Air–water fluxes and sources of carbon dioxide in the Delaware Estuary: spatial and seasonal variability

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Abstract. Distributions of surface water partial pressure of carbon dioxide (pCO₂) were measured on nine cruises in the Delaware Estuary (USA). The Delaware River was highly supersaturated in pCO₂ with respect to the atmosphere during all seasons, while the Delaware Bay was undersaturated in pCO₂ during spring and late summer and moderately supersaturated during mid-summer, fall, and winter. While the smaller upper tidal river was a strong CO₂ source (27.1 ± 6.4 mol-C m⁻² yr⁻¹), the much larger bay was a weak source (1.2 ± 1.4 mol-C m⁻² yr⁻¹), the latter of which had a much greater area than the former. In turn, the Delaware Estuary acted as a relatively weak CO₂ source (2.4 ± 4.8 mol-C m⁻² yr⁻¹), which is in great contrast to many other estuarine systems. Seasonally, pCO₂ changes were greatest at low salinities (0 ≤ S < 5), with pCO₂ values in the summer nearly 3-fold greater than those observed in the spring and fall. Undersaturated pCO₂ was observed over the widest salinity range (7.5 ≤ S < 30) during spring. Near to supersaturated pCO₂ was generally observed in mid- to high-salinity waters (20 ≤ S < 30) except during spring and late summer. Strong seasonal trends in internal estuarine production and consumption of CO₂ were observed throughout both the upper tidal river and lower bay. Positive correlations between river-borne and air–water CO₂ fluxes in the upper estuary emphasize the significance of river-borne CO₂ degassing to overall CO₂ fluxes. While river-borne CO₂ degassing heavily influenced CO₂ dynamics in the upper tidal river, these forces were largely compensated for by internal biological processes within the extensive bay system of the lower estuary.

1 Introduction

While, globally, the surface area of estuaries is only about 4 % that of continental shelves, recent studies have concluded that the carbon dioxide (CO₂) degassing flux from estuarine waters is as large as the CO₂ uptake by the continental shelf (Borges, 2005; Borges et al., 2005; Cai et al., 2006; Chen and Borges, 2009; Cai, 2011). Global estuarine waters are estimated to emit 0.10–0.45 Pg C yr⁻¹, while continental shelves take up 0.20–0.40 Pg C yr⁻¹ (Borges, 2005; Borges et al., 2005; Cai, 2011; Chen et al., 2013; Regnier et al., 2013; Laruelle et al., 2015). Such large estuarine CO₂ degassing suggests that much of the terrestrial organic carbon, including that from coastal wetlands, is respired to CO₂ during transport through the estuarine zone, though the relative importance of river-supplied CO₂ and organic carbon versus those from the coastal wetlands is debatable (Borges and Abril, 2011; Cai, 2011). In turn, estuarine waters are a major source of CO₂ to the atmosphere, with partial pressures of CO₂ (pCO₂) ranging from 350 to 10 000 µatm and air–water CO₂ fluxes ranging from −5 to 80 mol C m⁻² yr⁻¹ (Raymond et al., 1997; Cai and Wang, 1998; Frankignoull et al., 1998; Borges, 2005; Borges et al., 2006; Borges and Abril, 2011; Cai, 2011).

There is rising concern that global estuarine CO₂ degassing flux may be overestimated (Cai, 2011). Although substantial progress has been achieved over the past decade (Borges and Abril, 2011; Chen et al., 2013; and references therein), our knowledge of CO₂ degassing fluxes and their controlling processes in estuaries remains insufficient. Globally, the majority of past estuarine CO₂ studies have been conducted on small estuarine systems, which typically have...
high \( p\text{CO}_2 \). (Chen and Borges, 2009; Cai, 2011; Borges and Abril, 2011). Specifically, in the US east coast, high \( p\text{CO}_2 \) has been found in estuaries along the southeastern (Cai and Wang, 1998; Jiang et al., 2008a) and northeastern (Salisbury et al., 2008; Hunt et al., 2010) coastal regions. While high \( p\text{CO}_2 \) has also been found in small estuaries along the US mid-Atlantic coast (Raymond et al., 1997; Raymond et al., 2000), only a few estuarine \( \text{CO}_2 \) studies have been conducted in this region, such as Crosswell et al. (2012) in the Neuse River, NC; Raymond et al. (1997) in Hudson River, NY; and Raymond et al. (2000) in the York River, VA. Thus, there is limited research on \( \text{CO}_2 \) dynamics in large estuaries or bay systems with long freshwater residence times in the US mid-Atlantic coast (most notably the Chesapeake and Delaware estuaries). Presumably, these large estuaries have lower \( p\text{CO}_2 \) than small estuaries or bay systems with rapid freshwater transit times (Borges and Abril, 2011; Cai, 2011). Except for a few recent studies and the pioneering work of Sharp and Culberson, over the past 30 years there have been few inorganic carbon studies in the Delaware Estuary (Culberson, 1988; Sharp et al., 2009). Air–water \( \text{CO}_2 \) fluxes, total DIC fluxes, and ongoing evaluations of water acidification have not been consistently (via annual and seasonal surveys) studied. Overall, there is a lack of data and a pressing need to synthesize and expand global research to larger estuaries. Furthermore, of past estuarine \( \text{CO}_2 \) studies, many lack spatial and seasonal coverage of surface water \( p\text{CO}_2 \) and air–water \( \text{CO}_2 \) fluxes, making flux estimates highly uncertain.

The Delaware Estuary is divided into an upper 100 km long tidal Delaware River and lower Delaware Bay (Fig. 1; Sharp, 2010). With a relatively simple hydrology, the Delaware Estuary is fairly easy to characterize, and because of this it has served as a model estuary for biogeochemical studies (Cifuentes et al., 1988; Sharp et al., 2009). The tidal freshwater portion of the Delaware River flows from the head of the tide near Trenton, NJ, through the greater Philadelphia area, the sixth largest municipal region of the US, before passing into the saline Delaware Bay (Fig. 1; Sharp et al., 2009; Sharp, 2010). In turn, the upper Delaware River is heavily influenced by major industrial activity and continuously responding to a rapidly changing environment. For example, in the mid-20th century, the urban river of the Delaware Estuary suffered from severe hypoxia, with average summer dissolved oxygen (DO) concentrations near zero (Sharp, 2010). Fortunately, the implementation of the Clean Water Act (CWA) in the early 1970s helped promote efforts to improve water quality conditions in the Delaware River. With major upgrades to large sewage treatment plants, DO concentrations since the early 1990s have consistently been above the CWA standard of 3.5 mg L\(^{-1}\) (\(\approx 219 \mu\text{mol L}\(^{-1}\)); Sharp, 2010). Nonetheless, high \( p\text{CO}_2 \) is still expected to be associated with strong respiratory O\(_2\) consumption in the upper estuary. In contrast, the Delaware Bay is a large shallow embayment surrounded by salt marshes with minimal industrial or municipal inputs (Cifuentes et al., 1988). Thus, the Delaware Estuary is governed by the dynamic interaction between a river-dominated upper estuary and an ocean-dominated lower bay. This feature, typical for other large estuaries and, depending on river flow and geomorphology, smaller estuarine systems as well, provides us the opportunity to examine how contrasting geographical settings, physical mixing processes, and ecosystem metabolism in an extensive bay system can affect \( \text{CO}_2 \) gas exchange.

In this paper, we report the first seasonal distribution of \( p\text{CO}_2 \) and air–water \( \text{CO}_2 \) flux in the Delaware Estuary, which was surveyed nine times via various day- to week-long surveys from 2013 through 2014. We further assess the temperature and biological effects on \( p\text{CO}_2 \) distributions as well as the overall contribution of internal versus riverine sources on \( \text{CO}_2 \) inputs to the estuarine system. Finally, we present a summarized \( p\text{CO}_2 \) distribution over the study area and provide a conceptual model to illustrate the control mechanisms on surface water \( \text{CO}_2 \) dynamics in the Delaware Estuary.
2 Methods

2.1 Field measurements

The Delaware Estuary was surveyed on nine cruises: 8–10 June 2013, 8–15 August 2013, 17 October 2013, 17–22 November 2013, 23–24 March 2014, 3 July 2014, 27 August–1 September 2014, 30 October–2 November 2014, and 5 December 2014. Distributions of $pCO_2$, dissolved inorganic carbon (DIC), total alkalinity (TA), and pH were measured from the mouth of the bay to the near-zero salinity of the estuary in five of the nine cruises. During the August and October 2013 cruises, only surface water $pCO_2$ was measured.

To monitor levels of $pCO_2$, surface water was directly pumped from 1 to 2 m below the sea level through an undereway $pCO_2$ analyzer (AS-P2, Apollo Scitech) installed in the shipboard laboratory (Huang et al., 2015). Surface water flowed into a 1 L volume shower head equilibrator at a minimum rate of 1.7 L min$^{-1}$ to facilitate rapid gas exchange. A specifically designed water-drain system is attached to the equilibrator to insure that the pressure inside and outside remains balanced (Jiang et al., 2008b). The equilibrated gas was pumped through a water trap (Peltier cooler), which removed most of the water vapor, and then into a drying tube packed with magnesium perchlorate ($Mg(ClO_3)_2$) or Nafion tubing. Surface water $CO_2$ (mole fraction of dry air ($xCO_2$)) was measured approximately every 1.5 min using an undereway flow-through system equipped with a non-dispersive infrared (NDIR) gas analyzer (Li-Cor, model LI-7000, Lincoln, NE, USA). The LI-7000 was calibrated, every 3–6 h, against three or four $CO_2$ gas standards (151.5, 395.4, 982.6, and 1969 ppm $CO_2$ in air) referenced against standards traceable to those of the National Institute of Standards and Technology (NIST). Atmospheric $xCO_2$ was measured every 3–6 h using the same $CO_2$ system. In order to avoid contamination from the ship’s stack gases or other possible sources of air pollution, the inlet of the atmospheric $CO_2$ pipe was installed on the highest platform in the front of the ship. An onboard Sea-Bird thermosalinograph (SBE-45) measured surface water temperature and salinity. To calculate surface water and atmospheric $pCO_2$ values, all $xCO_2$ measurements were corrected to 100% saturation of water vapor pressure and the in situ surface water temperature (Dickson et al., 2007).

DIC and TA water samples were collected throughout the salinity gradient. Multiple samples were taken at near-zero salinity and at the mouth of the bay to obtain river and ocean end-member values. Samples for DIC and TA measurements were filtered through a cellulose acetate filter (0.45 µm) into 250 mL borosilicate bottles and then fixed with 100 µL of saturated mercury bichloride solution (Cai and Wang, 1998; Jiang et al., 2008a). When collecting water, all bottles were overflowed for at least twice its volume to minimize contact with the atmosphere. Afterwards, sample bottles were kept at 4 to 10 °C for future analysis. DIC was determined by acidifying 0.5–1.0 mL samples with phosphoric acid. The extracted $CO_2$ gas was subsequently quantified via an infrared gas analyzer (AS-C3 Apollo Scitech). TA was measured by Gran titration (Gran, 1952) using the open-cell method with a semi-automatic titration system (AS-ALK2, Apollo Scitech; Cai et al., 2010a; Huang et al., 2012). Both DIC and TA measurements were calibrated against certified reference material (CRM, provided by A. G. Dickson from Scripps Institution of Oceanography) at a precision level of about $\pm 2 \mu$mol kg$^{-1}$ (Huang et al., 2012).

2.2 Air–water $CO_2$ flux estimation

In this study, air–water $CO_2$ fluxes ($F$, mmol m$^{-2}$ d$^{-1}$) at pixel $i$ of a 0.01 longitude × 0.01 latitude grid were calculated as follows:

$$F_i = k_i \cdot K_{oi} \cdot \left( pCO_{2(water)} - pCO_{2(air)} \right),$$

where $k_i$ (cm h$^{-1}$) is the gas transfer velocity of $CO_2$; $K_{oi}$ is the solubility coefficient of $CO_2$ (mol L$^{-1}$ atm$^{-1}$), which can be calculated from in situ temperature and salinity (Weiss, 1974); and $pCO_{2(water)}$ and $pCO_{2(air)}$ (µatm) are the partial pressure of $CO_2$ in the water and the air, respectively. The mean atmospheric $xCO_2$ during each cruise and the sea surface temperature, salinity, and pressure were used to calculate the $pCO_{2(air)}$. A positive $F$ value indicates $CO_2$ transfer from water to the atmosphere.

Generally, two main issues arise when trying to accurately determine air–water $CO_2$ fluxes in coastal waters: (1) how to accurately represent surface turbulence and (2) obtaining spatial and temporal heterogeneity of $CO_2$ distributions. One of the greatest uncertainties when calculating air–water $CO_2$ fluxes is estimating gas transfer velocities (Wanninkhof et al., 2009). While gas transfer velocities primarily depend on wind regime in the open ocean, in coastal and shallower estuaries it is probably more complicated as other factors such as tidal currents, bottom stress, wave slope, turbidity, surface films, and fetch limitation can also influence gas exchange rates (Raymond and Cole, 2001; Borges et al., 2004; Zappa et al., 2007; Jiang et al., 2008a; Abril et al., 2009). Unfortunately, because there have not been many studies on gas transfer velocities in estuaries, we relied on wind speed dependence to estimate gas exchange rates. Moreover, limited research has been conducted at wind speeds less than 4 m s$^{-1}$. In turn, quadratic relationships that estimate $k$ often extrapolate to zero at low wind speeds (Wanninkhof et al., 2009). Increasing evidence suggests that $k$ does not approach zero at low wind speeds but rather asymptotically to a finite value due to various external factors such as buoyancy effects, chemical enhancements, and physical mixing processes (McGillis et al., 2001; McGillis et al., 2004; Wanninkhof et al., 2009). To avoid gas transfer velocities of zero in river and inland waters where wind speeds are typically low, we adopted the gas transfer relationship as proposed by
Wanninkhof et al. (2009):

\[ k_{660} = 3 + 0.1 \cdot U_{10} + 0.064 \cdot U_{10}^2 + 0.011 \cdot U_{10}^3, \]  
where \( k_{660} \) is the gas transfer velocity at the Schmidt number of 660, which can be calculated from in situ sea surface temperature (Wanninkhof, 1992), and \( U_{10} \) is the wind speed at 10 m above the water surface. Another challenge to accurately determining air–water CO\(_2\) fluxes is obtaining reliable spatial and temporal \( p\text{CO}_2 \) distributions. Unfortunately, while seasonal distributions of \( p\text{CO}_2 \) were measured from the mouth of the bay to the near-zero salinity of the estuary (north to south), our lack of cross-bay transects (east to west) limits our knowledge of CO\(_2\) dynamics in shallow water regions of the estuary. Thus, there is a pressing need to conduct more research near these shallow water boundaries.

In addition, because the relationship between \( k \) and mean wind speeds is nonlinear, temporal distributions of wind speeds influence gas transfer velocities (Wanninkhof, 1992; Wanninkhof et al., 2002). To accurately determine the effect of variability of winds over a month, Wanninkhof (1992) introduced the nonlinearity coefficient of the wind speeds (\( C_2 \)), which is calculated as follows (Wanninkhof et al., 2002; Jiang et al., 2008b):

\[ C_2 = \left( \frac{1}{n} \sum_{j=1}^{n} U_j^2 \right) / U_{\text{mean}}^2, \]  
where \( C_2 \) is the nonlinearity coefficient for quadratic terms of gas transfer relationships, \( U_j \) is the high-frequency wind speed collected at the buoy, \( U_{\text{mean}} \) is the monthly mean wind speed, and \( n \) is the total number of available wind speeds during that month. We used high-frequency wind speed data (measured every 6 min) obtained from four National Oceanic and Atmospheric Administration (NOAA) buoys (LWSD1, CMAN4, SJSN4. and DELD1) to calculate the nonlinearity coefficients at each buoy and extrapolate them to the entire estuary. Using the calculated nonlinearity coefficients, gas transfer relationships were corrected to obtain the most accurate relationship between gas transfer velocities and wind speeds during each month.

In order to calculate area-averaged CO\(_2\) flux throughout the Delaware Estuary, the system was divided into five geographic zones as defined by Sharp et al. (2009). However, due to rapid change in \( p\text{CO}_2 \) values across the mid-bay, this region was split into an upper and mid-bay zone to allow for a more robust comparison of \( p\text{CO}_2 \) and CO\(_2\) fluxes throughout the system (Fig. 1). Surface water \( p\text{CO}_2 \), temperature, salinity, wind speed, and pressure were interpolated onto a 0.01 x 0.01 grid. Following the same method as presented in Jiang et al. (2008b), flux \( F_i \) at each pixel was calculated:

\[ S_i = \frac{\Delta \text{Lon}}{2\pi} \cdot \frac{\Delta \text{Lat}}{2} \cdot \left[ \sin \left( \text{Lat}_i + \frac{1}{2} \Delta \text{Lat} \right) - \sin \left( \text{Lat}_i - \frac{1}{2} \Delta \text{Lat} \right) \right], \]  
where \( S_i \) is the total area surrounding pixel \( i \), \( \Delta \text{Lon} \) and \( \Delta \text{Lat} \) are the longitude and latitude intervals of the grid, respectively, \( \text{Lat}_i \) is the latitude at pixel \( i \), and \( R \) is the radius of the earth. The area-averaged CO\(_2\) flux was calculated as follows (Jiang et al., 2008b):

\[ F_{\text{area-averaged}} = \frac{1}{S_1 + S_2 + \ldots + S_n} \sum_{i=1}^{n} F_i \cdot S_i. \]  

Because there is no precise method to account for the uncertainties of air–water CO\(_2\) fluxes, we followed the same approach as described in Jiang et al. (2008b). Atmospheric measurements for each cruise and gas transfer velocities of Wanninkhof et al. (2009) and Wanninkhof (2014) were used to estimate standard deviations of the atmospheric CO\(_2\) and CO\(_2\) flux, respectively.

### 2.3 Temperature-normalized \( p\text{CO}_2 \) estimation

Temperature changes are important as they influence surface water \( p\text{CO}_2 \) by governing the thermodynamic equilibrium of the inorganic carbon system (Takahashi et al., 1993). If only controlled by temperature change and no other physical (mixing) or biogeochemical changes, \( p\text{CO}_2 \) in surface seawater would double for every 16°C increase (\( \partial \ln p\text{CO}_2 / \partial T = 0.0423 \text{°C}^{-1} \); Takahashi et al., 1993). The temperature constant above determined by Takahashi et al. (1993) works well for open-ocean waters with salinities between 34 and 36 as physical mixing with freshwater is generally minor. After temperature normalization, one may attribute the remaining \( p\text{CO}_2 \) change to non-thermal processes (mostly biological activity but possibly also mixing processes). However, in coastal oceans mixing is often serious and influences the interpretations of observed temperature dependences. For example, Jiang et al. (2008a) found that values of (\( \partial \ln p\text{CO}_2 / \partial T \)) in river- and marine-dominated estuaries were less (about 0.027–0.042°C\(^{-1}\)) than that determined by Takahashi et al. (1993). We suggest that a thermodynamic prediction for estuarine water should be used for such comparisons (Bai et al., 2015). We first derived temperature constants for a general estuarine system using the Excel macro CO2SYS (Pierrot, 2006) and inorganic carbon dissociation constants from Millero et al. (2006) for estuarine waters (\( S < 30 \)) and from Mehrbach et al. (1973) reﬁt by Dickson and Millero (1987) for high-salinity waters (\( S > 30 \)). Based on data collected over the past two years, river and ocean end-members of TA (900 and 2300 µmol kg\(^{-1}\), respectively) and of DIC (960 and 2000 µmol kg\(^{-1}\), respectively) were used. Calculated \( p\text{CO}_2 \) varied among different temperatures, from 5 to 30°C, with the largest difference in low salinities (0 to 5; Fig. 2). In turn, when binning salinities to intervals of 5 units, the greatest variability in temperature constants was observed in salinities 0–5 and 5–10 (Table 1). Averaged values of (\( \partial \ln p\text{CO}_2 / \partial T \)) for salinity intervals between 0 and 35 ranged from 0.0332 to 0.0420°C\(^{-1}\) (Table 1). Similar to the results found in Jiang et al. (2008a), temperature-derived constants were lower than the isochemical seawater constant 0.0423°C\(^{-1}\) determined by Takahashi.
et al. (1993). Thus, knowing the extensively complex nature of estuarine systems, it is important to note that derived variances in temperature-normalized $pCO_2$ provide only a relatively simple analysis of seasonal $pCO_2$ fluctuations due to temperature and biological processes as derived variances in temperature-normalized $pCO_2$ neglect the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on $pCO_2$ dynamics.

Using a similar approach to that in Takahashi et al. (2002), we also attempted to separate the temperature effect from other non-thermal effects on seasonal $pCO_2$ change. We first normalized the $pCO_2$ at in situ temperature to the 10-year (2004–2014) annual mean temperature of 13.3 °C via the following (Takahashi et al., 2002):

$$\frac{pCO_2}{pCO_2}_{mean} = \frac{\partial ln pCO_2}{\partial T} \cdot \frac{T_{obs} - T_{mean}}{T_{mean} - T_{obs}}.$$  

(6)

where $T$ is temperature (°C), $C_s$ is the averaged (\(\frac{\partial ln pCO_2}{\partial T}\)) value for the salinity interval, and subscripts “mean” and “obs” indicate the annual mean and observed values. Through this approach, we attributed any differences between calculated and observed $pCO_2$ values to be the result of biological activity and/or physical mixing processes (non-thermal). Because salinity gradients down the estuary vary greatly depending on the season, river discharge, tidal cycle, precipitation, and other circulation processes, salinity-binned climatologies can provide crucial insight into and a different perspective of the various physical and biological controls behind observed $pCO_2$ distributions that geographic boundaries may not. In turn, $pCO_2$ values from each survey were constructed into salinity-binned climatologies (intervals of 5 salinity units from 0 to 30) to better isolate and interpret the thermal versus non-thermal effects on seasonal $pCO_2$ fluctuations. Observed $pCO_2$ values during months with no surveys were estimated by linearly regressing data from adjacent months with sample measurements. In contrast, to best analyze the effect of temperature changes on observed $pCO_2$ values, annual mean $pCO_2$ values across each salinity interval were used in conjunction with the mean and observed temperatures via the following equation (Takahashi et al., 2002):

$$\frac{pCO_2}{pCO_2}_{mean} = \frac{\partial ln pCO_2}{\partial T} \cdot \frac{T_{obs} - T_{mean}}{T_{mean} - T_{obs}}.$$  

(7)

Using this method, we attributed any differences between calculated mean versus observed $pCO_2$ values as a result of seasonal temperature changes. To remove the temperature effect from observed in situ $pCO_2$, the observed $pCO_2$ values were normalized to a constant temperature of 13.3 °C, which was the 10-year annual mean water temperature measured in the Delaware Estuary from 2004 to 2014.

### 2.4 Estuarine and river CO₂ contributions

Due to various CO₂ sources such as the degradation of organic matter, discharge of sewage effluents, soil-induced respiration, freshwater runoff, and addition of humic substances, river water flowing into estuarine systems is typically supersaturated in CO₂ with respect to the atmosphere (Raymond et al., 2000; Abril and Borges, 2004; Borges et al., 2006). To investigate the influence of river-borne CO₂ input to overall air–water CO₂ fluxes, we used similar methods to those performed in Jiang et al. (2008a). In situ DIC and TA measurements were coupled using the Excel macro CO2SYS (Pierrot, 2006) and inorganic carbon dissociation constants from Millero et al. (2006) for estuarine waters to calculate dissolved CO₂ concentrations. We first estimated the contribution of the ocean end-member to the estuarine DIC alone as follows (Jiang et al., 2008a):

$$DIC_{mixing \ without ocean} = S_i \cdot DIC_{ocean}.$$  

(8)

where $DIC_{mixing \ without ocean}$ is the DIC concentration after the ocean end-member is diluted by fresh water with zero DIC and $S_i$ and $DIC_{ocean}$ are in situ and ocean end-member salinities, respectively (Fig. 3a). When DIC inputs from both the river and the ocean end-members were considered, estuarine DIC was estimated using a two-end-member mixing model as fol-
where DIC\textsubscript{mixing w/R} is the DIC concentration after mixing of river and ocean end-members and DIC\textsubscript{river} is the river end-member (Fig. 3a). With much of the DIC pool dominated by carbonate and bicarbonate ions, Sharp et al. (2009) observed small seasonal influences on DIC concentrations due to temperature affects and biological activity. They suggest that the majority of variability in DIC in the upper tidal river of the Delaware Estuary is due to the combined interaction of varying precipitation rates and prior meteorological conditions. This is expected as river DIC and TA are largely a dilution of weathering production by rain (Cai et al., 2008). However, at higher salinities, any drawdown of DIC relative to salinity is small since less than 1 % of the DIC pool exists as pCO\textsubscript{2} (Sharp et al., 2009). Thus, while total DIC concentrations illustrate some fluctuations in biological activity (which occurred mostly at the highly productive mid-bay), it is an integrated measurement of freshwater and seawater mixing (Sharp et al., 2009). TA\textsubscript{mixing w/o} and TA\textsubscript{mixing w/R} were also estimated using similar equations by replacing DIC with TA (Fig. 3b). Because CO\textsubscript{2} concentrations do not change linearly during mixing, they were estimated using corresponding DIC and TA mixing values (Fig. 3c; Jiang et al., 2008a). Moreover, since CO\textsubscript{2} concentrations fluctuate with temperature change, the 10-year (2004–2014) annual mean temperature of 13.3 °C was used in this work. Thus, the CO\textsubscript{2} contribution due to river input (ΔDIC\textsubscript{riv}) was estimated as follows:

$$\text{[CO}_2\text{]}_\text{riv} = \text{[CO}_2\text{]}_\text{mixing w/R} - \text{[CO}_2\text{]}_\text{mixing w/o}.$$  

Calculated river CO\textsubscript{2} inputs ([CO\textsubscript{2}]\textsubscript{riv}) and combined river discharges from the Schuylkill and Delaware rivers for each month were used to compute river-borne CO\textsubscript{2} fluxes in the upper tidal river. To further investigate the influence of CO\textsubscript{2} inputs from the river (external) versus production from within the estuary (internal), we used a similar but modified method as performed in Jiang et al. (2008a). The CO\textsubscript{2} contribution from within the estuarine zone ([CO\textsubscript{2}]\textsubscript{est}) was estimated as follows:

$$\text{[CO}_2\text{]}_\text{est} = \text{[CO}_2\text{]}_i - \text{[CO}_2\text{]}_\text{mixing w/R} + (\tau_i \cdot F_i),$$  

where [CO\textsubscript{2}]\textsubscript{i} is the in situ CO\textsubscript{2} concentration, τ\textsubscript{i} is the flushing time, and F\textsubscript{i} is the air-water CO\textsubscript{2} flux. Specifically, [CO\textsubscript{2}]\textsubscript{i} was calculated using in situ DIC and TA concentrations and τ\textsubscript{i} was estimated using river discharge rates and volume of each region (Table 3; Sheldon and Merryl, 2002). Surveys that did not contain sufficient river end-member DIC and TA measurements were excluded. Alternatively, Eq. (11) suggests that integrated CO\textsubscript{2} degassing (τ\textsubscript{i} × F\textsubscript{i}) is supported by the deficit or excess CO\textsubscript{2} concentration ([CO\textsubscript{2}]\textsubscript{mixing w/R}− [CO\textsubscript{2}]\textsubscript{i}) plus the internal estuarine CO\textsubscript{2} production or consumption ([CO\textsubscript{2}]\textsubscript{est}) exhibited across each region.

### 3 Results

#### 3.1 Hydrographic conditions

Measured surface water temperatures and river discharge during each cruise were compared with the 10-year (2004–2014) and 30-year (1980–2014) monthly averages for surface water temperatures and Delaware River discharge rates, respectively. Water temperatures were slightly cooler than the 10-year average during March 2014, June 2013, and July 2014, while water temperatures during the rest of the cruises were slightly warmer (Fig. 4a; USGS gauge 01463500). Discharge conditions during each survey were compared with the 30-year average discharges from 1980 to 2014 (Fig. 4b; USGS gauge 01463500). The Delaware River discharge was greatest during March 2014 and June 2013. Discharges were smallest during August 2014, October 2013, November 2013, and November 2014. Of the four low-flow months, all of them except for August 2014 had discharge rates less than 1 standard deviation of the 30-year average.

The surface water salinity distributions confirm the various river discharge conditions recorded throughout each sur-
Figure 4. (a) Surface water temperatures and (b) Delaware River discharge rates recorded in the Delaware Estuary during each sampling month. Error bars represent standard deviations of the 10-year (2004–2014) and 30-year (1980–2014) monthly averages for surface water temperatures and Delaware River discharge rates, respectively.

Figure 5. Spatial distributions of surface water salinity in the Delaware Estuary measured during each sampling month. The map was designed with the ODV software by R. Schlitzer (Ocean Data View software, 2015, http://odv.awi.de/).

3.2 Surface water \( p\text{CO}_2 \)

Generally, surface water \( p\text{CO}_2 \) in the Delaware Estuary increased from the ocean to the river end-member, with \( p\text{CO}_2 \) values ranging from about 150 to over 4000 µatm (Fig. 6a–i). Moreover, \( p\text{CO}_2 \) exhibited strong seasonal variations across both river and bay portions. The most pronounced shifts in surface water \( p\text{CO}_2 \) were observed within the lower urban river and turbidity maximum river zones of the Delaware River, with \( p\text{CO}_2 \) being lowest in the cool months (March, October, and November) and highest in the warm months (June, July, and August; Table 2). During all months, the turbidity maximum zone was supersaturated in \( \text{CO}_2 \) with respect to the atmosphere (atmospheric \( p\text{CO}_2 \): 375–398 µatm) except during March 2014 (Fig. 6a). Throughout the summer and early fall (June, July, and August), \( p\text{CO}_2 \) ranged from about 650 to over 4000 µatm across the turbidity and lower urban river zones (Fig. 6b–e). In late fall (October and November), \( p\text{CO}_2 \) dropped to as low as 500 µatm in the turbidity maximum zone and reached 1400 µatm within the lower urban river zone (Fig. 6f–h). However, the decrease in \( p\text{CO}_2 \) values was not always observed as temperatures cooled. During the winter (December), surface water \( p\text{CO}_2 \) values increased across the turbidity maximum zone, ranging from about 650 to 1000 µatm (Fig. 6i). As discussed later, this shift in \( p\text{CO}_2 \) during winter is likely a result of opposing timing of seasonal temperature cycles and respiration versus that of river discharge rates.
Surface water $pCO_2$ exhibited strong seasonal variations in the Delaware Bay as well (Fig. 6a–i). In March 2014, most likely due to a strong biological bloom and low temperature (Fig. 4a), the entire bay system (upper, middle, and lower) was undersaturated in CO$_2$ with respect to the atmosphere (Table 2). In particular, $pCO_2$ reached as low as 160 µatm in the mid-bay (Fig. 6a). During the warmer summer months (June, July, and August), $pCO_2$ in the bay remained around 400 to 500 µatm, with occasional undersaturation occurring in the mid-bay region (Fig. 6b–e). In August 2014, low $pCO_2$ ranging from about 200 to 350 µatm was observed throughout much of the mid- and lower bay regions (Fig. 6e). In contrast, during the late fall, $pCO_2$ values were fairly homogenous throughout the mid- and lower bay (400–450 µatm in October 2013 and 375–415 µatm in November 2013) and slightly higher $pCO_2$ occurring in the upper bay (Fig. 6f–h). In December 2014, $pCO_2$ increased throughout all regions of the bay, with $pCO_2$ values ranging from 500 to 650 µatm (Fig. 6i). While it remains unclear what supports these elevated $pCO_2$ values, stratification of subsurface waters in late fall followed by strong winter mixing during winter (December 2014) and a 2-fold increase in river discharge could explain the elevated $pCO_2$ values observed throughout the mid- and lower bay systems (Fig. 4b).

### 3.3 Air–water CO$_2$ fluxes

The urban river and turbidity maximum zone served as strong sources of CO$_2$ to the atmosphere and were positive during all months (Table 2). Across the upper to lower bay portions of the estuary, uptake of CO$_2$ from the atmosphere was greatest during spring (March), ranging from $F_{CO_2} = -12.1$ to $-20.0$ mmol m$^{-2}$ d$^{-1}$ (Table 2). The CO$_2$ uptake flux was highest in March 2014 in the mid-bay ($-20.0$ mmol m$^{-2}$ d$^{-1}$), while the highest CO$_2$ degassing flux occurred in June 2014 in the urban river ($144.8$ mmol m$^{-2}$ d$^{-1}$; Table 2). Air–water CO$_2$ fluxes in the upper to lower bay regions decreased in early winter (December) to a minimum in early spring (March), followed by an increase to an annual maximum in early summer (June). In the turbidity maximum zone and urban river, area-averaged CO$_2$ fluxes followed the same seasonal decrease in spring and increase in summer but reached an annual minimum in late fall instead of early spring. In winter (December), the mid- and lower bays, which were typically sinks or weak sources of CO$_2$, exhibited relatively strong CO$_2$ fluxes to the atmosphere.

### 3.4 CO$_2$ distribution across the salinity gradient

To further investigate $pCO_2$ variations along the Delaware Estuary, we examined distributions of $pCO_2$ across the salinity gradient. Due to limited area and salinity coverage, surveys conducted in August and October 2013 were excluded for this assessment. In all months, $pCO_2$ versus salinity followed a concave upward trend towards the river end-member (Fig. 7). The seasonal variation between $pCO_2$ values was largest at low salinities around 0 to 5, with $pCO_2$ values in the summer (June, July, and August) nearly 2-fold greater than those observed in the spring (March) and fall (October and November) seasons (Fig. 7). In all seasons, $pCO_2$ was supersaturated with respect to the atmosphere from salinities.

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**Table 2.** Area average, standard deviation, and range of $pCO_2$ and CO$_2$ flux ($F_{CO_2}$) in five of the six zones in the Delaware Estuary during each cruise.}

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<td>Mean SD</td>
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<tr>
<td></td>
<td>230 ± 23</td>
<td>477 ± 11</td>
<td>473 ± 52</td>
<td>384 ± 42</td>
<td>315 ± 59</td>
<td>421 ± 6</td>
<td>405 ± 8</td>
<td>387 ± 3</td>
<td>596 ± 11</td>
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<tr>
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<tr>
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<td>198 ± 8</td>
<td>540 ± 66</td>
<td>559 ± 97</td>
<td>530 ± 36</td>
<td>250 ± 16</td>
<td>465 ± 22</td>
<td>422 ± 2</td>
<td>390 ± 8</td>
<td>590 ± 21</td>
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<tr>
<td></td>
<td>289 ± 47</td>
<td>919 ± 192</td>
<td>917 ± 97</td>
<td>660 ± 58</td>
<td>470 ± 96</td>
<td>566 ± 39</td>
<td>463 ± 11</td>
<td>434 ± 11</td>
<td>658 ± 26</td>
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<tr>
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<tr>
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<td>686 ± 48</td>
<td>328 ± 163</td>
<td>2944 ± N/A</td>
<td>2542 ± N/A</td>
<td>2310 ± N/A</td>
<td>1199 ± N/A</td>
<td>816 ± 133</td>
<td>880 ± 179</td>
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</table>

**Average $F_{CO_2}$ (mmol m$^{-2}$ d$^{-1}$)**

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<tr>
<th>Zone</th>
<th>Mean SD</th>
<th>Mean SD</th>
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</thead>
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<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td></td>
<td>230 ± 23</td>
<td>477 ± 11</td>
<td>473 ± 52</td>
<td>384 ± 42</td>
</tr>
<tr>
<td><strong>Mid-bay</strong></td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td></td>
<td>198 ± 8</td>
<td>540 ± 66</td>
<td>559 ± 97</td>
<td>530 ± 36</td>
</tr>
<tr>
<td><strong>Upper bay</strong></td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td></td>
<td>289 ± 47</td>
<td>919 ± 192</td>
<td>917 ± 97</td>
<td>660 ± 58</td>
</tr>
<tr>
<td><strong>Turbidity</strong></td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td></td>
<td>2087 ± 499</td>
<td>1473 ± 162</td>
<td>1237 ± 139</td>
<td>1102 ± 317</td>
</tr>
<tr>
<td><strong>Urban river</strong></td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
<td>Mean SD</td>
</tr>
<tr>
<td></td>
<td>328 ± 163</td>
<td>2944 ± N/A</td>
<td>2542 ± N/A</td>
<td>2310 ± N/A</td>
</tr>
</tbody>
</table>

* Months when surveys did not extend into urban river. Area average was estimated by linearly extrapolating data from adjacent months with sample measurements. Standard deviations and range not available.
0 to 5. In spring, undersaturated $pCO_2$ was observed over the widest salinity range from 7.5 to 30. In summer, undersaturated $pCO_2$ was generally not observed except at moderate salinities around 17 to 28 in August. In fall, $pCO_2$ values were near atmospheric concentrations around mid-salinity waters and were only undersaturated at salinities greater than 25. In winter (December), $pCO_2$ values were always super-saturated with respect to the atmosphere across the entire salinity range. Seasonally, the Delaware Estuary served as a strong CO$_2$ sink ($-5.0 \pm 6.0 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) in the spring, a strong source ($4.9 \pm 8.1 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) in the summer, a weak source ($1.0 \pm 2.4 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) in the fall, and a strong source ($5.7 \pm 1.9 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) in the winter. While low-salinity waters were strong CO$_2$ sources, proportionally these upper regions ($0 \leq S < 10$) were small in comparison to the total estuarine study area. In turn, their area-averaged contribution ($27.1 \pm 6.4 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) to overall regional flux ($2.4 \pm 4.8 \text{ mol-C m}^{-2} \text{ yr}^{-1}$) is minor. Thus, the Delaware Estuary as a whole acts as a relatively weak CO$_2$ source ($2.4 \pm 4.8 \text{ mol-C m}^{-2} \text{ yr}^{-1}$), which is in great contrast to many river estuaries that are strong CO$_2$ sources ($26 \pm 21 \text{ mol-C m}^{-2} \text{ yr}^{-1}$; Borges and Abril, 2011).

3.5 Seasonal variations in temperature-normalized $pCO_2$

Seasonal distributions of $pCO_{2obs}$ at 13.3°C, which indicate impacts of non-thermal processes (biological and mixing), varied noticeably throughout the year and across salinity intervals (Fig. 8). Typically, $pCO_{2obs}$ at 13.3°C was greatest during the early and mid-winter season (December and January) except in the 0–5 salinity interval (mostly turbidity maximum zone and urban river) when $pCO_{2obs}$ at 13.3°C reached its maximum in June. Coupled with decreasing flow, in the 0–5 salinity interval, $pCO_{2obs}$ at 13.3°C decreased from June to an annual minimum in October. In the mid-salinity waters ($5 \leq S \leq 20$), $pCO_{2obs}$ at 13.3°C decreased from mid-winter to an annual minimum in March, followed by an increase to a secondary maximum in June. In contrast, in the high-salinity waters ($20 \leq S \leq 30$) of the lower bay, where biological removal of CO$_2$ was generally strong, annual minimums were observed in August. The annual distribution of $pCO_{2mean}$ at $T_{obs}$, which indicates the impact of the seasonal thermal cycle, followed typical bell-shaped curves across all salinity intervals, with the lowest values occurring in winter and an annual maximum occurring in July.

4 Discussion

The seasonal and spatial distributions of estuarine $pCO_2$ are governed by the dynamic interaction between water temperature; horizontal and vertical mixing processes; biological processes; and CO$_2$ contributions from the river, ocean, and estuarine zone (Jiang et al., 2008a; Borges and Abril, 2011; Hunt et al., 2014). In the estuarine zone, the addition or removal of CO$_2$ includes net ecosystem metabolism, DIC exchange with intertidal marshes, sediments, groundwater inputs, air–water gas exchanges, and other estuarine contributing processes (Jiang et al., 2008a). In the following sections, we evaluate the impact that seasonal temperature changes
and river discharge rates have on surface water \( pCO_2 \) distributions’ river and estuarine \( CO_2 \) inputs, and river-borne \( CO_2 \) fluxes throughout the Delaware Estuary.

### 4.1 Temperature vs. biological effects on \( pCO_2 \)

Similar to other estuaries (Borges and Abril, 2011), seasonal temperature changes provided a first control on the observed seasonal changes in \( pCO_2 \) (low in the winter and high in the summer, Figs. 4a and 7). This is further reflected in the fact that temperature-normalized \( pCO_2 \) was always higher than in situ \( pCO_2 \) in the winter but lower than in situ \( pCO_2 \) in the summer (Fig. 8). Presumably, then, seasonal patterns of the temperature-normalized \( pCO_2 \) reflect how non-thermal processes (mixing and biological) influence in situ \( pCO_2 \). For example, in the urban river and turbidity maximum zones (\( S < 5 \)), high \( pCO_2 \) at 13.3 °C in the spring and winter may reflect both river inputs and strong respiratory \( CO_2 \) production. Low \( pCO_2 \) at 13.3 °C during the warmer months likely reflects the removal of \( CO_2 \) due to various non-thermal processes. During the warmer months from May to October, Yoshiyama and Sharp (2006) found elevated nitrite (\( NO_2^- \)) concentrations in the urban river when nitrification and primary production were highest. In addition, high \( NO_2^- \) concentrations were observed in the mid-bay in summer, when primary production was maximal (Pennock and Sharp, 1994). Comparably, \( pCO_2 \) at \( T \) (changes due to the seasonal thermal cycle) trends were opposite to the trend of \( pCO_2 \) at 13.3 °C with lower than \( pCO_2 \) values in the winter and higher than \( pCO_2 \) values in the summer. These opposing signals suggest that increases in surface water \( pCO_2 \) due to winter-to-summer warming are partially compensated for by the reduction of surface water \( pCO_2 \) due to mixing processes and/or biological removal of \( CO_2 \) (Takahashi et al., 2002). Sharp et al. (2009) found that, during the March–April period, ammonium (\( NH_4^+ \)), phosphate (\( PO_4^- \)), and silicate (\( Si \)) concentrations were heavily depleted in the mid- and lower bay regions due to extensive spring blooms. Similarly, but in the opposite direction, the reduction in surface water \( pCO_2 \) due to fall-to-winter cooling is partially compensated for by the elevation of surface water \( pCO_2 \) caused by various non-thermal processes (Fig. 8).

We further examine the relative importance of the temperature and biological effects in each salinity interval by calculating the ratio of \( \Delta pCO_2 \) to \( pCO_2 \) (\( T/B \)). Using similar methods as performed in Takahashi et al. (2002), we calculate the thermal effects on surface water \( pCO_2 \) in each salinity interval as follows:

\[
\Delta pCO_2^{\text{thermal}} = (pCO_2^{\text{mean}} \text{ at } T_{\text{obs}})_{\text{max}} - (pCO_2^{\text{mean}} \text{ at } T_{\text{obs}})_{\text{min}},
\]

where \((pCO_2^{\text{mean}} \text{ at } T_{\text{obs}})_{\text{max}}\) and \((pCO_2^{\text{mean}} \text{ at } T_{\text{obs}})_{\text{min}}\) are the maximum and minimum \( pCO_2 \) values at \( T_{\text{obs}} \) values, respectively. In other words, the thermal effects on the mean annual \( pCO_2 \) value are represented by the seasonal amplitude of \((pCO_2^{\text{mean}} \text{ at } T_{\text{obs}})\) values computed using Eq. (7).

Likewise, the non-thermal effects (biological and mixing processes) on surface water \( pCO_2 \) were calculated as follows (Takahashi et al., 2002):

\[
\Delta pCO_2^{\text{non-thermal}} = (pCO_2^{\text{obs}} \text{ at } 13.3^\circ C)_{\text{max}} - (pCO_2^{\text{obs}} \text{ at } 13.3^\circ C)_{\text{min}},
\]

where \((pCO_2^{\text{obs}} \text{ at } 13.3^\circ C)_{\text{max}}\) and \((pCO_2^{\text{obs}} \text{ at } 13.3^\circ C)_{\text{min}}\) are the maximum and minimum \( pCO_2 \) values, respectively. Thus, the non-thermal effects on surface water \( pCO_2 \) at 13.3 °C are represented by the seasonal amplitude of \( pCO_2 \) values corrected to the 10-year (2004–2014) annual mean temperature using Eq. (6). The relative importance of these effects in each salinity interval can be expressed as the difference between \( \Delta pCO_2^{\text{thermal}} \) and \( \Delta pCO_2^{\text{non-thermal}}(T/B) \) or the ratio of \( \Delta pCO_2^{\text{thermal}} \) to \( \Delta pCO_2^{\text{non-thermal}}(T/B) \). In estuarine regions where thermal effects on surface water \( pCO_2 \) exceed non-thermal effects, the \((T/B)\) ratio is greater than 1 or \((T/B)\) is positive, whereas in areas where non-thermal effects dominate, the \((T/B)\) ratio is less than 1 or \((T/B)\) is negative. Based on our results, temperature was a dominant factor in controlling surface water \( pCO_2 \) in low-salinity waters (0 ≤ \( S \) ≤ 10; mainly the urban river and turbidity maximum zone), with \( T/B \) ratios ranging from 1.30 to 1.68 (Table 4). As salinity increased, both \( \Delta pCO_2^{\text{thermal}} \) and \( \Delta pCO_2^{\text{non-thermal}} \) decreased (Table 4). The decrease in \( \Delta pCO_2^{\text{thermal}} \) may be attributed to the reduction in river water temperatures at the ocean end-member (Hunt et al., 2014). In comparison to the upper tidal river, low \( T/B \) ratios ranging from 0.69 to 0.80 were observed in mid-salinity waters (15 ≤ \( S \) ≤ 25; mainly the mid- and lower bay), suggesting that \( pCO_2 \) distributions in the Delaware Bay are largely governed by biological and/or mixing processes.

### 4.2 Influence of river-borne \( CO_2 \) on estuarine degassing

The potential emission of river-borne \( CO_2 \) was estimated based on the concept of excess \( CO_2 \), the difference between the in situ DIC at zero salinity and a theoretical DIC value at atmospheric equilibrium (\( \Delta DIC \); Abril et al., 2000; Borges et al., 2006). The theoretical DIC was computed using in situ TA values and an atmospheric \( pCO_2 \) of 395 µatm. River-borne \( CO_2 \) fluxes were calculated as the product of \( ADIC \) and the combined river discharges from the Schuylkill and Delaware rivers for each month divided by the estuarine surface area. Generally, as freshwater residence time increases (river discharge decreases), river-borne \( CO_2 \) fluxes decrease (Borges et al., 2006). As more river-borne \( CO_2 \) is released into the atmosphere in the upper estuary due to increased residence time, leaving less river-borne \( CO_2 \) for degassing in the lower estuary, the overall contributions of \( CO_2 \) emissions are largely shaped by the net community production in the mixed layer (ML NCP) in the mid- to high-salinity estuarine
zones (Abril et al., 2000; Borges et al., 2006). In comparison, as freshwater residence time decreases (river discharge increases), DIC enrichment from ML NCP is reduced and river-borne CO$_2$ fluxes increase. In certain cases, such as the Rhine Estuary or other systems with extremely rapid flushing times, residence time is so short that not all of the river-borne CO$_2$ is ventilated to the atmosphere in the estuarine zone (Borges and Frankignoulle, 2002; Borges et al., 2006). In turn, the potential emission of river-borne CO$_2$ is higher than the actual observed air–water CO$_2$ fluxes from the estuary (Borges et al., 2006).

Positive correlations between river-borne and air–water CO$_2$ fluxes illustrate the importance of river inputs to CO$_2$ degassing fluxes (Fig. 9). In the Delaware Estuary, the largest river-borne CO$_2$ flux was observed during the highest flow month of June 2013, with river CO$_2$ flux accounting for 119 and 60 % of the overall CO$_2$ degassing flux in the urban river and turbidity maximum zone, respectively (Fig. 9). Moreover, during the high-flow month of March 2014, river-borne CO$_2$ fluxes exceeded 200 and 150 % of the overall CO$_2$ degassing flux in the urban river and turbidity maximum zone, respectively (Fig. 9). Presumably, the higher river-borne CO$_2$ fluxes than overall CO$_2$ fluxes in March are due to the combined influence of increased river discharge coupled with large CO$_2$ consumption in the estuary (Figs. 4b and 5a). This is consistent with the observed low $p$CO$_2$ and high O$_2$ values (Fig. 6a; Cai, unpublished data). In contrast, in July and August 2014, air–water CO$_2$ fluxes exceeded river-borne CO$_2$ fluxes, indicating strong estuarine CO$_2$ production. Such internal estuarine CO$_2$ production is most likely due to respiration in the water column, but may also include other inputs such as benthic respiration and net respiration from surrounding intertidal marshes. In turn, while correlations between river-borne and air–water CO$_2$ fluxes were exhibited, differences between the two fluxes suggest that the input of CO$_2$ from other estuarine sources is important.

### 4.3 Internal estuarine production versus river CO$_2$ input

Our results illustrate that both the river and the estuarine zone contribute to CO$_2$ inputs in the Delaware Estuary (Fig. 10). Combined river CO$_2$ input and internal estuarine production was highest in the urban river (87.8 to 255.4 µmol L$^{-1}$) and lowest in the lower bay (−38.8 to 7.0 µmol L$^{-1}$; Fig. 10). In the tidal river, internal estuarine production exhibited clear
seasonal trends, with CO₂ contributions being lowest in the spring (March), highest in the summer (June and August), and medium in the fall (October and November). Strong seasonal trends in internal estuarine production were also observed in the bay regions. During spring and late summer (March and August 2014), internal estuarine CO₂ signals were negative in the mid- and lower bay zones and reached as much as 8-fold greater than total river CO₂ inputs, ranging from $-22.9$ to $-100.4 \mu\text{mol L}^{-1}$ (Fig. 10). Thus, the majority of river CO₂ input was heavily compensated for by the biological removal of CO₂ in the bay waters. In addition, during the spring season (March), high CO₂ consumption was also observed in the upper bay, with internal estuarine CO₂ signals ($-30.7 \mu\text{mol L}^{-1}$) exceeding total river CO₂ contribution ($25.7 \mu\text{mol L}^{-1}$; Fig. 10). Depending on river discharge rates, the freshwater residence time in the Delaware Estuary ranges from about 40 to 90 days (Ketchum, 1952). Due to smaller physical sizes, freshwater residence time in the upper tidal river is much shorter (Table 3). Thus, the percentage of river-borne CO₂ in the upper Delaware Estuary is large (Fig. 10), and that percentage decreases in the mid- and lower bays, which have longer residence times and high biological CO₂ removal (Sharp, 1983).

4.4 Assumptions and limitations

While this study serves as the first air–water CO₂ flux product in the Delaware Estuary, there are several limitations. First, the lack of cross-bay transects (east to west), except in December 2014, limits our knowledge of surface water $p\text{CO}_2$ distributions in shallow water regions of the bay system. Due to various biological and physical processes (i.e., influence from nearby tidal marshes, tributaries, or estuarine circulation forces), surface water $p\text{CO}_2$ may vary from within the main channel to the perimeters of the estuary. Jiang et al. (2008a) found that surface water $p\text{CO}_2$ and air–water CO₂ flux in the marine-dominated Sapelo and Doboy sounds paralleled seasonal temperature changes and net CO₂ inputs from within the estuarine zone. Due to intense productivity of vegetation in the surrounding salt marshes, extensive accumulation of organic carbon occurs during spring and early summer (Dai and Wiegert, 1996; Jiang et al., 2008a). During late summer and early fall, increased surface water temperatures coupled with tidal flushing of intertidal marsh waters and the decomposition of dead plants contribute to high CO₂ degassing in these estuaries (Dai and Wiegert, 1996; Cai and Wang, 1998; Cai et al., 1999; Neubauer and Anderson, 2003; Wang and Cai, 2004). However, due to the much broader geographic size of the Delaware Bay compared to the marine-dominated Sapelo and Doboy sounds, in-water biological processes are most likely important. In turn, the impact from the growth and decay of marsh plants on surface water $p\text{CO}_2$ and CO₂ flux dynamics may not be as influential in the Delaware Bay, except near the shorelines, where tides regularly flush marsh boundaries. Culberson et al. (1987) and Lebo et al. (1990) performed several cross-bay
It is important to note that derived variables in temperature-normalized $pCO_2$ provide only a relatively simple analysis of seasonal $pCO_2$ fluctuations due to thermal and non-thermal processes as it neglects the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on $pCO_2$ dynamics. However, as mentioned before, since salinity fluctuates greatly depending on factors such as season, river discharge, and tidal cycle, salinity-binned climatologies can provide crucial insight into various physical and biological controlling mechanisms behind $pCO_2$ distributions that geographic boundaries may not. Unfortunately, due to the lack of winter surveys and unusually high $pCO_2$ values in December, interpolated temperature-normalized $pCO_2$ during cooler months may be biased and slightly overestimated. Moreover, the temperature-derived constants ($\partial \ln pCO_2/\partial T$) derived in this study were based on river and ocean end-member TA and DIC concentrations collected in the Delaware Estuary over the past 2 years. Thus, it is important to note that derived temperature constants here are applicable for general estuarine systems and may not be suitable for coastal environments with different hydrological and/or geochemical characteristics.

In situ DIC and TA measurements were coupled using the Excel macro CO2SYS (Pierrot, 2006) and inorganic carbon dissociation constants from Millero et al. (2006) for estuarine waters to calculate dissolved CO2 concentrations. While river and ocean end-members were obtained at near-zero salinity and at the mouth of the bay, respectively, no fixed end-member sampling locations were established. This marginal difference in end-member location could slightly increase or decrease estimated CO2 concentrations. In the chemical model of the CO2SYS, NH3, $NH_4^+$, and organic matter contribution to TA were not included (Cai et al., 1998; Cai et al., 2010b), which were likely high in low-salinity waters. Thus, lower calculated than observed CO2 was expected as the observed TA included other acid–base components (Fig. 3c). However, due to the very high $pCO_2$, such uncertainty is deemed unimportant in our consideration. Another factor that may contribute to the lower calculated than observed CO2 could be the use of mercuric chloride as a preservative in low-salinity samples ($S < 10$; Trabalka and Reichle, 2013). Excess alkalinity generated via the dilution of mercuric chloride could contribute to conservative CO2 flux estimates (Trabalka and Reichle, 2013), although, due to the

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<td>11.7</td>
<td>26.5</td>
<td>23.8</td>
<td>36.2</td>
<td>21.9</td>
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<td>16.1</td>
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<td>22.9</td>
<td>54.5</td>
<td>38.2</td>
<td>64.1</td>
<td>41.3</td>
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<td>28.3</td>
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<tr>
<td>Turbidity maximum zone</td>
<td>7.6</td>
<td>7.5</td>
<td>11.9</td>
<td>13.3</td>
<td>18.5</td>
<td>19.9</td>
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<td>Urban river</td>
<td>2.5</td>
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<td>3.7</td>
<td>6.1</td>
<td>6.9</td>
<td>6.5</td>
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relatively high TA in the Delaware River, we believe this effect is small.

5 Summary and concluding remarks

While the urban river and turbidity maximum zone are strong CO$_2$ sources to the atmosphere, these upper regions are small in comparison to the bay regions of the Delaware Estuary. Thus, overall the Delaware Estuary acts as a relatively weak CO$_2$ source ($2.4 \pm 4.8$ mol-C m$^{-2}$ yr$^{-1}$) in comparison to many other estuarine systems that serve as strong CO$_2$ sources to the atmosphere ($26 \pm 21$ mol-C m$^{-2}$ yr$^{-1}$; Borges and Abril, 2011). Of the 62 estuaries compiled in Borges and Abril (2011), only the Aby Lagoon, a permanently stratified system, served as a sink for atmospheric CO$_2$. Seasonal temperature cycles influence the rise and fall of surface water $p$CO$_2$ throughout the Delaware Estuary, but these effects are partially compensated for by opposing cycles of biological removal and addition of CO$_2$. Moreover, positive correlations between river-borne degassing to overall CO$_2$ fluxes in the upper subsections of the estuary (the urban river and turbidity maximum zone) illustrate the importance of river-borne CO$_2$ to overall CO$_2$ degassing fluxes. Such features are typical for rapidly flushing river-dominated estuaries. While river-borne CO$_2$ degassing fluxes heavily impact CO$_2$ dynamics throughout the upper Delaware Estuary, these forces are largely compensated for by internal biological processes within the extensive bay system of the lower estuary.

Along the eastern Georgia (USA) coast, Jiang et al. (2008a) identified the Altamaha Sound as a river-dominated estuary with CO$_2$ fluxes driven by river discharge. Comparably, the Kennebec Estuary, located on the central Maine (USA) coast, exhibited high river CO$_2$ inputs and short freshwater residence times ($\sim$ 4 days), suggesting that CO$_2$ sources in the estuary were mainly controlled by the degassing of river-borne DIC (Hunt et al., 2014). The upper Delaware Estuary showed similar results, with high river CO$_2$ contributions and rapid freshwater transit times during all months (Fig. 10 and Table 3). In contrast, in systems with long freshwater residence times (i.e., the Delaware Bay and Scheldt Estuary), much, if not all, of the river-borne CO$_2$ is released into the atmosphere (Abril et al., 2000; Borges et al., 2006). In turn, overall CO$_2$ emission from the estuary is largely controlled by net community production in the mixed layer (ML NCP; Borges et al., 2006). In the case of the European Scheldt Estuary, long freshwater residence time (30–90 days) leads to extensive DIC enrichment in the water column and high CO$_2$ emissions to the atmosphere (Abril et al., 2000; Borges et al., 2006). Similarly, and in contrast to the rapidly flushing Altamaha Sound, Jiang et al. (2008a) identified the marsh-surrounded Sapelo Sound as a marine-dominated estuary with CO$_2$ fluxes driven by seasonal temperature and metabolic cycles.

With its extensive geographic size, the Delaware Estuary features both a river-dominated upper estuary and an ocean-dominated lower bay. In this case, air–water CO$_2$ fluxes in the heterotrophic upper estuary are significantly influenced by intense river-borne CO$_2$ degassing akin to the river-dominated Altamaha Sound and Kennebec Estuary. The autotrophic lower estuary is governed by water-column biological processes and seasonal temperature cycles akin to the marine-dominated Sapelo Sound and Scheldt Estuary (though the Delaware Estuary and other large estuarine systems are orders of magnitude more productive than smaller marine-dominated estuaries).

The continuation of research cruises on estuarine and coastal margins can provide crucial insight into the physical and biological changes in the past, present, and future ocean systems. With such extensive surveys, collection of carbonate parameters, and comparison of carbonate parameters over time, we can significantly broaden our understanding of the processes that govern these coastal zones. In turn, such knowledge can be used to help predict and hopefully regulate the rise of current and future threats to our coastal ocean systems.

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