cm hr}^{-1}$, whereas equation (17), k 's measured at current speeds less than 0.35 m s^{-1} , has a standard error of $\pm 4.3 \text{ cm hr}^{-1}$. Both models increase with wind speeds, however the model in equation (17) predicts higher gas transfer velocities at lower wind speeds. This relationship holds up to wind speeds of 12.3 m s^{-1} where the two models converge and equation (16) then yields higher gas transfer velocities at given wind speeds.

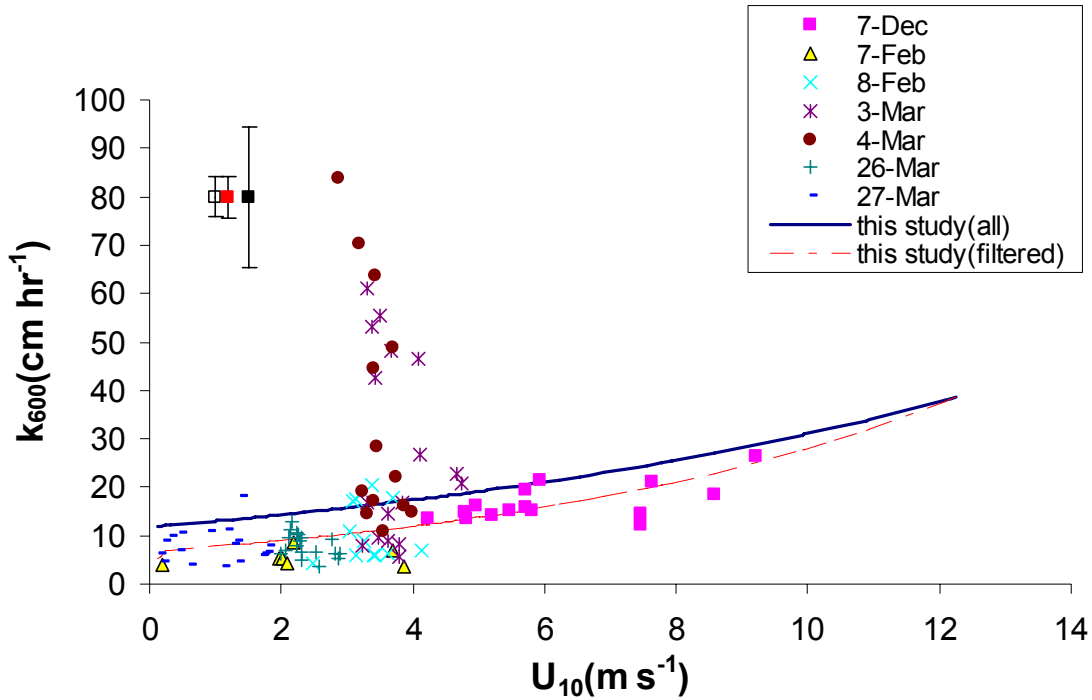


Fig. 24. Total gas transfer velocities normalized to a Sc of 600 with wind speed at a ten meter height. Two empirical models for this study have been plotted; one for all k 's measured and the second for k filtered to current speeds less than 0.35 m s^{-1} . The errors reported are $\pm 4 \text{ cm hr}^{-1}$ (open square) which is commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007), $\pm 4.3 \text{ cm hr}^{-1}$ (this study filtered; red box) and $\pm 14.5 \text{ cm hr}^{-1}$ (this study all; black box).

Regression of current speeds (u) to k_{600}

Based on k_{600} values from category 1, filtered wind speeds and current speeds, a simple power function (equation 18) has been created in the same manner as Borges et al. (2004b) and O'Connor and Dobbins (1956) :

$$k_{600} = 46.6 \sqrt{\frac{u}{h}} \quad (18)$$

The standard error of equation (18) is $\pm 4.6 \text{ cm hr}^{-1}$.

Multi-linear regression of current speeds (u) and wind speeds (U_{10}) to k_{600}

Two multi-linear regressions of k_{600} values with current and wind speeds are presented; one based on all gas transfer velocities measured and a second based on those measured in current speeds under 0.35 m s^{-1} . The model, based on all measured values of k_{600} , follows the 1:1 relationship of measured vs. modeled gas transfer velocities up to k_{600} values of 25 cm hr^{-1} (Fig. 25). Above this value, measured gas transfer velocities reach to an 84 cm hr^{-1} maximum while modeled values of k_{600} remain around 26 cm hr^{-1} .

$$k_{600} = 61.13 \sqrt{\frac{u}{h}} + 0.722 U_{10} \quad (19)$$

In contrast, the model determined in the case of gas transfer velocities with the filtered current speeds (equation 20) leads maximum values in measured k_{600} of 26 cm hr^{-1} and modeled k_{600} of 24 cm hr^{-1} (Fig. 26).

$$k_{600} = 29.01\sqrt{\frac{u}{h}} + 1.47U_{10} \quad (20)$$

Equation (20) predicts a greater role from wind speeds in governing the magnitude of the gas transfer velocities and decreased role of the tidal currents in the magnitude of k_{600} as opposed to equation (19).

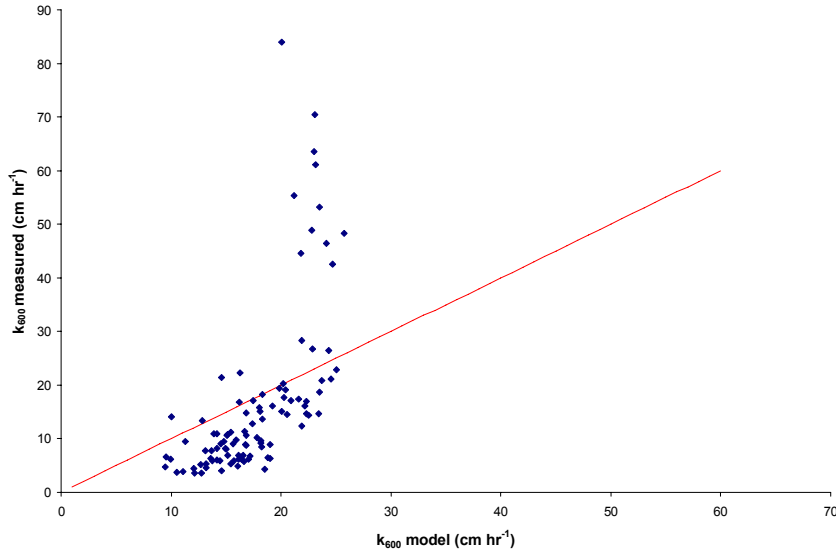


Fig. 25. Modeled data from multi-linear regression model based on all gas transfer velocities measured plotted against measured k_{600} with 1:1 line represented in red (equation 19).

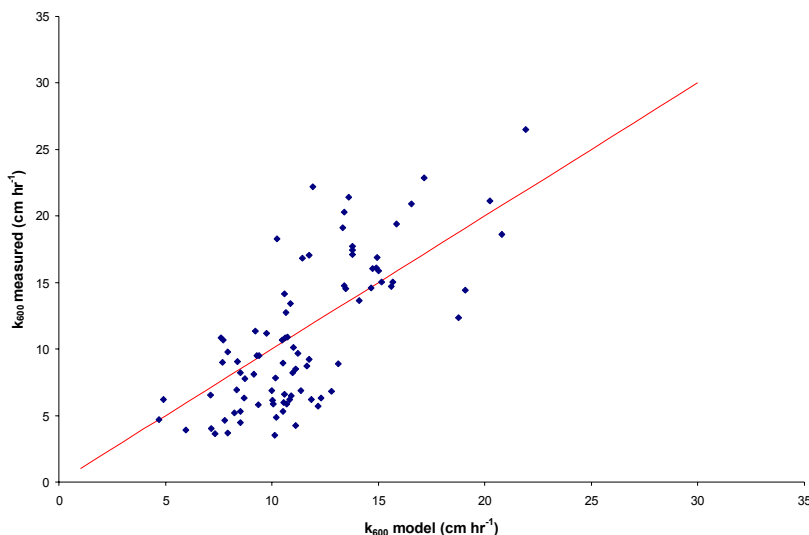


Fig. 26. Modeled data from multi-linear regression model based on gas transfer velocities measured with current speeds less than 0.35 m s^{-1} (equation 20) plotted against measured k_{600} with 1:1 line represented in red.

Fluxes

Fluxes are reported for every deployment by time and order of release time (Fig. 27). December 7 had the highest CO_2 fluxes with a maximum of $260 \text{ mmol m}^{-2} \text{ d}^{-1}$. For the two February dates, CO_2 fluxes are into the estuary the exception of the last two deployments on February 7th. The March deployments exhibited CO_2 fluxes with an average value of $33.48 \text{ mmol m}^{-2} \text{ d}^{-1}$ where individual fluxes over each deployment generally reflected the average values. Exceptions to this were the high tide measurements of CO_2 fluxes that were lower ($\sim 10 \text{ mmol m}^{-2} \text{ d}^{-1}$) than the lower tide values due to the decreased interfacial pCO_2 gradient caused by lower ocean pCO_2 levels. These low flux deployments can be seen (Fig. 27) as the early values in March 3 and 4 and the later values in March 26 and 27.

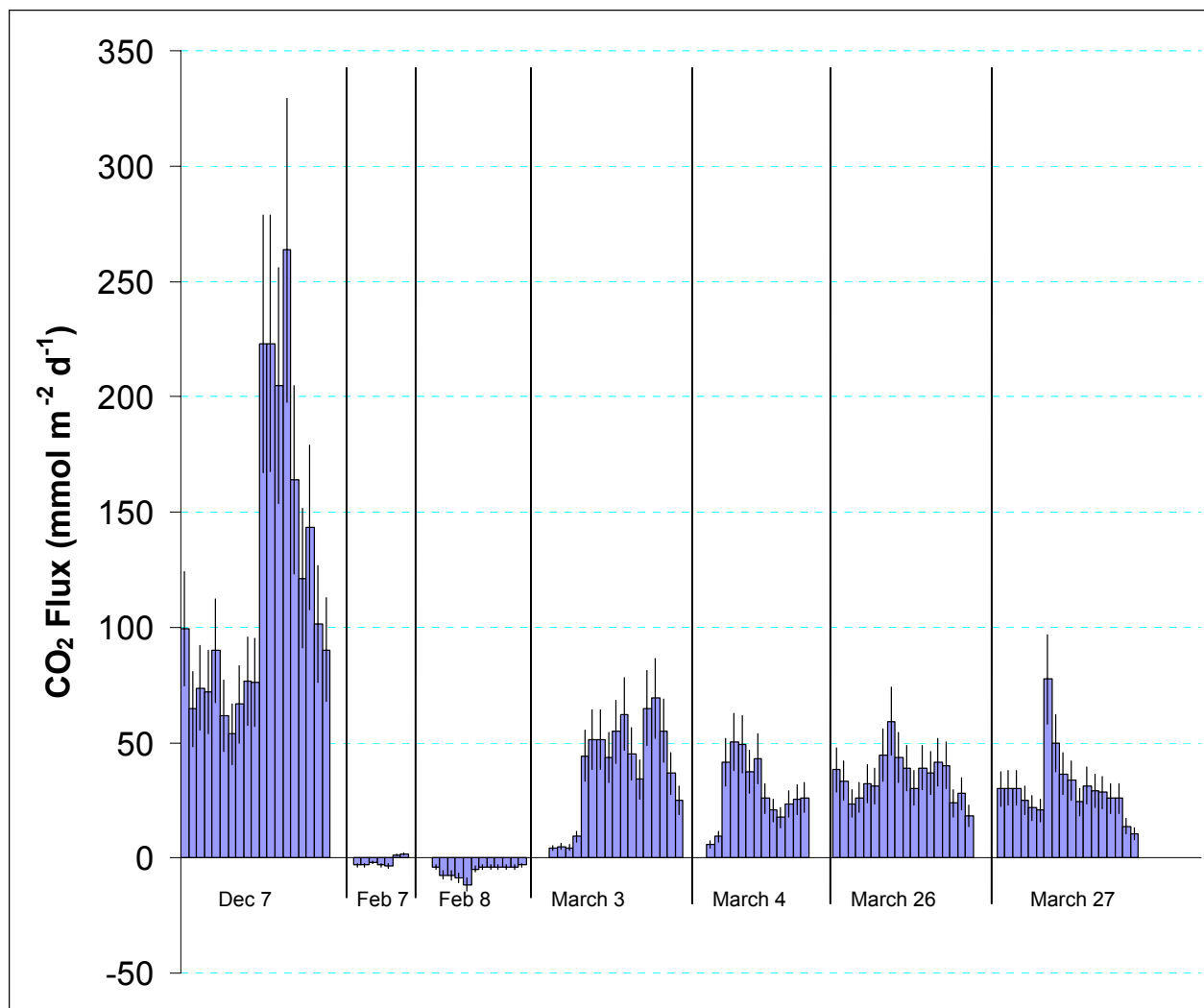


Fig. 27. CO₂ fluxes over the range of the entire study by deployment day. Chamber fluxes are reported in order of deployment. An error of 25% in fluxes measured from floating chambers is assumed based on Frankignoulle (1988).

Ebb and flood tidal velocities effect on k

The acoustic doppler current profiler was always deployed on the southern side of Marsh Landing Dock. Because of this, the ebbing tidal currents were measured after traveling underneath the dock. Therefore, there is the potential for large eddies to form on the southern side of the dock and the current speeds measured may have been affected. Based on

comparisons of the regression coefficients between the flooding and ebbing tides between gas transfer velocities and current speeds it can be seen that the values of the regression coefficient and the 95% confidence intervals (40.5 ± 17.4 for the flooding tide and 49.5 ± 26 for the ebbing tide) of the ebbing currents fall within the values predicated for the flooding currents and therefore are statistically similar. Thus the dock pylons do not appear to be skewing the current speeds collected over the ebbing tides.

CHAPTER 4

DISCUSSION

Current speed (u) and wind speed (U_{10}) vs. k_{600} and k_m (total)

As was discussed previously, Schmidt numbers measured were often significantly higher than 600. Therefore for k 's reported at low temperatures, k_m and k_{600} (Figs. 21a, 22b, 21a and 22b) may differ by as much as 33% (see Sc results section for error on individual dates). As stated in the results section, current speeds and gas transfer velocities were well related, and at current speeds greater than 0.35 m s^{-1} the gas transfer velocities increase sharply (Figs. 21a and 22a). This sharp upturn is in contrast to the square root dependence developed in the surface renewal model. The upturn may be the consequence of all measured gas transfer velocities occurring on March 3rd and 4th, which coincided with a spring tide, the only one captured during this study. As stated in the introduction, Hahm et al. (2005) reports that spring tides can be responsible for gas transfer velocities up to 42 cm hr^{-1} , closer to the maximum values of k reported here, however, still well below the maximum k_{600} determined in this study (84 cm hr^{-1}). The water depth ($\sim 12\text{m}$) in the Hahm et al. (2005) study was much deeper than the Duplin River (see Results), which may dissipate turbulent energy generated from bottom friction over a greater depth. Therefore the depth difference could explain the lower k values found in that study. Hahm et al. (2005) proposed that on spring tides, mixing happens over much larger scales where bottom water is quickly mixed with the surface water leading to elevated values of k .

Another possible explanation for the sharp increase in k , is that the limit of the method was reached and the gas transfer coefficients are caused by chamber wall generated turbulence and thus are artificially high. However, it may be incorrect to discount these very high k_{600} values because other estuarine studies have yielded results that suggest current-derived turbulence may have a great influence on gas transfer velocities (Hartman and Hammond 1985; Borges et al. 2004a; Borges et al. 2004b; Guerin et al. 2007). For example, in Borges et al. (2004a) there is a wide range of transfer velocities around wind speeds of 7 m s^{-1} that reach over 60 cm hr^{-1} then reduce to under 30 cm hr^{-1} at subsequent higher wind speeds suggesting a similar phenomena. In addition, a recent study (Guerin et al. 2007) that tracked gas transfer velocities from a tropical reservoir in French Guiana down river towards the ocean, demonstrated that gas transfer velocities in the riverine and estuarine portion of the study reach three times the k values derived in the reservoir where there is a deeper depth and weaker current strength. In conjunction these values of k (Guerin et al. 2007) were still well correlated with wind speeds suggesting, possibly, that bottom friction-induced turbulence has a large additive effect on gas transfer. For coastal regions, spikes or bumps in k with wind are common in prior studies (Marino and Howarth 1993; Borges et al. 2004b; Tokoro et al. 2007), however these bumps are often in the range of $20\text{-}40 \text{ cm hr}^{-1}$ (Marino and Howarth 1993; Tokoro et al. 2007) and rarely exceed values of 60 cm hr^{-1} (Borges et al. 2004a) in contrast with the maximum of 84 cm hr^{-1} measured in this study. Chamber wall derived turbulence is a major concern in all floating dome studies and turbulence from the chamber wall may have affected data derived at current speeds above 0.35 m s^{-1} . Therefore, because the chamber wall may have contributed artificially to k at high current speeds, for comparison between models determined in this study and those determined in other estuarine areas, k_{600} has been filtered to current speeds below 0.35 m s^{-1} .

Table 8. Common models used for estuarine k_{600} as a function of current and wind speeds determination along with models determined in the Duplin River.

Model	n	r^2	P value	reference
$k_{600} = 1.91e^{0.35U_{10}}$	-	-	-	(Raymond and Cole 2001)
$k_{600} = 0.045 + 2.20277U_{10}$	4	0.8870	0.037	(Carini et al. 1996)
$k_{600} = 0.94e^{(1.09+0.249U_{10})}$	9	0.5500	0.0001	(Marino and Howarth 1993)
$k_{600} = 6.97e^{0.20U_{10}}$	86	0.2200	<0.0001	(Guerin et al. 2007)
$k_{600} = 11.82e^{0.0965U_{10}}$	100	0.0377	0.0296	This study (all)
$k_{600} = 6.77e^{0.142U_{10}}$	87	0.3788	<0.0001	This study ($u < 0.35 \text{ m s}^{-1}$)
$k_{600} = 14.6\sqrt{\frac{u}{h}}$	-	-	-	(O'connor and Dobbins 1956)
$k_{600} = 46.6\sqrt{\frac{u}{h}}$	87	0.2680	0.0025	This study ($u < 0.35 \text{ m s}^{-1}$ $U_{10} < 5 \text{ m s}^{-1}$)
$k_{600} = 6.1 + 18.7\sqrt{\frac{u}{h}}$	9	0.7250	<0.0001	(Borges et al. 2004a)
$k_{600} = 1.0 + 17.19\sqrt{\frac{u}{h}} + 2.58U_{10}$	10	0.9600	<0.0001	(Borges et al. 2004b)
$k_{600} = 61.13\sqrt{\frac{u}{h}} + 0.722U_{10}$	100	0.2540	<0.0001	This study (all)
$k_{600} = 29.01\sqrt{\frac{u}{h}} + 1.47U_{10}$	87	0.4773	<0.0001	This study (filtered)

Table 9. Comparison of common models used for estuarine k_{600} as a function of current and wind speeds compared with measured k_{600} determined in the Duplin River.

Model	r^2 between modeled and measured k_{600}	The mean of the absolute residual value	conditions for comparison	reference
$k_{600} = 1.91e^{0.35U_{10}}$	0.35	5.73	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Raymond and Cole 2001)
$k_{600} = 0.045 + 2.20277U_{10}$	0.27	4.97	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Carini et al. 1996)
$k_{600} = 0.94e^{(1.09+0.249U_{10})}$	0.30	5.00	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Marino and Howarth 1993)
$k_{600} = 6.97e^{0.20U_{10}}$	0.32	5.04	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Guerin et al. 2007)
$k_{600} = 11.82e^{0.0965U_{10}}$	0.34	6.11	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	This study (all)
$k_{600} = 6.77e^{0.142U_{10}}$	0.33	3.78	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	This study ($u < 0.35 \text{ m s}^{-1}$)
$k_{600} = 14.6\sqrt{\frac{u}{h}}$	0.98	7.81	($u < 0.35 \text{ m s}^{-1}$ $U_{10} < 5 \text{ m s}^{-1}$)	(O'connor and Dobbins 1956)
$k_{600} = 46.6\sqrt{\frac{u}{h}}$	0.84	4.02	($u < 0.35 \text{ m s}^{-1}$ $U_{10} < 5 \text{ m s}^{-1}$)	This study
$k_{600} = 6.1 + 18.7\sqrt{\frac{u}{h}}$	0.33	4.47	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Borges et al. 2004a)
$k_{600} = 1.0 + 17.19\sqrt{\frac{u}{h}} + 2.58U_{10}$	0.44	4.09	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	(Borges et al. 2004b)
$k_{600} = 61.13\sqrt{\frac{u}{h}} + 0.722U_{10}$	0.49	6.26	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	This study (all)
$k_{600} = 29.01\sqrt{\frac{u}{h}} + 1.47U_{10}$	0.54	3.36	($u < 0.35 \text{ m s}^{-1}$ all U_{10})	This study (filtered)

Values for k_{600} are compared to an empirical relationship derived by Borges et al. (2004b) as a function of current and wind speeds in Fig. 28. It is seen in Fig. 28 and Table 9 that there is

a considerable amount of agreement (lowest residual value for any model comparison) between the equation found in Borges (2004b) and k_{600} determined in the Duplin River, suggesting the viability of Borges' model in the Georgia estuarine zone. This agreement between Borges' model and k_{600} (Table 9) measured in the Duplin River may also represent a verification that turbulence from the chamber wall at current speeds less than 0.35 m s^{-1} does not contribute to overestimations of k_{600} in this study.

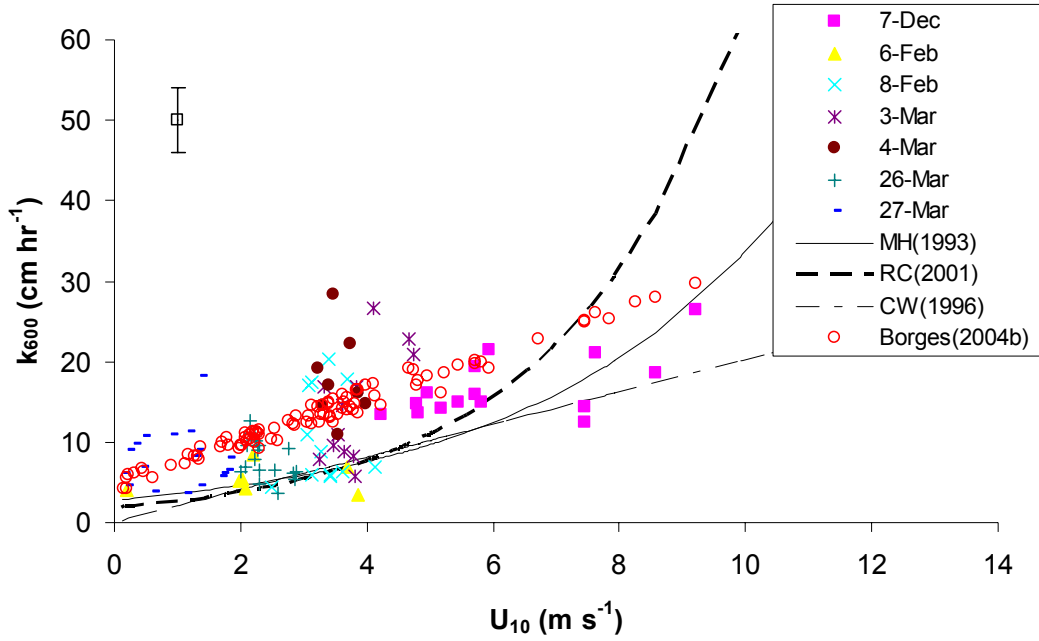


Fig. 28. Total gas transfer velocities with wind speeds at a ten meter height by date filtered for current speeds less than 0.35 m s^{-1} . For comparison Marino and Howarth (1993) [MH(1993)] based on floating chamber-derived fluxes in the tidal freshwater portion of the Hudson River, Raymond and Cole (2001) [RC(2001)] based on the combination of multiple data sets of floating chamber and natural tracers and Carini et al. (1996) [CW(1996)] determined with SF_6 have been plotted. A model from Borges et al. (2004a) determined with a floating chamber is seen to predict filtered gas exchange velocities. The error reported is $\pm 4 \text{ cm hr}^{-1}$ commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007).

High wind speeds ($> 5 \text{ m s}^{-1}$) only occurred on one sampling date, December 7, 2006 and therefore the relationship between k_{600} and wind speed is not as robust on that date as many of the other days. With the exception of the dates corresponding to spring tides, the lowest mean residuals for any of the models which relate wind speed to k are associated with relationships derived in the Parker River estuary (Table 9, Fig 29) from SF_6 tracer measurements (Carini et al. 1996).

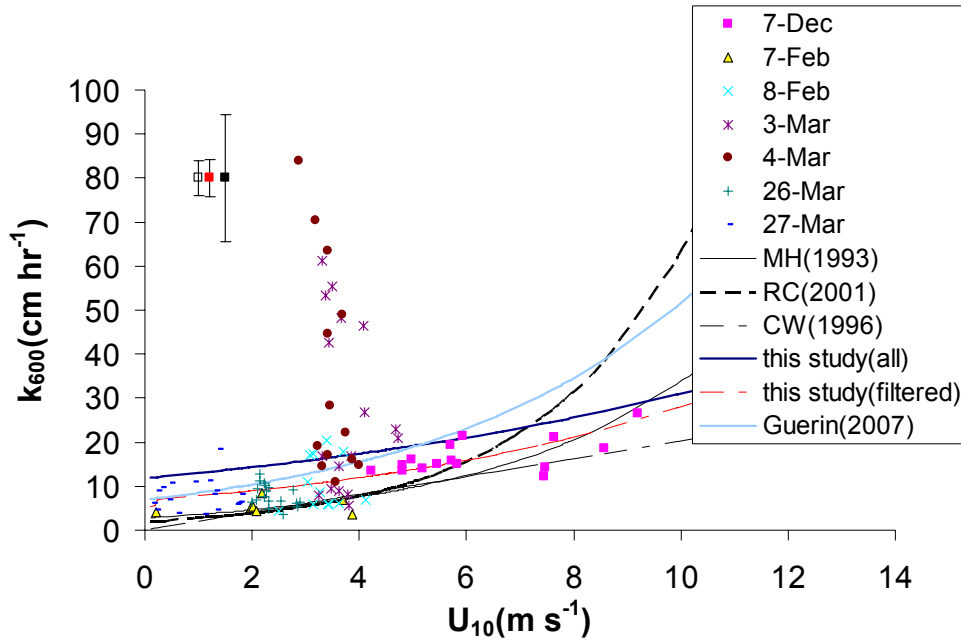


Fig. 29. Total gas transfer velocities normalized to a Sc of 600 with wind speeds at a ten meter height by date. For comparison Marino and Howarth (1993) [MH(1993)] based on floating chamber-derived fluxes in the tidal freshwater portion of the Hudson River, Raymond and Cole (2001) [RC(2001)] based on the combination of multiple data sets of floating chamber and natural tracers and Carini et al. (1996) [CW(1996)] determined with SF_6 have been plotted. In addition two empirical models for this study have been plotted; one for all k 's measured and the second for k filtered to current speeds less than 0.35 m s^{-1} . The errors reported are $\pm 4 \text{ cm hr}^{-1}$ (open square) which is commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007), $\pm 4.3 \text{ cm hr}^{-1}$ (this study filtered; red box) and $\pm 14.5 \text{ cm hr}^{-1}$ (this study all; black box).

Another study (Marino and Howarth 1993) based on floating chamber-derived fluxes in the tidal freshwater portion of the Hudson River (Table 9, Fig 29) also agrees with the relationship between k_{600} and U_{10} derived from this study, however, the Marino and Howarth (1993) study has slightly higher mean residuals and lower correlation coefficients. The model generated from riverine and estuarine derived k_{600} 's (Raymond and Cole 2001) based on a combination of multiple data sets and methods (floating chamber and natural tracers) overestimates gas transfer velocities in the Duplin River for wind speeds above 6 m s^{-1} and exhibits some of the highest residuals seen in any of the model comparisons (Table 9, Fig 29).

Filtered data (Current speed (u) vs. k_{600} (total))

Category 1 represents k measured in low current and wind speeds ($u < 0.35 \text{ m s}^{-1}$ & $U_{10} < 5 \text{ m s}^{-1}$) and therefore the role of tidal currents in generating k may potentially be isolated by modeling k with u in this category. Based on k_{600} values from category 1, filtered wind speeds and current speeds, a simple power function (equation 18) has been created in the same manner as Borges et al. (2004b) and O'Connor and Dobbins (1956) and plotted in Fig. 30.

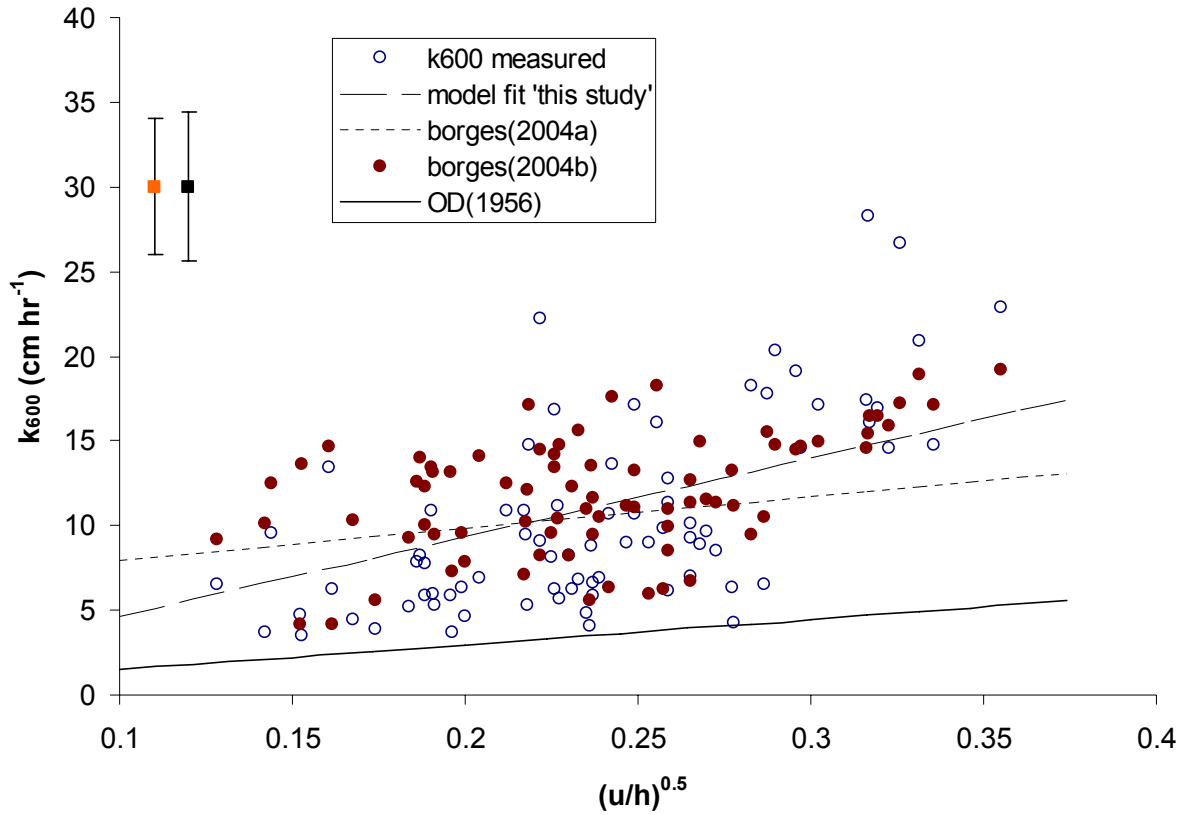


Fig. 30. Gas transfer velocities with $u/h^{0.5}$ filtered for $u < 0.35 \text{ m s}^{-1}$ and wind speeds $< 5 \text{ m s}^{-1}$ (open circles). The modeled fit (equation 18) is represented by the broken line and the Borges (2004a) relationship is represented by the hashed line, while O'Connor and Dobbins (1958) is plotted as the solid black line. The black square represents the standard error associated with the model $\pm 4.6 \text{ cm hr}^{-1}$ and the red square represents a commonly assumed error of $\pm 4 \text{ cm hr}^{-1}$ associated with chamber flux measurements (Kremer et al. 2003; Tokoro et al. 2007).

Measured gas transfer velocities are compared to gas transfer velocities determined by the theoretical surface renewal model (developed in the introduction) and empirical relationships determined in two other tidal estuaries (Borges et al. 2004a; Borges et al. 2004b), the Randers Fjord and Scheldt River estuaries (Fig. 30). The surface renewal model (O'Connor and Dobbins 1956) under represents the measured k (Fig 30., Table 9) in this study potentially due to the renewal term being underestimated by u/h . This underestimation may also be because of a high

degree of bottom roughness or wind shear contributing significantly to k even at low wind speeds. Both of Borges' models represent relationships between k , u and h determined from empirical fits in the estuary and both factor in the influence of wind (U_{10}) on k . The first equation (Table 8) by Borges et al. (2004a) determined a background influence of wind as contributing 6.1 cm hr^{-1} to the gas transfer velocities measured in the Randers Fjord river estuary in conjunction with an empirical fit for the currents contribution to k developed the similarly to equation (18, Table 8). The second model (Borges 2004b) assumes the tidal currents contribution to k_{600} as calculated by the surface renewal model (O'Connor and Dobbins 1956) in addition to the wind contribution determined by a linear regression to measured k 's and U_{10} in the Scheldt river estuary. While both of Borges' models predict k_{600} measured in this study based on the residuals reported in Table 9, the second model (Borges 2004b) agrees better, suggesting that wind shear cannot be neglected when determining gas transfer velocities in the Duplin River under the current speeds of $0\text{-}0.35 \text{ m s}^{-1}$ and wind speeds less than 5 m s^{-1} .

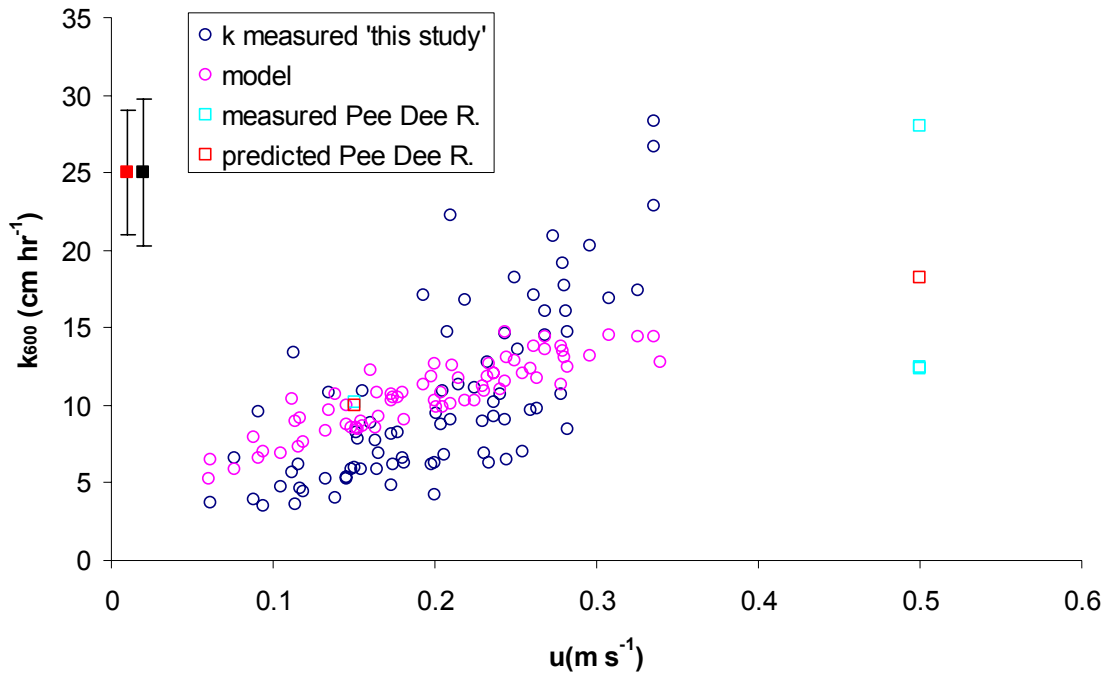


Fig. 31. Total gas transfer velocities with current speeds less than 0.35 m s^{-1} and wind speeds less than 5 m s^{-1} compared with modeled results from equation (18) and experiment results from Elsinger and Moore (1983). The error reported is $\pm 4 \text{ cm hr}^{-1}$ (red square) commonly assumed to be the uncertainty in floating chamber studies (Kremer et al. 2003; Tokoro et al. 2007). The standard error of ± 4.6 of the model regression is represented by the black square.

Along with the gas transfer velocities measured in this study, gas transfer velocities from the Pee Dee River on the South Carolina Coast (Elsinger and Moore 1983) have been plotted in Fig. 31. Transfer velocities from that study were obtained by measuring ^{222}Rn evasion based on the loss of a terrestrial radon signal towards the ocean and represent the only other investigation of gas transfer velocities along the near-shore southeastern coast. Wind data for the Pee Dee river study was not reported so it is difficult to directly compare gas transfer velocities measured over the whole spectrum of wind speeds. The absence of the wind data in Elsinger and Moore (1983) is most likely because the study was based on more than just the estuarine zone, encompassing the upriver portions as well; and due to fetch limitation, wind is not as likely to be

as important as bottom friction generated turbulence in controlling gas transfer velocities. Thus, Elsinger and Moore (1983) may be used as an estimate for k measured in higher current speeds and lower wind speeds, as compared with k measured in this study. The model derived from category 1 (equation 18) predicts k 's measured in the Pee Dee river almost exactly at lower current speeds ($u = 0.15 \text{ m s}^{-1}$) and falls in between the two gas transfer velocities measured at current speeds of 0.5 m s^{-1} (Fig. 31).

Multi-linear regression of current speeds (u) and wind speeds (U_{10}) to k_{600}

Two multi-linear regressions of k_{600} measured with current and wind speeds are presented. One based on all gas transfer velocities measured and a second based on those measured in current speeds under 0.35 m s^{-1} . The model from equation (19), based on all measured values of k_{600} , incurs a large error in predicted gas transfer velocities over 25 cm hr^{-1} (Fig. 25). In contrast, based on the residuals calculated in Table 9, equation (20) predicts k measured significantly better than the fit derived from all k 's measured (Fig. 26, Table 9), again suggesting that the measured gas transfer velocities in high current speeds may be inaccurate or, at least, that the square root dependence of u to k is insufficient to explain the spring tides. The second model (equation 20) represents the best fit in this study over any regression calculated (Table 8) where the coefficient in the currents contribution to k_{600} is the closest to that of the surface renewal theory (Table 9). The coefficient determined by regression for the current speed term (29.01) in equation (20) is more similar to that developed by O'Connor and Dobbins (1956) (14.6) than the coefficient (44.6) in equation (18), suggesting that this relationship represents a

better fit for k_{600} on u in the Duplin River and may adequately predict gas transfer velocities there without the influence of wind.

Given that equation (20) is the best predictor of k , the fractional contribution to k can be calculated from bottom generated turbulence and from wind. The % k current term and % k wind term can be calculated by equation (21) for bottom generated turbulence and equation (22) for wind based on the measured values of u , h and U_{10} .

$$\%current = 29.01 \sqrt{\frac{u}{h}} / k_{600} \quad (21)$$

$$\%wind = 1.47 U_{10} / k_{600} \quad (22)$$

For wind speeds over 5 m s^{-1} the wind contributes over 50% of k_{600} (Fig. 32a) and as seen in Fig. 32b throughout the majority of deployments, current speeds contribute over 50% of k . In addition, under conditions measured in this study, current speeds are the dominant variable in determining k . Assuming that this study represents ordinary wind and current conditions, current speeds cannot be neglected when determining k or dissolved gas fluxes in the Duplin River. However, wind speeds also have a large contribution to k , particularly at wind speeds in excess of 4 m s^{-1} ; therefore, in the Duplin River current speeds and wind speeds both require attention in the proper estimation of k .

In addition, the variance explained by the model (equation 20) for both currents and wind was calculated. This was calculated by taking the difference between the total variance (the standard deviation of k_{600} squared) and the error variance (the standard deviation of the residuals squared). The variance explained by the currents influence on k_{600} is 33.7% and from the winds influence on k_{600} is 33.1%, leaving 29.9 % of the variance in k_{600} unexplained by the equation (20). Thus, the current has a larger affect on the total magnitude of k and plays a slightly larger role in the variance as well.

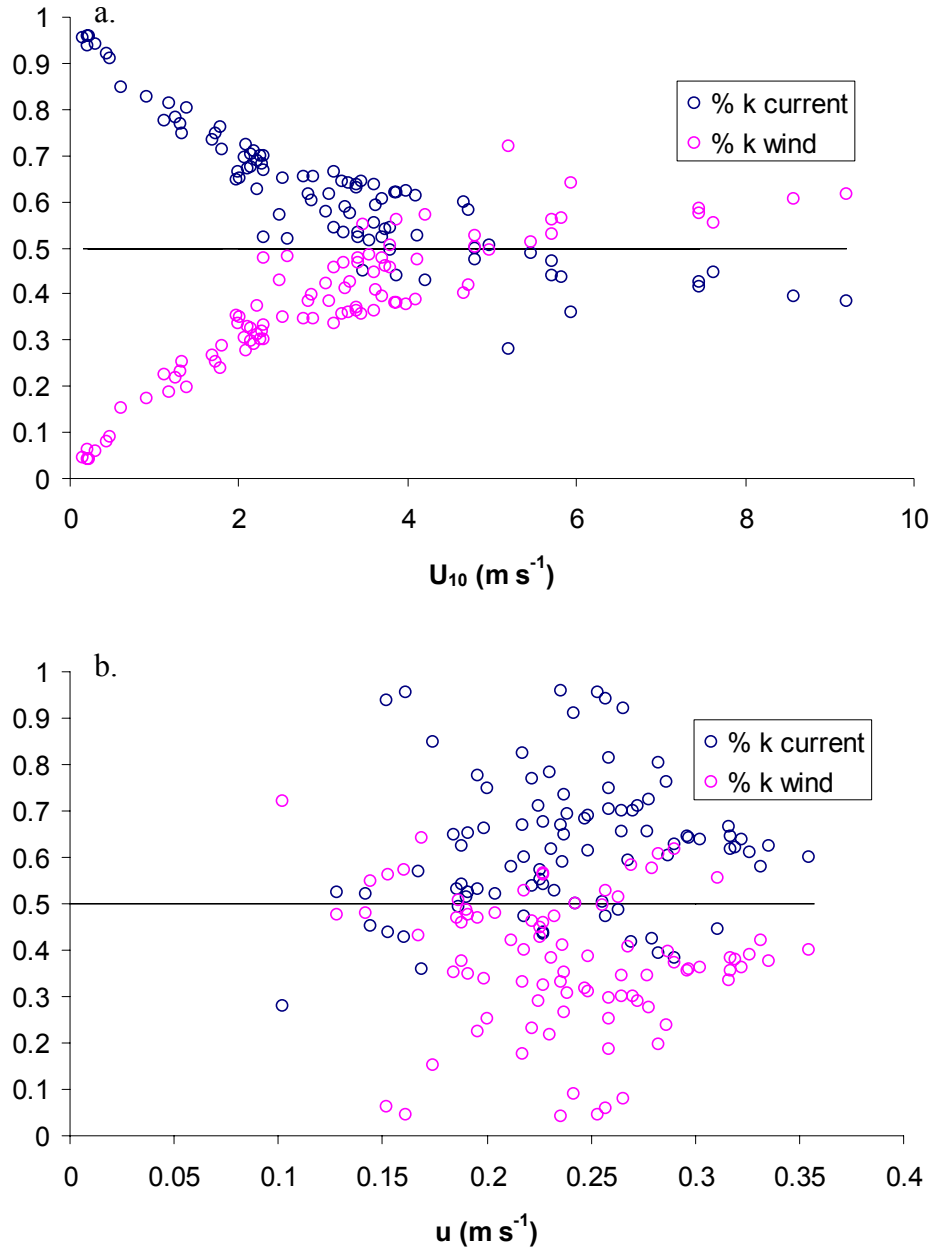


Fig 32. (a) k_{600} plotted in terms of the fractional contribution from currents and from wind against wind speeds measured in this study; all points are based on the measured u , h , and U_{10} calculated by equation (20, Table 8). (b) k_{600} plotted in terms of the fractional contribution from currents and from wind against current speeds measured in this study.

Fluxes

Over the study period individual fluxes per chamber deployment are plotted in Fig. 27. On February 7th and 8th the Duplin was a weak sink for CO₂ (-1 to -3 mmol m⁻² d⁻¹) while the only other study of CO₂ fluxes (Wang and Cai 2004) estimated the Duplin River to be a year-round CO₂ source. Throughout all of March measured CO₂ fluxes agreed well with fluxes (30 to 90 mmol m⁻² d⁻¹) estimated in Wang and Cai (2004) with the exception of high tide values. CO₂ fluxes during December 7 exhibit the largest exchange over the entire study, much larger than the 2004 study previously mentioned. However, in the 2004 study, average monthly wind speeds of 3-4 m s⁻¹ were applied to determine gas flux based on interfacial CO₂ gradients while for December 7th wind speeds in this study were much higher (6-12 m s⁻¹) than the calculated average and therefore yielded much higher fluxes.

CHAPTER 5

CONCLUSIONS

Fluxes were determined directly, using a floating chamber, for fifteen minute intervals over the winter between 2006 and 2007 from Marsh Landing Dock on Sapelo Island, Georgia. Interfacial $p\text{CO}_2$ concentrations were measured alongside the fluxes using a coupled equilibrator and infrared gas detector whereby gas transfer velocities were calculated. In addition, current speeds were measured using an acoustic doppler current profiler and correlated with gas transfer velocities along side wind speeds.

The objectives for this study were to measure gas transfer velocities in an important estuarine zone (the Duplin River) and to determine relationships with known relevant variables (current and wind speeds) in estimating gas transfer velocities. While this study covered a relatively short period of time a number of useful conclusions may be derived; primarily that in the Duplin River, with the exception of spring tides, wind is an important variable controlling k in agreement with prior empirical measurement of estuarine k values from Carini et al.(1996) and Marino and Howarth (1993). However, bottom generated turbulence was responsible for more than half of the gas transfer velocity during almost all of the deployments. In addition, gas transfer during spring tides may be able to substantially increase k , well above that of the theoretically derived values by O'connor and Dobbins (1956). However, more gas transfer measurements in the Duplin River with free floating chambers will be required to verify this.

In order to better parameterize global CO₂ gas exchange between the oceans and atmosphere resulting from estuarine degassing, gas transfer velocities in these regions must be critically investigated. However, one of the reasons models are still so uncertain is the high number of variables controlling k_{600} in these regions. Hydrodynamic qualities such as bottom generated turbulence are still poorly constrained and may vary due to heterogeneities in stream bed slope and bottom roughness. Wind shearing effects on k are also hard to constrain due to different fetch limitations and the interplay between current derived turbulence and wind shear.

Chamber studies, while highly debated, have proven consistent with geochemical tracer studies and mass balance methods. In addition, due to the high temporal resolution of the deployment, they make ideal candidates for gas transfer studies with rapidly changing current speeds and geochemical settings. Newer methods such as eddy correlation and the controlled flux technique are rapidly replacing the need for floating dome studies due to the equally high temporal resolution and higher accuracy. However, floating chamber studies may still be around for quite some time because more accurate studies for k are technically more rigorous and considerably more expensive. In addition, they still incur large errors due to the difficulty in determining a whole new set of uncertain terms, for example air side eddy diffusion coefficients in the controlled flux technique or high precision turbulent velocity fluctuations in the air layer for eddy correlation studies.

There were two major obstacles in this study. The first is that turbulence from the chamber wall may have contributed to the magnitude of k_m and errors associated with this phenomenon are un-quantified. The second is the location of the study; chamber deployments should float freely near the center of the estuary away from obstructions in the stream flow. Due mainly to financial constraints this study was limited to dock deployments from the side of the

estuary where the max current speed is expected to be less than the center channel suggesting a greater role in bottom generated stream turbulence. All steps possible were taken to ensure no artifacts in the dock deployments affected the measured gas transfer velocities. However, chamber deployments from a free floating boat and attached to a drogue would be ideal.

Future work in estuarine gas transfer velocities need to rely on classifying estuaries and rivers in terms of relevant physical properties involved in air-sea gas exchange. Fetch limitation, stream depth, bottom topography, current speed, and wind friction seem to all be relevant factors. With an increase in empirically determined gas transfer velocity measurements and a better understating of the relevant variables in the world's coastal zones in determining them, general fits for particular estuaries may be achievable and thus higher resolution in global CO₂ air-sea cycling calculations will be obtainable.

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APPENDIX A. DERIVATION OF THE SURFACE RENEWAL MODEL.

Given the distribution of surface ages capable of gas exchange as a function of renewal rate in equation (1A).

$$flux = -D_{gas} r \int_0^{\infty} \left(\frac{\partial C}{\partial z} \right)_{z=0} e^{-rt} dt \quad (1A)$$

It is seen that equation (1A) can be rewritten in term of its Laplace transform in equation (2A).

$$flux = -D_{gas} r \left[\frac{\partial}{\partial z} \int_0^{\infty} e^{-rt} (C) dt \right]_{z=0} \quad (2A)$$

And written explicitly in equation (3A).

$$flux = -D_{gas} r \left[\frac{\partial \bar{C}}{\partial z} \right]_{z=0} \quad (3A)$$

Before the flux can be calculated, $C(t,z)$ is derived in terms of exchange over the whole water column. Where C_0 represents the initial concentration in the water column and C_a represents the concentration in the air. Where at time 0 the entire water column is of concentration C_0 and any time dt the concentration is equal to the air side concentration (C_a). In addition there is a 'no flux' boundary condition at $z=h$ for all time.

$$at \ t=0; \ C=C_0; \ 0 < z < h$$

$$at \ t>0; \ C=C_a; \ z=0$$

$$\frac{\partial C}{\partial z} = 0; \ t>0; \ z=h$$

Transformed boundary conditions can be applied by developing a new C

$C' = C - C_w$. Therefore the new boundary conditions are written in terms of C' rather than C .

$$\text{at } t=0; C'=0; 0 < z < h$$

$$\text{at } t>0; C'=C_a-C_0; z=0$$

$$\frac{\partial C'}{\partial z} = 0; t>0; z=h$$

Given the diffusion equation in terms of the transformed concentrations

$$\frac{\partial^2 C'}{\partial z^2} = \frac{1}{D} \frac{\partial C'}{\partial t} = 0 \quad (4A)$$

Applying a Laplace transform to equation (4A).

$$\int_0^\infty e^{-rt} \frac{\partial^2 C'}{\partial z^2} dt - \frac{1}{D} \int_0^\infty e^{-rt} \frac{\partial C'}{\partial t} dt = 0 \quad (5A)$$

Equation (6A) is developed in terms of the Laplace transform.

$$\frac{\partial^2 \bar{C}'}{\partial z^2} - \frac{1}{D} (r \bar{C}') = 0 \quad (6A)$$

Where the general solution is given in equation 7A.

$$\bar{C}' = A \sinh\left(\sqrt{\frac{r}{D}} z\right) + B \cosh\left(\sqrt{\frac{r}{D}} z\right) \quad (7A)$$

Applying the second transformed (in terms of transformed coordinate system and the Laplace

transform) boundary condition (at $t>0; \bar{C}' = \frac{C_a - C_0}{r}; z=0$). At $z=0$ the sinh term goes to 0 and

the cosh term goes to 1 leaving $\bar{C}' = B$.

$$\overline{C'} = \frac{C_a - C_0}{r} = A \sinh\left(\sqrt{\frac{r}{D}} z\right) + B \cosh\left(\sqrt{\frac{r}{D}} z\right) = B \quad (8A)$$

Then applying the third boundary condition where there is no flux at the bottom of the stream or

estuary at $Z=h$; $\frac{\partial \overline{C'}}{\partial z} = 0$

$$\frac{\partial \overline{C'}}{\partial z} = A \cosh\left(\sqrt{\frac{r}{D}} h\right) + B \sinh\left(\sqrt{\frac{r}{D}} h\right) = 0 \quad (9A)$$

And rearranging in terms of A.

$$A = -B \frac{\sinh\left(\sqrt{\frac{r}{D}} h\right)}{\cosh\left(\sqrt{\frac{r}{D}} h\right)} \quad (10A)$$

After solving and substituting out the integration constants A and B specific solution (equation 11A) is calculated for equation (7A).

$$\overline{C'} = \left(\frac{C_a - C_0}{r}\right) \frac{\cosh\left(\sqrt{\frac{r}{D_{gas}}} (h - z)\right)}{\cosh\left(\sqrt{\frac{r}{D_{gas}}} h\right)} \quad (11A)$$

The derivative of equation (11A) is equation (14A) which is incorporated back into equation (1A) and evaluated at $z = 0$ to give equation (15A). Given that the change in concentration with depth is the same in terms of the transformed boundary conditions as in the original boundary conditions.

$$\frac{\partial \bar{C}}{\partial z} = \frac{\partial \bar{C}'}{\partial z} \quad (12A)$$

Equation one can be rewritten in terms of a Laplace transform. In order to derive these terms

$\bar{C}'$ needs to be derived in terms of transport properties in the water column.

$$flux = -D_{gas} r \left[\frac{\partial \bar{C}'}{\partial z} \right]_{z=0} \quad (13A)$$

where

$$\frac{\partial \bar{C}'}{\partial z} = \left(-\sqrt{\frac{r}{D_{gas}}} \right) \left(\frac{C_a - C_0}{r} \right) \frac{\sinh \left(\sqrt{\frac{r}{D_{gas}}} (h - z) \right)}{\cosh \left(\sqrt{\frac{r}{D_{gas}}} h \right)} \quad (14A)$$

After substituting equation (14A) into equation (13A) the model for gas transfer is developed and written (equation 15A) in terms of gas transfer velocities, k (equation 16A).

$$flux = (C_a - C_o) \sqrt{Dr} \tanh \left(\frac{rh^2}{D_{gas}} \right) \quad (15A)$$

$$k = \sqrt{Dr} \tanh \left(\frac{rh^2}{D_{gas}} \right) \quad (16A)$$