**Referee #1**

We thank you for the very thorough and constructive reviews. The positive encouragement to expand on certain sections that needed additional explanation or supporting evidence has significantly improved the clarity of the paper and reinforced the validity of our results. With your suggestions, we have made great efforts to improve the methods section, incorporate variability statistics to Table 1 (now Table 2 due to the incorporation of appendixes into the main paper), and expand on why this $CO_2$ study (the Delaware Estuary) is so important. To help address the uncertainties and limitations to our study, we have added a new assumptions and limitations section (4.4) in the discussion.

**Major Comments**

My greatest criticism of the manuscript is in the presentation of the data; specifically, the lack of information about variability. The most glaring example of this is Table1. The authors present area-averaged pCO2 and CO2 flux estimates from five subsections of the estuary, but present no information about the range of these data, the standard deviation, or the median. These statistics seem vital to include in order to develop a total picture of estuary conditions. This is particularly important in light of the data presented in Figure 5, panel I. Most of the estuary transects follow a general north-south route, presumably following the main channel of the estuary. However, in December 2014 the authors made the wise decision to add some east-west transects as well, which show considerable variability. This makes intuitive sense, as the map of the Delaware Estuary (Figure 1) seems to show a number of smaller contributing rivers flowing into the bay from the east and west. Presumably if ranges and/or standard deviations were included in Table 1, the results would show much more variability during the December 2014 cruise than other cruises which only followed the north-south line. I suspect that this system is more complex than the presented data indicate, which is interesting! The authors acknowledge this "lack of cross-bay transects" in their Concluding Remarks, but this is a limitation that should be discussed much earlier and much more thoroughly. Some of the pCO2 variability may be distinguishable in Figure 7, but this figure is so small, and the error bars so light, that I can't make much sense out of it. The authors even specifically mention that standard deviations of atmospheric pCO2 and CO2 flux were calculated (P10907L2-5), but I do not see these standard deviations presented anywhere. This overall lack of variability discussion really limits the discussion of the data, as well as the relevancy of the results.

<span style="color:red">We agree that the lack of information about variability is indeed limiting to the discussion and relevancy of our results. To help strengthen our findings, we have followed your suggestions and have added the range and standard deviations to all $pCO_2$ and $CO_2$ flux estimates in Table 2. In addition, we agree that the "lack of cross-bay transects" should be an issue addressed. Incorporating suggestions from both referees, we have added a new section (4.4 Assumptions and limitations) that addresses the various limitations in this study in more detail (please see below). We reference a few studies that investigate the influence of tidal marshes to the carbonate system and some that have done previous cross bay transects in the Delaware Bay to support the issue of cross bay variability.</span>

Table 2. Area-averaged, standard deviation, and range of $pCO_2$ and $CO_2$ flux ($F_{CO2}$) in five of the six zones in the Delaware Estuary during each cruise.

| | | Mar 2014 | Jun 2013 | Jul 2014[*] | Aug 2013[*] | Aug 2014 | Oct 2013[*] | Oct 2014 | Nov 2013 | Dec 2014[*] | Annual Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Average $pCO_2$ (µatm)** | | | | | | | | | | | |
| Lower Bay | Mean ± SD | 230 ± 23 | 477 ± 11 | 473 ± 52 | 384 ± 42 | 315 ± 59 | 421 ± 6 | 405 ± 8 | 387 ± 3 | 596 ± 11 | 410 |
| | Range | 194 – 267 | 456 – 528 | 397 – 648 | 317 – 491 | 243 – 432 | 413 – 437 | 395 – 419 | 380 – 393 | 570 – 627 | |
| Mid-Bay | Mean ± SD | 198 ± 8 | 540 ± 66 | 559 ± 97 | 530 ± 36 | 250 ± 16 | 465 ± 22 | 422 ± 2 | 390 ± 8 | 590 ± 21 | 438 |
| | Range | 187 - 232 | 464 – 759 | 402 – 777 | 464 – 607 | 223 – 310 | 429 – 516 | 417 – 431 | 378 – 415 | 566 – 654 | |
| Upper Bay | Mean ± SD | 289 ± 47 | 919 ± 192 | 917 ± 97 | 680 ± 58 | 470 ± 98 | 566 ± 39 | 463 ± 19 | 434 ± 11 | 658 ± 26 | 599 |
| | Range | 225 - 401 | 645 – 1374 | 768 – 1149 | 594 – 846 | 312 – 697 | 508 – 651 | 428 - 483 | 411 – 461 | 597 – 744 | |
| Turbidity Maximum Zone | Mean ± SD | 595 ± 121 | 2087 ± 499 | 1473 ± 162 | 1237 ± 139 | 1102 ± 317 | 726 ± 34 | 575 ± 79 | 542 ± 61 | 786 ± 39 | 1014 |
| | Range | 397 - 854 | 1327 – 2981 | 1141 – 1680 | 837 – 1370 | 689 – 1866 | 645 – 754 | 481 – 737 | 457 – 709 | 711 – 1000 | |
| Urban River | Mean ± SD | 868 ± 48 | 3287 ± 163 | 2994 ± N/A | 2542 ± N/A | 2310 ± 589 | 1199 ± N/A | 816 ± 133 | 880 ± 179 | 878 ± N/A | 1753 |
| | Range | 762 – 945 | 3007 – 3600 | N/A | N/A | 1822 – 4000 | N/A | 640 – 1330 | 615 – 1450 | N/A | |
| **Average $F_{CO2}$ (mmol m$^{-2}$ d$^{-1}$)** | | | | | | | | | | | |
| Lower Bay | Mean ± SD | -15.4 ± 2.3 | 3.8 ± 0.5 | 4.4 ± 2.5 | 3.8 ± 1.9 | -3.0 ± 2.7 | 1.6 ± 0.4 | 0.8 ± 0.6 | -1.2 ± 0.3 | 13.5 ± 1.0 | 0.9 |
| | Range | -19.4 - (-12.0) | 2.8 – 6.2 | 0.5 – 13.1 | 0.8 – 8.5 | -6.4 – 2.5 | 1.1 – 2.6 | 0.1 – 1.8 | -1.9 – (-0.7) | 11.6 – 15.7 | |
| Mid-Bay | Mean ± SD | -20.0 ± 0.6 | 6.8 ± 3.2 | 11.1 ± 6.8 | 10.2 ± 1.6 | -6.7 ± 0.7 | 4.8 ± 1.8 | 2.0 ± 0.1 | -1.1 ± 0.7 | 13.5 ± 2.0 | 2.3 |
| | Range | -21.0 - (-17.8) | 3.2 – 17.4 | 0.8 – 27.8 | 7.3 – 13.6 | -8.0 – (-3.9) | 2.1 – 9.0 | 1.6 – 2.7 | -2.1 – 1.3 | 11.2 – 19.3 | |
| Upper Bay | Mean ± SD | -12.1 ± 4.9 | 25.3 ± 9.5 | 39.5 ± 7.3 | 16.8 ± 2.6 | 5.7 ± 6.0 | 13.0 ± 2.9 | 5.0 ± 1.4 | 3.4 ± 1.2 | 19.7 ± 2.0 | 12.9 |
| | Range | -18.4 – (-0.5) | 11.8 – 48.0 | 26.9 – 54.7 | 13.0 – 24.3 | -3.8 – 19.0 | 8.4 – 18.6 | 2.5 – 6.5 | 0.9 – 5.9 | 14.2 – 25.1 | |
| Turbidity Maximum Zone | Mean ± SD | 15.9 ± 9.6 | 83.9 ± 25.2 | 63.5 ± 2.9 | 42.2 ± 6.9 | 37.1 ± 13.9 | 21.1 ± 0.9 | 12.3 ± 5.1 | 10.1 ± 3.0 | 26.7 ± 1.9 | 34.8 |
| | Range | -0.9 – 36.9 | 45.6 – 129.1 | 54.3 – 65.5 | 23.9 – 47.6 | 18.6 – 71.9 | 18.3 – 21.7 | 6.3 – 23.6 | 5.6 – 19.7 | 23.3 – 44.8 | |
| Urban River | Mean ± SD | 38.3 ± 4.3 | 144.8 ± 8.1 | 131.0 ± N/A | 109.8 ± N/A | 98.9 ± 25.9 | 52.1 ± N/A | 30.2 ± 8.6 | 31.0 ± 8.1 | 32.1 ± N/A | 74.2 |
| | Range | 33.6 – 45.5 | 130.4 – 160.0 | N/A | N/A | 83.0 – 175.4 | N/A | 17.8 – 64.1 | 20.9 – 66.4 | N/A | |

[*]Months when surveys did not extend into Urban River. Area averaged was estimated by linearly regressing data from adjacent months with sample measurements. Standard deviation and range not available.

## 4.4 Assumptions and limitations

"While this study serves as the first air-water $CO_2$ 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 $pCO_2$ distributions in shallow waters 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 $pCO_2$ may vary from within the main channel to the perimeters of the estuary. Jiang et al., (2008a) found that surface water $pCO_2$ and air-water $CO_2$ flux in the marine-dominated Sapelo and Doboy sounds paralleled seasonal temperature changes and net $CO_2$ 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 $CO_2$ 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 $pCO_2$ and $CO_2$ flux dynamics may not be as influential in the Delaware Bay except near the shorelines where tides regularly flush marsh

boundaries. Studies conducted by Culberson et al., (1987) and Lebo et al., (1990) performed several cross bay transects sampled at various depths, over diel cycles, within tributaries, and periodically offshore. Results showed that cross-bay gradients were inconsistent and relatively small, except in shallow waters near the shoreline when total suspended sediment and chlorophyll concentrations were frequently elevated (Culberson et al., 1987; Lebo et al., 1990; Sharp et al., 2009). Thus, the impact from marsh input of DIC to the Delaware Bay on overall $pCO_2$ distributions and associated $CO_2$ degassing fluxes are most likely small. During December 2014, $pCO_2$ measurements were not only collected in the main channel, but also near the Delaware and New Jersey perimeters of the bay (Fig. 6I). While slight variability was observed across the bay, $pCO_2$ values from the lower to upper bay regions remained within about 150 µatm (Fig. 6I and Table 2).

In addition to the lack of cross bay transects, there is a pressing need to conduct more winter and early spring surveys to fully cover seasonal ranges in key properties such as temperature and river discharge rates. Moreover, cruises or moored sensor studies at or around large discharge events are needed. Recent study by Voynova and Sharp (2012) found that in the past century there have been a recorded 54 extreme discharges (defined by the average daily discharge as recorded in Trenton, NJ from 1 Oct 1912 to 30 Sept 2011 plus 10 standard deviations); 46% of these occurring in the past decade (Voynova and Sharp, 2012). With increasing evidence suggesting that extreme weather events will occur more frequently with climate change, it is important to maintain routine seasonal surveys to learn how such subsequent conditions (i.e. increased summer stratification, riverine $CO_2$ fluxes, removal of oxygen in bottom waters) impact various coastal environments (Allan and Soden, 2008; Yoana and Sharp, 2012). Furthermore, more research is needed in the urban and upper river sections of the estuary to better understand $CO_2$ dynamics throughout the whole estuarine gradient. The lack of inorganic carbon data in these upper regions limits syntheses of regional $CO_2$ fluxes and generalizations to underlying mechanisms. Routine sampling along small tributaries and river systems could provide crucial insight to the biogeochemistry in the upper tidal river.

There are also several limitations to the temperature-normalized and end-member mixing models that need to be addressed. First, 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 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, 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 additional insight to the various physical and biological controls behind observed $pCO_2$ 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 two 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 $CO_2$ 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 $CO_2$ concentrations. In the chemical model of the CO2SYS, $NH_3$, $NH_4^+$, 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ flux estimates (Trabalka and Reichle, 2013) although due to the relatively high TA in the Delaware River we believe this effect is small."

The use of interpolation is somewhat unclear in this manuscript, and sometimes may not be appropriate. Specifically, on P10908L15-17 the authors state: "Temperature normalized pCO2 values during months with no surveys were estimated by linearly regressing data from adjacent months with sample measurements." However, Figure 7 does not show this. There were no cruises in January or February, but the plots in Figure 7 clearly show a non-linear patterns between December and March, when the plot should have shown a straight line according to the above description. How is this possible? There were also no cruises in April or May, but the same conflicting pattern is shown in Figure 7.

You are correct. We mistakenly wrote that we interpolated temperature normalized $pCO_2$ when we never intended to. We meant to say that "Observed $pCO_2$ values during months with no surveys were estimated by linearly regressing data from adjacent months with sample measurements." We have corrected these problems in the graph and have made the errors bars darker (black lines) so that they are more visible.

We have also made pCO_2(obs) line the boldest. To help highlight times of addition (red) or removal (blue) of $CO_2$, we have inserted colored arrows in the first panel. Moreover, each arrow is accompanied with either a T or B symbol to indicate whether this $pCO_2$ change was governed by thermal or non-thermal processes.

I am also confused about the '0.01x0.01' latitude by longitude grid (P10906L16, P10904L15-16) employed in the analysis. Does this grid cover the entire Delaware Estuary, including those areas not occupied by the ship? If so, it seems unwise to extrapolate air-water CO2 fluxes from the center of the estuary out to the eastern and western fringes where no data were taken and conditions may be quite different, and the east-west variability is essentially unknown. It seems much more reasonable to calculate overall pCO2 levels and CO2 fluxes (with accompanying variability statistics) for each of the five estuary sub areas, instead of trying to interpolate the north-south transect data over the entire estuary. But perhaps I misunderstood the manuscript and the grid only covered those areas occupied by the ship.

Yes, you are correct. We did interpolate the data for each section of the estuary to the land-water boundary (perimeter). This is definitely a huge limitation to our study (extrapolating to areas where our ship did not cover) given we were unable to do east and west transects in the bay for all of our cruises except in December 2014. We agree that our data begs for accompanying variability statistics. We have added additional variability statistics to Table 2, which really highlight the north-south variability especially the rapid and extensive range in values in the upper tidal river (as shown above). A reason why we decided to extrapolate to the boundaries is that we wanted to account for the extensive size of the bay system. We tried to avoid having our measurements biased or heavily skewed towards the upper estuarine system that is so much smaller in size than the Delaware Bay. As you pointed out, addressing the uncertainties and limitations to our study is crucial. In turn, we have discussed in more detail the limitations to the lack of east to west transects in the new 4.4 limitations section (see above) as well as our lack of winter and upper estuarine data.

**Minor Comments**

Abstract

P10900L6: change to "the smaller upper tidal river..."

Now reads as, "While the smaller upper tidal river was a strong $CO_2$ source ($24.6 \pm 2.2$ mol-C m$^{-2}$ yr$^{-1}$)…"

P10900L7: change to "the much larger bay was a weak..."

Now is, "the much larger bay was a weak source ($1.8 \pm 0.2$ mol-C m$^{-2}$ yr$^{-1}$)…"

Introduction

P10902L10-13: are there any estimates of how far up the Delaware River the tidal prism extends?

Pass studies have recognized Trenton, NJ as the head of the tide (Sharp et al., 2009; Sharp, 2010).

Sentence now reads as, "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 U.S., before passing into the saline Delaware Bay (Fig. 1) (Sharp et al., 2009; Sharp, 2010)."

P10902L16-18: this dynamic interaction can be a common feature in smaller estuary systems as well, depending on river flow and geomorphology

Good point. We have incorporated this idea and now reads as follows:

"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 $CO_2$ gas exchange."

P10919L17-19: What does this sentence mean? Where is the evidence for this?

"Due to increasing urbanization and industrial activities, the biogeochemistry of the Delaware Estuary may respond differently to the rapidly changing environment than it did in the past."

We agree that this is somewhat unclear. We have edited this and inserted it into the Introduction along with some supporting evidence of how the urban river is continuously responding to a rapid changing environment.

"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 U.S., 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 value (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 (~219 μmol L-1) illustrating significant recovery from post hypoxic conditions (Sharp, 2010). Nonetheless, high $pCO_2$ is still expected to associate with strong respiratory $O_2$ consumption in the upper estuary."

P10919L17-25: This last paragraph seems ill-conceived. Are there historical data in the Delaware Estuary? If so, why were they not mentioned in the Introduction? If not, how are the past conditions known?

We have moved part of the last paragraph (as shown above) to the Introduction. We have also added more information on why we should study the Delaware Estuary to emphasize the importance of this research.

"Thus, there is limited research on $CO_2$ dynamics in large estuaries or bay systems with long freshwater residence times in the U.S. Mid-Atlantic coast (most notably the Chesapeake and Delaware estuaries). Presumably, these large estuaries have lower $pCO_2$ 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, 2009). Air-water $CO_2$ 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 pressing need to synthesize and expand global research to larger estuaries. Furthermore, of past

estuarine $CO_2$ studies, many lack spatial and seasonal coverage of surface water $pCO_2$ and air-water $CO_2$ fluxes, making flux estimates highly uncertain."

<u>Methods</u>

How deep was the seawater intake on the ship?

<span style="color:red">About 1 to 2 meters below the sea surface. I have added this and now reads as:</span>

<span style="color:red">"To monitor levels of $pCO_2$, surface water was directly pumped from 1 to 2 meters below the sea level through an underway $pCO_2$ analyzer"</span>

Some description of the equilibration method used by the AS-P2 is needed

<span style="color:red">Agreed. We have expanded on this section as follows:</span>

<span style="color:red">"To monitor levels of $pCO_2$, surface water was directly pumped from 1 to 2 meters below the sea level through an underway $pCO_2$ 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 water-drain system is attached to the equilibrator to insure balanced pressure (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 [$Mg(ClO_4)_2$] or Nafion tubing. Surface water $CO_2$ (mole fraction of dry air [$xCO_2$]) was measured approximately every one and a half minutes using an underway flow-through system equipped with a non-dispersive infrared (NDIR) gas analyzer (Li-Cor Model Li-7000, Lincoln, NE, USA)."</span>

P10903L16- The LI-7000 is not a spectrometer

<span style="color:red">Now reads as, "underway flow-through system equipped with a non-dispersive infrared (NDIR) gas analyzer…"</span>

P10906L5-9: Can you show the NOAA buoy locations on the map in Figure 1?

<span style="color:red">Good idea. We have put the NOAA buoy locations on the map.</span>

P10908L5: pCO2 was presumably normalized to the annual mean temperature, and temperature was not normalized to the annual mean temperature as indicated

<span style="color:red">The sentence is now, "We first normalized $pCO_2$ to the annual mean temperature of 13.3ºC via the following…"</span>

P10908L5: Give the mean annual temperature (13.3◦C) here.

<span style="color:red">Now is, "We first normalized $pCO_2$ to the annual mean temperature of 13.3ºC via the following…"</span>

P10908L11: Change 'as a result of" to "to be the result of"

Now reads, "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)."

P10908L12-13: "pCO2 data obtained during each cruise was rarely stationary..." What does this mean?

Deleted. "Stationary" didn't mean anything and was unnecessary. Now reads:

"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 and a different perspective to 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 five units from 0-30) to better isolate and interpret the thermal versus non-thermal effects on seasonal $pCO_2$ fluctuations."

P10910L3: This is the first mention of the Schuylkill River, which is not shown on the map. Were some river sites samples which are not discussed?

We have inserted the Schuylkill River on the map. River samples were not collected here only along the Delaware River. We used river discharge from the Schuylkill River to get a more accurate estimate of total river discharge out of the system (together the Delaware and Schuylkill River combine for about 75% of the total discharge).

P10910L7-8: How were in situ DIC and TA measurements coupled? In CO2SYS or some other program? Which carbonate K values were used? Much more description is needed here.

Agreed. More description is needed. Now reads as:

"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 $CO_2$ concentrations."

P10910L8: awkward: "The CO2 production or its contribution..."

Agreed. We have deleted "production" to avoid confusion. Now reads as:

"The $CO_2$ contribution from within the estuarine zone ($[CO_2]_{est}$) was estimated as follows…"

Results

P10910L21-24: These water temperatures are just for the Delaware River, right? Show the USGS gage used for these measurements on the map.

Correct. These water temperatures are only for the Delaware River. We have inserted the USGS gage station located at the head of the tide on the map.

P10911L1: "The Delaware River discharged was..."

Now reads, "The Delaware River discharge was greatest during March 2014 and June 2013"

P10912L20-21: Why did pCO2 go up in December 2014? It looks like low-salinity waters from the Delaware River stretch further south that usual, and flow in Figure 3 seems pretty high. Did a storm precede the survey that month?

No storm was observed only increased (strong) winds. Reasons to explain the high $pCO_2$ are still unclear but we have some theories.

"While reasons to support the elevated $pCO_2$ values remain unclear, stratification of subsurface waters in late fall followed by strong winter mixing during winter (December 2014) and a two-fold increase in river discharge could explain the elevated $pCO_2$ values observed throughout the mid- and the lower bay systems (Fig. 4)."

P10912L24: "atmosphere positive during all..."

The sentence is now, "The urban river and turbidity maximum zone served as strong sources of $CO_2$ to the atmosphere and was positive during all months"

P10913L25: Give the magnitude of the contribution, even if it is minor.

Now reads as, "In turn, their contribution (24.6 ± 2.2 mol-C m$^{-2}$ yr$^{-1}$) to overall regional flux (2.4 ± 0.3 mol-C m$^{-2}$ yr$^{-1}$) is minor."

Discussion

P10915L13: How is the removal of CO2 attributed to biology here? No evidence of biological activity is presented. Were oxygen data taken as well? O2 data are mentioned later (P10916L18), but never presented.

Agreed. We cannot attribute any removal or addition of $CO_2$ to biology without substantial evidence. We realized that in this paragraph we want to contrast the thermal versus non-thermal effects (which includes mixing) on pCO2. Thus, we attributed any reduction or elevation of $pCO_2$ in $pCO_{2obs}$ at 13.3°C to be the result of various non-thermal processes. We also added some historical data on biological activity throughout the system.

"For example, in the urban river and turbidity maximum zones (S < 5), high $pCO_{2obs}$ at 13.3 °C in the spring and winter may reflect both river inputs and strong respiratory $CO_2$ production.

Low $pCO_{2obs}$ at 13.3 ºC during the warmer months likely reflect 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, $pCO_{2mean}$ at $T_{obs}$ (changes due to the seasonal thermal cycle) trends were opposite to that of $pCO_{2obs}$ at 13.3 ºC with lower than $pCO_{2obs}$ values in the winter and higher than $pCO_{2obs}$ values in the summer. These opposing signals suggest that increases in surface water $pCO_2$ due to winter-to-summer warming are partially compensated 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 by the elevation of surface water $pCO_2$ caused by various non-thermal processes (Fig. 8)."

P10916L11-14: I don't understand what these percentages represent, or how they were calculated. This section could use some work to make the terms discussed more clear.

Agreed. We have added some more details/information to this section and now reads as:

"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 $\Delta$DIC 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 contribution 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)."

P10917L13: "during spring season..."

Now reads, "In addition, during spring season (March) high $CO_2$ consumption was also observed…"

P10917L23: Strong CO2 sources to the atmosphere, or the Delaware Estuary?

Strong $CO_2$ sources to the atmosphere. The sentence is now, "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."

P10917L25: relatively weak compared to what? Put this number in some context. The following paragraph discusses relative CO2 sources in some other estuaries, but gives no actual numbers.

Good point. We have added relevant values and comparisons and now reads as follows:

"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 $CO_2$."

P10918L24: "to the rapid flushing..."

Now is, "Similarly, and in contrast to the rapidly flushing Altamaha Sound…"

P10918L4-5: "to overall CO2 fluxes". Are these fluxes for the entire estuary, or just these smaller sub-sections?

These fluxes are just for these smaller sub-sections.

"Moreover, positive correlations between river-borne and air-water $CO_2$ fluxes in the upper tidal river emphasize the significance of river-borne $CO_2$ degassing to overall $CO_2$ fluxes in the upper sub-sections of the estuary (the urban river and turbidity maximum zone)."

P10918L26-29: This section is awkwardly written.

"Due to its extensive geographic size, one may conceptually model the Delaware Estuary, and in some circumstances, other large estuarine systems as being a funnel-shaped estuary."

The sentence now reads, "With its extensive geographic size, the Delaware Estuary features both a river dominated upper estuary and an ocean dominated lower bay."

FIGURE 7- The error bars on this plot are unreadable. In general, this plot is too small.

Agreed. We were also a little disappointed in the "readability"of the figures. We have tried to increase figure and text sizes.

FIGURE 8- Is a linear fit in the top panel really appropriate for five data points? Also, the different a-axis and y-axis scales should be clearly noted, or the panels should be depicted on the

same scales. It might be interesting to plot the data from both panels in one plot- how would the Urban River points line up with those from the Turbidity Maximum Zone?

Good call. We have clearly noted the different x-axis and y-axis. We believe the smaller ratio of river borne to air water $CO_2$ fluxes in the Turbidity Maximum Zone illustrates the rapid degassing of $CO_2$ in the upper estuary. When plotting data from both panels in one plot we can see this as all the data points from the Turbidity Maximum Zone fall to the left of the Urban River points. However, when using the same axes, the Turbidity Maximum points become clumped and it's hard to distinguish between the various months. Because of this, we have kept the data in separate panels.

FIGURE 9-This figure is totally unreadable – the colors of the bars are indistinguishable from one another. The different y-axis scales need to be noted. Also, are some data omitted from this figure? Table 1 shows data from June 2013 and December 2014, but those months have no results in Figure 9

We have changed the colors of the bars and have noted the different y-axis scales. For the months of July and December, we were unable to reach near zero salinity or the river-end member. In turn, we were unable to accurately produce theoretical dilution and river mixing lines for DIC and TA since we had no end-member data. We could not accurately calculate river nor estuarine $CO_2$ contributions and thus had to unfortunately omit these months.

**Referee #2**

We thank you for the very insightful and thorough responses, which have greatly strengthened the overall flow and organization of our manuscript. Following your suggestions, we have made great efforts to improve the methods section and expand on why this $CO_2$ study (the Delaware Estuary) is so important. In addition, to help address the uncertainties and limitations to our study, we have composed a new assumptions and limitations section (4.4) in the discussion.

**Major Comments**

In calculating temperature-normalized pCO2, it is necessary to define an annual mean temperature against which seasonal fluctuations can be measured. Here, the authors use the mean water temperature measured in the Delaware Estuary from 2013-2015, which covers the span of their sampling. Others have adopted a more climatological approach that uses a long-term annual mean temperature, as may be provided by the 10-year average temperature cycle the authors show in Figure 3. Especially since there important seasonal gaps in the authors' analysis (e.g., January and February - the two lowest temperature months), it is my instinct to suggest using a more resolved temperature product for this calculation, such as a USGS record (e.g., that given in Figure 3a if it can be applied to the entire estuary) or a satellite-derived mean. If the authors used a similar temporal interpolation to get an annual temperature despite months without data (as in the calculation of annual CO2 fluxes including months without data, which could also be better shown and described itself), this should be more directly stated. A broad recalculation of this result constitutes a major revision.

Agreed. In order to obtain a more solid representation of the annual mean surface water temperature in the Delaware Estuary against which seasonal fluctuations can be measured, a longer annual record (10-yr average) of surface water temperature cycles would be more appropriate. This would help smoothen out any anomalies that a shorter record would have trouble accounting for. Thus, we have decided to use the 10-year average temperature (13.3°C) as shown in Figure 3a for the annual mean surface water temperature in my calculations.

Throughout the description of their techniques, the authors take care to point out weaknesses. However, they provide no systematic error analysis. A consolidated summary of methods, assumptions, caveats and gaps at least is integral to the readers understanding, and what was missed. For example, I was left wondering how the salinity-binned temperature-normalized $pCO_2$ related to the area-averaged $CO_2$ flux. This seemed out of place next to the other area-based considerations (e.g., Tables 1 and 2, Figures 8 and 9), and the implications of this choice were not well explained either for the method itself or for the interpretation of the data. For additional examples, see the annual mean temperature choice highlighted above, and the absence of discussion about any weakness in the river $CO_2$ contribution calculations, as well as additional points listed in the minor comments below. I consider additional discussion of assumptions and caveats a major revision, whether it involves additional text or additional calculations.

To resolve these comments, I highly recommend that the authors include a conceptual sketch to summarize their calculations, and consolidate the information about their assumptions and caveats in a clear, concise additional section. An excellent reference would be the recent manuscript published by W. Evans and colleagues, which required a similar methodological description and error calculation to underpin their observations of coastal $CO_2$ fluxes. See http://onlinelibrary.wiley.com/wol1/doi/10.1002/2015GB005153/abstract.

We agree that the assumptions and limitations in our study need to be better addressed. Taking your responses into consideration, we have added a new assumptions and caveats section (4.4) to better address these issues (please see below).

**4.4 Assumptions and limitations**

"While this study serves as the first air-water $CO_2$ 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 $pCO_2$ distributions in shallow waters 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 $pCO_2$ may vary from within the main channel to the perimeters of the estuary. Jiang et al., (2008a) found that surface water $pCO_2$ and air-water $CO_2$ flux in the marine-dominated Sapelo and Doboy sounds paralleled seasonal temperature changes and net $CO_2$ 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 $CO_2$ 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 $pCO_2$ and $CO_2$ flux dynamics may not be as influential in the Delaware Bay except near the shorelines where tides regularly flush marsh boundaries. Studies conducted by Culberson et al., (1987) and Lebo et al., (1990) performed several cross bay transects sampled at various depths, over diel cycles, within tributaries, and periodically offshore. Results showed that cross-bay gradients were inconsistent and relatively small, except in shallow waters near the shoreline when total suspended sediment and chlorophyll concentrations were frequently elevated (Culberson et al., 1987; Lebo et al., 1990; Sharp et al., 2009). Thus, the impact from marsh input of DIC to the Delaware Bay on overall $pCO_2$ distributions and associated $CO_2$ degassing fluxes are most likely small. During December 2014, $pCO_2$ measurements were not only collected in the main channel, but also near the Delaware and New Jersey perimeters of the bay (Fig. 6I). While slight variability was observed across the bay, $pCO_2$ values from the lower to upper bay regions remained within about 150 µatm (Fig. 6I and Table 2).

In addition to the lack of cross bay transects, there is a pressing need to conduct more winter and early spring surveys to fully cover seasonal ranges in key properties such as temperature and river discharge rates. Moreover, cruises or moored sensor studies at or around large discharge events are needed. Recent study by Voynova and Sharp (2012) found that in the past century there have been a recorded 54 extreme discharges (defined by the average daily discharge as recorded in Trenton, NJ from 1 Oct 1912 to 30 Sept 2011 plus 10 standard deviations); 46% of these occurring in the past decade (Voynova and Sharp, 2012). With increasing evidence suggesting that extreme weather events will occur more frequently with climate change, it is important to maintain routine seasonal surveys to learn how such subsequent conditions (i.e. increased summer stratification, riverine $CO_2$ fluxes, removal of oxygen in bottom waters) impact various coastal environments (Allan and Soden, 2008; Yoana and Sharp, 2012). Furthermore, more research is needed in the urban and upper river sections of the estuary to better understand $CO_2$ dynamics throughout the whole estuarine gradient. The lack of inorganic carbon data in these upper regions limits syntheses of regional $CO_2$ fluxes and generalizations to underlying mechanisms. Routine sampling along small tributaries and river systems could provide crucial insight to the biogeochemistry in the upper tidal river.

There are also several limitations to the temperature-normalized and end-member mixing models that need to be addressed. First, 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 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, 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 additional insight to the various physical and biological controls behind observed $pCO_2$ 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 two 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 $CO_2$ 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 $CO_2$ concentrations. In the chemical model of the CO2SYS, $NH_3$, $NH_4^+$, 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ flux estimates (Trabalka and Reichle, 2013) although due to the relatively high TA in the Delaware River we believe this effect is small."

**Minor Comments**

<u>Introduction</u>

Page 10900 Line 24: Nice note about industrialization and future change at the end of this manuscript that could be included up front.

Thanks. We wanted to emphasis the point that the system is continuously responding to a rapidly changing environment (i.e. industrialization) and have moved this part and added some supporting evidence to the Introduction. Now reads as follows:

"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 U.S., 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 value (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 (~219 µmol L-1) illustrating significant recovery from post hypoxic conditions (Sharp, 2010). Nonetheless, high $pCO_2$ is still expected to associate with strong respiratory $O_2$ consumption in the upper estuary. In contrast, the Delaware Bay is a large shallow embayment surrounded by partially undeveloped salt marshes (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 $CO_2$ gas exchange."

Page 10902 Line 5/6: Great statement. Lead this section with that, and then clearly state the gaps that contribute to this concern (spatially, not a lot done in Mid-Atlantic; theoretically, not a lot done in large, fast-moving estuaries), and how the Delaware Estuary could help address these issues. That would lead well into the review of the Delaware R. Estuary in the next section.

This paragraph is structured as follows:

"There is rising concern that global estuarine $CO_2$ 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; references therein), our knowledge of $CO_2$ degassing fluxes and their controlling processes in estuaries remains insufficient. Globally, the majority of past estuarine $CO_2$ studies have been conducted on small estuarine systems, which typically have high $pCO_2$. (Chen and Borges, 2009; Cai, 2011; Borges and Abril, 2011)…"

In addition, I have added the following to address the importance and lack of $CO_2$ studies conducted in the Delaware Estuary:

"…Thus, there is limited research on $CO_2$ dynamics in large estuaries or bay systems with long freshwater residence times in the U.S. Mid-Atlantic coast (most notably the Chesapeake and Delaware estuaries). Presumably, these large estuaries have lower $pCO_2$ 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, 2009). Air-water $CO_2$ 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 pressing need to synthesize and expand global research to larger estuaries. Furthermore, of past estuarine $CO_2$ studies, many lack spatial and seasonal coverage of surface water $pCO_2$ and air-water $CO_2$ fluxes, making flux estimates highly uncertain."

Page 10902 Line 9/10: Later you point out that your manuscript represents the first carbon work, so it is important here to state that too.

In addition to the added information (above) about the lack of inorganic carbon studies in the Delaware Estuary, I have stated that this is the first paper that summarizes a $CO_2$ flux product for the system.

"In this paper, we report the first seasonal distribution of $pCO_2$ and air-water $CO_2$ 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 $pCO_2$ distributions as well as the overall contribution of internal versus riverine sources on $CO_2$ inputs

to the estuarine system. Finally, we present a summarized $pCO_2$ distribution over the study area and provide a conceptual model to illustrate the control mechanisms on surface water $CO_2$ dynamics in the Delaware Estuary."

Page 10902 Line 14: Why does industrialization matter? It is better stated at the conclusion of the paper, but should be explained here too.

Agreed. Please see above response (Page 10900 Line 24) where I address industrialization and the systems continuous response to a rapidly changing environment (with historical examples).

Page 10903 Line 3: Sampling bias implied by lack of Jan/Feb data. This should be discussed in reorganized methods section.

The lack of winter data indeed limits our seasonal coverage of the system. We've tried our best to address this issue in the new caveats section (please see 4.4 Assumptions and limitations)

Methods

Page 10904 Line 3/4: Sampling method reference for filtration?

The same sampling technique as in Cai and Wang (1998) and Jiang et al. (2008a) was used. We have added these references. When collecting water, all bottles were overflowed for at least twice its volume to minimize contact with the atmosphere.

Page 10904 Line 5: There is some internal discussion among the carbon community about use of mercuric chloride as a preservative in low-salinity samples. The challenge is that the mercury salt impacts alkalinity concentrations at salinities less than 10. The excess alkalinity from the HgCl2 may have lowered calculated CO2 concentrations, and as a result these flux estimates are likely conservative. Important to point this out in new assumptions/caveats section.

Please see new 4.4 Assumptions and limitations section. As mentioned earlier, due to the relatively high TA in the Delaware River, we believe this effect is small.

Page 10904 Line 26: Starting out this section strong by trying stating these challenges directly, but need a clearer description or summary of how they were addressed.

To address the challenge of estimating gas transfer velocities, we adopted an established method based on wind speed that avoided calculations of zero gas transfer velocities ($k$) at low wind speeds (Wanninkhof et al., [2009]). Now reads as follows:

"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…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)…"

<span style="color:red">In order to address the challenge of obtaining spatial and temporal heterogeneity of $pCO_2$ distributions we have added the following details:</span>

<span style="color:red">"Another challenge to accurately determining air-water $CO_2$ fluxes is obtaining reliable spatial and temporal $pCO_2$ distributions. Unfortunately, while seasonal distributions of $pCO_2$ were measured from the mouth of the bay to 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"</span>

Page 10906 Line 14: Why split the upper and mid-bay regions? Are these salinity binned designations, or geographically...?

<span style="color:red">We noticed rapid changes and range in $pCO_2$ values (salinity as well) across these regions and felt that if we divided the area into one more region (now upper, mid-, and lower bay) that this would allow for a more thorough comparison of $pCO_2$ and $CO_2$ fluxes throughout the system.</span>

<span style="color:red">These are geographically binned designations. Now reads as follows:</span>

<span style="color:red">"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 $pCO_2$ values across the mid-bay, this region was split into an upper and mid-bay zone to allow for a more robust comparison of $pCO_2$ and $CO_2$ fluxes throughout the system (Fig. 1)."</span>

Page 10907 Line 24: stating the temperature constant here is redundant

"Similar to the results found in Jiang et al. (2008a), temperature derived constants were lower than the isochemical seawater constant $0.0423 \circ C{-}1$ determined by Takahashi et al. (1993)"

<span style="color:red">This is now replaced with, "Similar to the results found in Jiang et al. (2008a), temperature derived constants were lower than that determined by Takahashi et al. (1993)."</span>

Page 10907 Line 25-27: Address with other caveats in new section

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 pCO2 fluctuations due to temperature and biological processes as it neglects the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on $pCO_2$ dynamics.

<span style="color:red">We have addressed this issue and other caveats in new limitations section (please see 4.4 Assumptions and limitations)</span>

Page10908Line13: Not sure what "stationary" signifies here. The salinity bin rationale needs more detail, and more description of how salinity-bins and geographic bins relate to each other in the data interpretation.

Page 10914 Line 6: Why is the salinity interval more important than the geographical interval? I'm still confused by the salinity binning as described in Section 2.3 and the results here are not helping clarify why this was important or what it showed.

"Stationary" has been removed as it only brought confusion and is unnecessary. More information on the difference and importance between salinity and geographic bins has been added. This section now reads as follows:

"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 and a different perspective to 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 five units from 0-30) to better isolate and interpret the thermal versus non-thermal effects on seasonal $pCO_2$ fluctuations."

Page 10909 Line 20-22: Clever way of calculating this, but is it the ideal way? What are the challenges here? Good thing to discuss in caveats section.

Good point. We have added some discussion on the limitations of using TA and DIC to calculate $CO_2$ in our new caveats section.

Page 10910 Line 15: Very interesting comment in the caption for Figure 2 concerning panel C, but panel C is not discussed here. Another important point for the assumptions and caveats section, especially since CO2SYS was again used for the calculation of riverine contribution to fluxes (Section 2.4; Page 10909, line 20-22).

We have included part of the caption into the main paper to assist with clarification. In addition, we have added some discussion about assumptions and limitations in this part to the new caveats section. We also note how the addition of mercuric chloride to low salinity samples may result in lower calculated then observed $CO_2$ concentrations. This section now reads as follows:

"Because $CO_2$ concentrations do not change linearly during mixing, they were estimated using corresponding DIC and TA mixing values (Fig. 3C) (Jiang et al., 2008a). In the chemical model of the CO2SYS, $NH_3$, $NH_4^+$, 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 $CO_2$ than observed $CO_2$ was expected as the observed TA included other acid-base components (Fig. 3C). Another factor that may contribute to the lower calculated $CO_2$ than observed $CO_2$ 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 $CO_2$ flux estimates (Trabalka and Reichle, 2013) although due to the relatively high TA in the Delaware River we believe this effect is small."

Results

Page 10910 Line 21-25: Why different time ranges for discharge and temperature? Directly mention differences in the data record.

We felt that the variability in monthly mean water temperatures could be sufficiently captured within the past 10-year average records. However, due to the irregularity of weathering and various external events, river discharge fluctuations are much larger from year to year than monthly mean surface water temperatures. Thus, we believe a longer 30-year monthly discharge record is necessary to capture the general trend and range of seasonal river discharge rates.

"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."

Page 10911 Line 1: Change "The Delaware River discharged..." to "The Delaware River discharge..."

Now the sentence is, "The Delaware River discharge was greatest during March 2014 and June 2013."

Page 10912 Line 10: Difficult to see any DIC drawdown relative to salinity in Figure 2a that would also indicate a bloom... unusual for such a strong bloom. If entire water column/estuary was affected by the bloom, how does this affect your calculation of the DIC endmember? Since much of the seasonal cycle you describe relies on this point, the biological production should be better shown or explained.

Agreed. We have added some research on the variability of DIC at the end-members. It appears that for the most part, precipitation rates are the dominant controlling processes effecting DIC variability at the river end-member with minimal impact from biological activity. This is actually expected as river DIC and TA are largely a dilution of weathering production by rain (Cai et al., 2008). Now reads as follows:

"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). On the other hand, at higher salinities, any drawdown of DIC relative to salinity is small since less than 1% of the DIC pool exists as $p$CO$_2$ (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)."

Page 10913 Section 3.4: Temporal questions here could be better addressed, such as definition of seasons as well as the temporal averaging for the annual estimates.

Good point. We have defined each season and given annual estimates for each of them.

"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 two-fold greater than those observed in the spring (March) and fall (October and November) seasons (Fig. 7)…" "In winter (December), $pCO_2$ values were always supersaturated with respect to the atmosphere across the entire salinity range."

"Seasonally, the Delaware Estuary served as a strong $CO_2$ sink (-5.0 ± 6.0 mol-C m$^{-2}$ yr$^{-1}$) in the spring, a strong source (4.9 ± 8.1 mol-C m$^{-2}$ yr$^{-1}$) in the summer, a weak source (1.0 ± 2.4 mol-C m$^{-2}$ yr$^{-1}$) in the fall, and a strong source (5.7 ± 1.9 mol-C m$^{-2}$ 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 ± 6.4 mol-C m$^{-2}$ yr$^{-1}$) to overall regional flux (2.4 ± 4.8 mol-C m$^{-2}$ yr$^{-1}$) is minor. Thus, the Delaware Estuary as a whole acts as a relatively weak $CO_2$ source (2.4 ± 4.8 mol-C m$^{-2}$ yr$^{-1}$), which is in great contrast to many river estuaries that are strong $CO_2$ sources (26 ± 21 mol-C m$^{-2}$ yr$^{-1}$) (Borges and Abril, 2011)."

Page 10914 Line 13/14: How does this bloom timing relate to other observations of the seasonal biological cycles in the Delaware Estuary?

Good question. We've added a little more information about historical production data to the discussion section as shown below.

"For example, in the urban river and turbidity maximum zones ($S < 5$), high $pCO_{2obs}$ at 12.7 °C in the spring and winter may reflect both river inputs and strong respiratory $CO_2$ production. Low $pCO_{2obs}$ at 12.7 °C during the warmer months likely reflect 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, $pCO_{2mean}$ at $T_{obs}$ (changes due to the seasonal thermal cycle) trends were opposite to that of $pCO_{2obs}$ at 12.7 °C with lower than $pCO_{2obs}$ values in the winter and higher than $pCO_{2obs}$ values in the summer. These opposing signals suggest that increases in surface water $pCO_2$ due to winter-to-summer warming are partially compensated 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 by the elevation of surface water $pCO_2$ caused by various non-thermal processes (Fig. 8)."

Discussion

Page 10915 Appendix B could be expanded and would be a worthy inclusion in the main paper.

It appears that the need for Appendixes is probably unnecessary (similar comments made by other referee) since space is not a critical issue for Biogeosciences. We have included both Appendixes back into the main paper and tried to make some expansions for clarification. Now reads as follows:

"We further examine the relative importance of the temperature and biological effects in each salinity interval by calculating the ratio of $\Delta pCO_{2temp}$ to $\Delta pCO_{2bio}$ (*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:

$$\Delta pCO_{2thermal} = (pCO_{2mean} \text{ at } T_{obs})_{max} - (pCO_{2mean} \text{ at } T_{obs})_{min} \tag{12}$$

where $(pCO_{2mean} \text{ at } T_{obs})_{max}$ and $(pCO_{2mean} \text{ at } T_{obs})_{min}$ are the maximum and minimum $pCO_{2mean}$ at $T_{obs}$ values, respectively. In other words, the thermal effects on the mean annual $pCO_2$ value is represented by the seasonal amplitude of $(pCO_{2mean} \text{ at } T_{obs})$ 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):

$$\Delta pCO_{2non\text{-}thermal} = (pCO_{2obs} \text{ at } 13.3 \,°C)_{max} - (pCO_{2obs} \text{ at } 13.3 \,°C)_{min} \tag{13}$$

where $(pCO_{2obs} \text{ at } 13.3 \,°C)_{max}$ and $(pCO_{2obs} \text{ at } 12.7 \,°C)_{min}$ are the maximum and minimum $pCO_{2obs}$ at 12.7 °C values, respectively. Thus, the non-thermal thermal effects on surface water $pCO_2$ ($pCO_{2obs}$ at 13.3 °C) is represented by the seasonal amplitude of $pCO_2$ values corrected to the annual mean temperature using Eq. (6). The relative importance of these effects in each salinity interval can be expressed as the difference between $\Delta pCO_{2thermal}$ and $\Delta pCO_{2non\text{-}thermal}$ (*T − B*) or the ratio of $\Delta pCO_{2thermal}$ to $\Delta pCO_{2non\text{-}thermal}$ (*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.

Summary and Concluding Remarks

Page 10919 Line 6: Great statement! Belongs at the top of the paper.

"While this study serves as the first air–water $CO_2$ flux product in the Delaware Estuary, there are several limitations."

Thanks! We have included this in the beginning of our new caveats sections (please see 4.4 Assumptions and limitations)

Page 10919 Line 6-16: This section needs to be broadly expanded to turn it into an appropriate assumptions and caveats section (consider it section 4.4). Some of the points made here could then receive more attention, such as some review of how nearby marshes might influence pCO2

Please see new 4.4 Assumptions and limitations section

Tables and Figures

Table 1. Area-weighted average flux in an additional column.

Table 2. Area-averaged, standard deviation, and range of $pCO_2$ and $CO_2$ flux ($F_{CO2}$) in five of the six zones in the Delaware Estuary during each cruise.

| | | Mar 2014 | Jun 2013 | Jul 2014[*] | Aug 2013[*] | Aug 2014 | Oct 2013[*] | Oct 2014 | Nov 2013 | Dec 2014[*] | Annual Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Average $pCO_2$ (µatm) | | | | | | | | | | | |
| Lower Bay | Mean ± SD | 230 ± 23 | 477 ± 11 | 473 ± 52 | 384 ± 42 | 315 ± 59 | 421 ± 6 | 405 ± 8 | 387 ± 3 | 596 ± 11 | 410 |
| | Range | 194 – 267 | 456 – 528 | 397 – 648 | 317 – 491 | 243 – 432 | 413 – 437 | 395 – 419 | 380 – 393 | 570 – 627 | |
| Mid-Bay | Mean ± SD | 198 ± 8 | 540 ± 66 | 559 ± 97 | 530 ± 36 | 250 ± 16 | 465 ± 22 | 422 ± 2 | 390 ± 8 | 590 ± 21 | 438 |
| | Range | 187 - 232 | 464 – 759 | 402 – 777 | 464 – 607 | 223 – 310 | 429 – 516 | 417 – 431 | 378 – 415 | 566 – 654 | |
| Upper Bay | Mean ± SD | 289 ± 47 | 919 ± 192 | 917 ± 97 | 680 ± 58 | 470 ± 98 | 566 ± 39 | 463 ± 19 | 434 ± 11 | 658 ± 26 | 599 |
| | Range | 225 - 401 | 645 – 1374 | 768 – 1149 | 594 – 846 | 312 – 697 | 508 – 651 | 428 - 483 | 411 – 461 | 597 – 744 | |
| Turbidity Maximum Zone | Mean ± SD | 595 ± 121 | 2087 ± 499 | 1473 ± 162 | 1237 ± 139 | 1102 ± 317 | 726 ± 34 | 575 ± 79 | 542 ± 61 | 786 ± 39 | 1014 |
| | Range | 397 - 854 | 1327 – 2981 | 1141 – 1680 | 837 – 1370 | 689 – 1866 | 645 – 754 | 481 – 737 | 457 – 709 | 711 – 1000 | |
| Urban River | Mean ± SD | 868 ± 48 | 3287 ± 163 | 2994 ± N/A | 2542 ± N/A | 2310 ± 589 | 1199 ± N/A | 816 ± 133 | 880 ± 179 | 878 ± N/A | 1753 |
| | Range | 762 – 945 | 3007 – 3600 | N/A | N/A | 1822 – 4000 | N/A | 640 – 1330 | 615 – 1450 | N/A | |
| Average $F_{CO2}$ (mmol m$^{-2}$ d$^{-1}$) | | | | | | | | | | | |
| Lower Bay | Mean ± SD | -15.4 ± 2.3 | 3.8 ± 0.5 | 4.4 ± 2.5 | 3.8 ± 1.9 | -3.0 ± 2.7 | 1.6 ± 0.4 | 0.8 ± 0.6 | -1.2 ± 0.3 | 13.5 ± 1.0 | 0.9 |
| | Range | -19.4 - (-12.0) | 2.8 – 6.2 | 0.5 – 13.1 | 0.8 – 8.5 | -6.4 – 2.5 | 1.1 – 2.6 | 0.1 – 1.8 | -1.9 – (-0.7) | 11.6 – 15.7 | |
| Mid-Bay | Mean ± SD | -20.0 ± 0.6 | 6.8 ± 3.2 | 11.1 ± 6.8 | 10.2 ± 1.6 | -6.7 ± 0.7 | 4.8 ± 1.8 | 2.0 ± 0.1 | -1.1 ± 0.7 | 13.5 ± 2.0 | 2.3 |
| | Range | -21.0 - (-17.8) | 3.2 – 17.4 | 0.8 – 27.8 | 7.3 – 13.6 | -8.0 – (-3.9) | 2.1 – 9.0 | 1.6 – 2.7 | -2.1 – 1.3 | 11.2 – 19.3 | |
| Upper Bay | Mean ± SD | -12.1 ± 4.9 | 25.3 ± 9.5 | 39.5 ± 7.3 | 16.8 ± 2.6 | 5.7 ± 6.0 | 13.0 ± 2.9 | 5.0 ± 1.4 | 3.4 ± 1.2 | 19.7 ± 2.0 | 12.9 |
| | Range | -18.4 – (-0.5) | 11.8 – 48.0 | 26.9 – 54.7 | 13.0 – 24.3 | -3.8 – 19.0 | 8.4 – 18.6 | 2.5 – 6.5 | 0.9 – 5.9 | 14.2 – 25.1 | |
| Turbidity Maximum Zone | Mean ± SD | 15.9 ± 9.6 | 83.9 ± 25.2 | 63.5 ± 2.9 | 42.2 ± 6.9 | 37.1 ± 13.9 | 21.1 ± 0.9 | 12.3 ± 5.1 | 10.1 ± 3.0 | 26.7 ± 1.9 | 34.8 |
| | Range | -0.9 – 36.9 | 45.6 – 129.1 | 54.3 – 65.5 | 23.9 – 47.6 | 18.6 – 71.9 | 18.3 – 21.7 | 6.3 – 23.6 | 5.6 – 19.7 | 23.3 – 44.8 | |
| Urban River | Mean ± SD | 38.3 ± 4.3 | 144.8 ± 8.1 | 131.0 ± N/A | 109.8 ± N/A | 98.9 ± 25.9 | 52.1 ± N/A | 30.2 ± 8.6 | 31.0 ± 8.1 | 32.1 ± N/A | 74.2 |
| | Range | 33.6 – 45.5 | 130.4 – 160.0 | N/A | N/A | 83.0 – 175.4 | N/A | 17.8 – 64.1 | 20.9 – 66.4 | N/A | |

[*]Months when surveys did not extend into Urban River. Area averaged was estimated by linearly regressing data from adjacent months with sample measurements. Standard deviation and range not available.

Figures1-9. In general, sizing here could be made a little more uniform. In some cases text sizes were extremely difficult to read (see especially the legends in Figures 7 and 9). Increasing the size of Figure 2 might also be able to highlight any potential DIC drawdown influencing biological production.

Figure 2. Panel c not discussed in manuscript.

Figure 4, 5. ODV stamp required on figures generated using that program, as well as a Schlitzer citation.

Figure 7. Not sure this is the best way to show differences between temperature and biological forcing, salinity binning aside. Firstly, the variables need better labels (use T and B as in Appendix B) and the pCO2(obs) line should be the boldest. I would also consider plotting T and B as anomalies from pCO2(obs), or showing a vector diagram, or using color to highlight times when warming, cooling, production, and respiration are clearly factors so that the interpretation of this figure immediately jumps out.

**Relevant Changes**

- The removal of Appendixes A and B. Now Appendix A is incorporated into section 2.3 (Temperature normalized $p\mathrm{CO_2}$ estimation) and Appendix B is incorporated into section 4.1 (Temperature vs. biological effects on $p\mathrm{CO_2}$).

- The addition of section 4.4 (Assumptions and limitations) was added to help address the uncertainties and limitations faced during this study such as the lack of cross bay and nearshore transects, the need for more winter and upper estuarine surveys, and the various assumptions and limitations to our chemical models that may not have been clear.

- To allow for more variability statistics (mean, range, and standard deviation), there is now one table (Table 2) investigating the area-averaged $p\mathrm{CO_2}$ and air-water $\mathrm{CO_2}$ fluxes throughout each section of the estuary and another table (Table 3) exploring the estimated flushing times in each region of the estuary.

- In order to obtain a more solid representation of the annual mean surface water temperature in the Delaware Estuary against which seasonal fluctuations can be measured, the 10-year average surface water temperature (13.3°C) instead of the 2-year average temperature (12.7 C) recorded during our study was used throughout our calculations.

- Additional description of the equilibration method used to measured surface water $p\mathrm{CO_2}$ has been added in the methods section.

- Figure 1 now includes the location of the four NOAA buoys used for wind speed data, the USGS gauging station used for surface water temperature and river discharge, and the Schuylkill River.

- Red and blue arrows accompanied with either a T or B symbol have been added to Figure 8 to indicate whether $p\mathrm{CO_2}$ change was governed by thermal or non-thermal processes.

# 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 ($pCO_2$) were measured on nine cruises in the Delaware Estuary (USA). The Delaware River was highly supersaturated in $pCO_2$ with respect to the atmosphere during all seasons while the Delaware Bay was undersaturated in $pCO_2$ during spring and late summer and moderately supersaturated during midsummer, fall, and winter. While the smaller upper tidal river was a strong $CO_2$ source ($27.1 \pm 6.4$ mol-C m$^{-2}$ yr$^{-1}$), the much larger bay was a weak source ($1.2 \pm 1.4$ 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 $CO_2$ source ($2.4 \pm 4.8$ mol-C m$^{-2}$ yr$^{-1}$), which is in great contrast to many other estuarine systems. Seasonally, $pCO_2$ changes were greatest at low salinities ($0 \leq S < 5$) with $pCO_2$ values in the summer nearly three-fold greater than those observed in the spring and fall. Undersaturated $pCO_2$ was observed over the widest salinity range ($7.5 \leq S < 30$) during spring. Near to supersaturated $pCO_2$ was generally observed in mid- to high salinity waters ($20 \leq S < 30$) except during spring and late summer. Strong seasonal trends in internal estuarine production and consumption of $CO_2$ were observed throughout both the upper tidal river and lower bay. Comparably, positive correlations between river-borne and air-water $CO_2$ fluxes in the upper estuary emphasize the significance of river-borne $CO_2$ degassing to overall $CO_2$ fluxes. While river-borne $CO_2$ degassing heavily influenced $CO_2$ dynamics in the upper tidal river, these forces were largely compensated 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 ($CO_2$) degassing flux from estuarine waters is as large as the $CO_2$ 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, 2013; Laruelle et al., 2015). Such large estuarine $CO_2$ degassing suggests that much of the terrestrial organic carbon, including that from coastal wetlands, is respired to $CO_2$ during transport through the estuarine zone, though the relative importance of river supplied $CO_2$ and organic carbon verses those from the coastal wetlands is debatable (Borges and Abril, 2011; Cai, 2011). In turn, estuarine waters are a major source of $CO_2$

to the atmosphere, with partial pressures of $CO_2$ ($pCO_2$) ranging from 350 to 10,000 µatm and air-water $CO_2$ fluxes ranging from -5 to 80 mol C m$^{-2}$ yr$^{-1}$ (Raymond et al., 1997; Cai and Wang, 1998; Frankignoulle et al., 1998; Borges, 2005; Borges et al., 2006; Borges and Abril, 2011; Cai 2011).

There is rising concern that global estuarine $CO_2$ 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; references therein), our knowledge of $CO_2$ degassing fluxes and their controlling processes in estuaries remains insufficient. Globally, the majority of past estuarine $CO_2$ studies have been conducted on small estuarine systems, which typically have high $pCO_2$. (Chen and Borges, 2009; Cai, 2011; Borges and Abril, 2011). Specifically, in the U.S. east coast, high $pCO_2$ was found in estuaries along the southeastern (Cai and Wang, 1998; Jiang et al., 2008) and northeastern (Salisbury et al., 2008; Hunt et al., 2010) coastal regions. While high $pCO_2$ was also found in small estuaries along the U.S. Mid-Atlantic coast (Raymond et al., 1997; Raymond et al., 2000), only a few estuarine $CO_2$ 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 $CO_2$ dynamics in large estuaries or bay systems with long freshwater residence times in the U.S. Mid-Atlantic coast (most notably the Chesapeake and Delaware estuaries). Presumably, these large estuaries have lower $pCO_2$ 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, 2009). Air-water $CO_2$ 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 pressing need to synthesize and expand global research to larger estuaries. Furthermore, of past estuarine $CO_2$ studies, many lack spatial and seasonal coverage of surface water $pCO_2$ and air-water $CO_2$ fluxes, making flux estimates highly uncertain.

The Delaware Estuary is composed of a 100-km-long tidal Delaware River and the 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 study (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 U.S., 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 value (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 $L^{-1}$ (~219 µmol $L^{-1}$) illustrating significant recovery from post hypoxic conditions (Sharp, 2010). Nonetheless, high $p$CO$_2$ is still expected to associate with strong respiratory O$_2$ consumption in the upper estuary. In contrast, the Delaware Bay is a large shallow embayment surrounded by partially undeveloped salt marshes (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 CO$_2$ gas exchange.

In this paper, we report the first seasonal distribution of $p$CO$_2$ and air-water 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 $p$CO$_2$ distributions as well as the overall contribution of internal versus riverine sources on CO$_2$ inputs to the estuarine system. Finally, we present a summarized $p$CO$_2$ distribution over the study area and provide a conceptual model to illustrate the control mechanisms on surface water CO$_2$ dynamics in the Delaware Estuary.


## 2 Methods

### 2.1 Field measurements

The Delaware Estuary was surveyed on nine cruises: 08-10 June 2013, 08-15 August 2013, 17 October 2013, 17-22 November 2013, 23-24 March 2014, 03 July 2014, 27 of August to 01 of September 2014, 30 of October to 02 November 2014, and 05 December 2014. Distributions of $p$CO$_2$, 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 meters below the sea level through an underway $pCO_2$ 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 [$Mg(ClO_4)_2$] or Nafion tubing. Surface water $CO_2$ (mole fraction of dry air [$xCO_2$]) was measured approximately every one and a half minutes using an underway flow-through system equipped with a non-dispersive infrared (NDIR) gas analyzer (Li-Cor Model Li-7000, Lincoln, NE, USA). This LICOR 7000 was calibrated, every 3-6 hours, 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 hours 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 on-board 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 salinity zero 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 in 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 x 0.01 latitude grid were calculated as follows:

$$F_i = k_i \cdot K_{oi} \cdot (pCO_{2(water)i} - pCO_{2(air)i}) \tag{1}$$

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 $pCO_{2(water)i}$ and $pCO_{2(air)i}$ ($\mu$atm) 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 $pCO_{2(air)i}$. 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: how to accurately represent surface turbulence and obtaining spatial and temporal heterogeneity of $pCO_2$ 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 asymptotes 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):

$$k_{660} = 3 + 0.1 \cdot U_{10} + 0.064 \cdot U_{10}^2 + 0.011 \cdot U_{10}^3 \tag{2}$$

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 meters above the water surface. Another challenge to accurately determining air-water $CO_2$ fluxes is obtaining reliable spatial and temporal $pCO_2$ distributions. Unfortunately, while seasonal distributions of $pCO_2$ were measured from the mouth of the bay to 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):

$$C_2 = (\frac{1}{n}\sum_{j=1}^{n} U_j^2)/U_{mean}^2 \tag{3}$$

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 buoys, $U_{mean}$ 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 six minutes) 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 $pCO_2$ values across the mid-bay, this region was split into an upper and mid-bay zone to allow for a more robust comparison of $pCO_2$ and $CO_2$ fluxes throughout the system (Fig. 1). Surface water $pCO_2$, temperature, salinity, wind speed, and pressure were interpolated onto 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:

$$S_i = \frac{\Delta Lon}{2\pi} \cdot 2 \cdot \pi \cdot R^2 \cdot [\sin (Lat_i + \frac{1}{2}\Delta Lat) - \sin (Lat_i - \frac{1}{2}\Delta Lat)] \tag{4}$$

where $S_i$ is the total area surrounding pixel i; $\Delta$Lon and $\Delta$Lat are the longitude and latitude intervals of the grid respectively, $Lat_i$ is the latitude at pixel i, and $R$ is the radius of the earth. The area-averaged $CO_2$ flux was calculated as followed (Jiang et al., 2008b):

$$F_{\text{area-averaged}} = \frac{1}{S_1 + S_2 + \dots S_n} \cdot \sum_{i=1}^{n} F_i \cdot S_i \qquad (5)$$

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 $pCO_2$ estimation

Temperature changes are important as they influence surface water $pCO_2$ 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, $pCO_2$ in surface seawater would double for every 16°C increase ($\partial \ln pCO_2/\partial T = 0.0423°C$) (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 $pCO_2$ 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 $(\partial \ln pCO_2/\partial T)/pCO_2$ 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 $pCO_2$ varied among different temperatures, from 5 to 30ºC, 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 $(\partial \ln p CO_2 / \partial T) / p CO_2$ for salinity intervals between 0-35 ranged from 0.0332 to 0.0420 ºC$^{-1}$ (Table 1). Similar to the results found in Jiang et al., (2008a), temperature derived constants were lower than the isochemical seawater constant 0.0423ºC$^{-1}$ 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 $p CO_2$ provide only a relatively simple analysis of seasonal $p CO_2$ fluctuations due to temperature and biological processes as it neglects the impact that various physical processes, turbulent forces, and tidal mixing scenarios have on $p CO_2$ dynamics.

Using a similar approach as in Takahashi et al., (2002), we also attempted to separate the temperature effect from other non-thermal effects on seasonal $p CO_2$ change. We first normalized the $p CO_2$ at in-situ temperature to the 10-year (2004-2014) annual mean temperature of 13.3ºC via the following (Takahashi et al., 2002):

$$(p CO_{2obs} \text{ at } T_{mean}) = (p CO_2)_{obs} \cdot \exp[C_s(T_{mean} - T_{obs})] \tag{6}$$

where $T$ is temperature (°C), $C_s$ is the averaged $(\partial \ln p CO_2 / \partial T) / p CO_2$ value for the salinity interval, and subscripts "mean" and "observed" indicate the annual mean and observed values, respectively. Through this approach, we attributed any differences between calculated and observed $p CO_2$ 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 and a different perspective to the various physical and biological controls behind observed $p CO_2$ distributions that geographic boundaries may not. In turn, $p CO_2$ values from each survey were constructed into salinity-binned climatologies (intervals of five units from 0-30) to better isolate and interpret the thermal versus non-thermal effects on seasonal $p CO_2$ fluctuations. Observed $p CO_2$ 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 $p CO_2$ values, annual mean $p CO_2$ values across each salinity interval were used in conjunction with the mean and observed temperatures via the following equation (Takahashi et al., 2002):

$$(p CO_{2mean} \text{ at } T_{obs}) = (p CO_2)_{mean} \cdot \exp[C_s(T_{obs} - T_{mean})] \tag{7}$$

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 13.3ºC, which was the 10-year annual mean water temperature measured in the Delaware Estuary from 2004 to 2014.

**2.4 Estuarine and river $CO_2$ contributions**

Due to various $CO_2$ 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 are typically supersaturated in $CO_2$ with respect to the atmosphere (Raymond et al., 2000; Abril and Borges, 2004; Borges et al., 2006). To investigate the influence of river-borne $CO_2$ input to overall air-water $CO_2$ fluxes, we used similar methods as 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 $CO_2$ concentrations. We first estimated the contribution of the ocean end-member to the estuarine DIC alone as follows (Jiang et al., 2008a):

$$\text{DIC}_{\text{mixing w/o}} = \frac{S_i}{S_{\text{ocean}}} \cdot \text{DIC}_{\text{ocean}} \tag{8}$$

where $\text{DIC}_{\text{mixing w/o}}$ is the DIC concentration after the ocean end-member is diluted by fresh water with zero DIC and $S_i$ and $S_{\text{ocean}}$ 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 follows (Jiang et al., 2008a):

$$\text{DIC}_{\text{mixing w/R}} = \frac{S_i}{S_{\text{ocean}}} \cdot \text{DIC}_{\text{ocean}} + (1 - \frac{S_i}{S_{\text{ocean}}}) \cdot \text{DIC}_{\text{river}} \tag{9}$$

where $\text{DIC}_{\text{mixing w/R}}$ is the DIC concentration after mixing of river and ocean end-members and $\text{DIC}_{\text{river}}$ 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). On the other hand, at higher salinities, any drawdown of DIC relative to salinity is small since less than 1% of the DIC pool exists as $pCO_2$ (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). $TA_{mixing\ w/o}$ and $TA_{mixing\ w/R}$ were also estimated using similar equations by replacing DIC with TA (Fig. 3B). Because $CO_2$ 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 $CO_2$ concentrations fluctuate with temperature change, the 10-year (2004-2014) annual mean temperature of 13.3 ℃ was used in this work. Thus, the $CO_2$ contribution due to river input ($\Delta[CO_2]_{riv}$) was estimated as follows:

$$[CO_2]_{riv} = [CO_2]_{mixing\ w/R} - [CO_2]_{mixing\ w/o} \tag{10}$$

Calculated river $CO_2$ inputs ($[CO_2]_{riv}$ ) and combined river discharges from the Schuylkill and Delaware Rivers for each month were used to compute river-borne $CO_2$ fluxes in the upper tidal river.

To further investigate the influence of $CO_2$ 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 $CO_2$ contribution from within the estuarine zone ($[CO_2]_{est}$) was estimated as follows:

$$[CO_2]_{est} = [CO_2]_i - [CO_2]_{mixing\ w/R} + (\tau_i \cdot F_i) \tag{11}$$

where ($[CO_2]_i$) is the in situ $CO_2$ concentration, $\tau_i$ is the flushing time, and $F_i$ is the air-water $CO_2$ flux. Specifically, ($[CO_2]_i$) was calculated using in situ DIC and TA concentrations and $\tau_i$ was estimated using river discharge rates and volume of each region (Table 3) (Sheldon and Alber, 2002). Surveys that did not contain sufficient river end-member DIC and TA measurements were excluded. Alternatively, Eq. (11) suggests that integrated $CO_2$ degassing ($\tau_i \cdot F_i$) is supported by the deficit or excess $CO_2$ concentration ($[CO_2]_{mixing\ w/R} - [CO_2]_i$) plus the internal estuarine $CO_2$ production or consumption ($[CO_2]_{est}$) 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 one standard deviation of the 30-year average. The surface water salinity distributions confirm the various river discharge conditions recorded throughout each survey (Fig. 5A-I). Salinity < 1.0 was reached on six of the nine cruises (Fig. 5A, 5B, 5C, 5E, 5G, and 5H). The July 2014, August 2013 and October 2013 cruises only transected as far north as the Chesapeake-Delaware Canal (about 39.55°N) (Fig. 1). Salinity < 1.0 (a minimum of 0.98) was only observed during the July 2014 excursion, which had the highest river discharge of the three partial surveys (Fig. 5C). Generally, high salinity waters (25-32.5) were observed in the lower bay and salinities around 20 to 25 in the mid-bay. The upper bay had a much broader scale ranging from salinities 10 to 20 and during the high flow months of March 2014 and June 2013 salinities < 10 were observed (Fig. 5A and 5B). Salinities did not reach less than 0.25 in the turbidity maximum zone. Salinity distributions in the urban river were limited due to the lack of surveys conducted in this region.

**3.2 Surface water $p$CO$_2$**

Generally, surface water $p$CO$_2$ in the Delaware Estuary increased from the ocean to the river end-member with $p$CO$_2$ values ranging from about 150 to over 4000 µatm (Fig. 6A-I). Moreover, $p$CO$_2$ exhibited strong seasonal variations across both river and bay portions. The most pronounced shifts in surface water $p$CO$_2$ were observed within the lower urban river and turbidity maximum river zones of the Delaware River with $p$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 CO$_2$ with respect to the atmosphere (atmospheric $p$CO$_2$: 375-398 µatm) except during March 2014 (Fig. 6A). Throughout the summer and early fall (June, July, and August), $p$CO$_2$ ranged from about 650 µatm to over 4000 µatm across the turbidity and lower urban river zones (Fig. 6B-E). In late fall (October and November), $p$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 $p$CO$_2$ values were not always observed as temperatures cooled. During the winter (December), surface water $p$CO$_2$ values increased across the turbidity maximum zone ranging from about 650 to 1000 µatm (Fig. 6I). As

discussed later, this shift in $pCO_2$ 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, mid-, and lower) was under-saturated 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 2014 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 reasons to support the elevated $pCO_2$ values remain unclear, stratification of subsurface waters in late fall followed by strong winter mixing during winter (December 2014) and a two-fold increase in river discharge could explain the elevated $pCO_2$ values observed throughout the mid- and the 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 was 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 two-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 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 supersaturated with respect to the atmosphere across the entire salinity range. Seasonally, the Delaware Estuary served as a strong $CO_2$ sink (-5.0 ± 6.0 mol-C m$^{-2}$ yr$^{-1}$) in the spring, a strong source (4.9 ± 8.1 mol-C m$^{-2}$ yr$^{-1}$) in the summer, a weak source (1.0 ± 2.4 mol-C m$^{-2}$ yr$^{-1}$) in the fall, and a strong source (5.7 ± 1.9 mol-C m$^{-2}$ 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 ± 6.4 mol-C m$^{-2}$ yr$^{-1}$) to overall regional flux (2.4 ± 4.8 mol-C m$^{-2}$ yr$^{-1}$) is minor. Thus, the Delaware Estuary as a whole acts as a relatively weak $CO_2$ source (2.4 ± 4.8 mol-C m$^{-2}$ yr$^{-1}$), which is in great contrast to many river estuaries that are strong $CO_2$ sources (26 ± 21 mol-C m$^{-2}$ yr$^{-1}$) (Borges and Abril, 2011).

**3.5 Seasonal variations in temperature normalized $pCO_2$**

Seasonal distributions of $pCO_{2obs}$ at 13.3 ℃, 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 ℃ was greatest during 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 ℃ reached its maximum in June. Coupled with decreasing flow, in the 0-5 salinity interval, $pCO_{2obs}$ at 13.3 ℃ decreased from June to an annual minimum in October. In the mid-salinity waters ($5 \leq S \leq 20$), $pCO_{2obs}$ at 13.3 ℃ 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 $pCO_2$ is 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 $CO_2$ include net ecosystem metabolism, DIC exchange between intertidal marshes, 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 $pCO_{2obs}$ (low in the winter and high in the summer, Fig. 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 $pCO_{2obs}$ at 13.3 °C in the spring and winter may reflect both river inputs and strong respiratory $CO_2$ production. Low $pCO_{2obs}$ at 13.3 °C during the warmer months likely reflect 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, $pCO_{2mean}$ at $T_{obs}$ (changes due to the seasonal thermal cycle) trends were opposite to that of $pCO_{2obs}$ at 13.3 °C with lower than $pCO_{2obs}$ values in the winter and higher than $pCO_{2obs}$ values in the summer. These opposing signals

suggest that increases in surface water $p$CO$_2$ due to winter-to-summer warming are partially compensated by the reduction of surface water $p$CO$_2$ 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 $p$CO$_2$ due to fall-to-winter cooling is partially compensated by the elevation of surface water $p$CO$_2$ 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 $\Delta p$CO$_{2\text{temp}}$ to $\Delta p$CO$_{2\text{bio}}$ ($T/B$). Using similar methods as performed in Takahashi et al., (2002), we calculate the thermal effects on surface water $p$CO$_2$ in each salinity interval as follows:

$$\Delta p\text{CO}_{2\text{thermal}} = (p\text{CO}_{2\text{mean}} \text{ at } T_{\text{obs}})_{\text{max}} - (p\text{CO}_{2\text{mean}} \text{ at } T_{\text{obs}})_{\text{min}} \tag{12}$$

where ($p$CO$_{2\text{mean}}$ at T$_{\text{obs}}$)$_{\text{max}}$ and ($p$CO$_{2\text{mean}}$ at T$_{\text{obs}}$)$_{\text{min}}$ are the maximum and minimum $p$CO$_{2\text{mean}}$ at T$_{\text{obs}}$ values, respectively. In other words, the thermal effects on the mean annual $p$CO$_2$ value is represented by the seasonal amplitude of ($p$CO$_{2\text{mean}}$ at $T_{\text{obs}}$) values computed using Eq. (7). Likewise, the non-thermal effects (biological and mixing processes) on surface water $p$CO$_2$ were calculated as follows (Takahashi et al., 2002):

$$\Delta p\text{CO}_{2\text{non-thermal}} = (p\text{CO}_{2\text{obs}} \text{ at } 13.3\,°\text{C})_{\text{max}} - (p\text{CO}_{2\text{obs}} \text{ at } 13.3\,°\text{C})_{\text{min}} \tag{13}$$

where ($p$CO$_{2\text{obs}}$ at 13.3 °C)$_{\text{max}}$ and ($p$CO$_{2\text{obs}}$ at 13.3 °C)$_{\text{min}}$ are the maximum and minimum $p$CO$_{2\text{obs}}$ at 13.3 °C values, respectively. Thus, the non-thermal thermal effects on surface water $p$CO$_2$ ($p$CO$_{2\text{obs}}$ at 13.3 °C) is represented by the seasonal amplitude of $p$CO$_2$ 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 $\Delta p$CO$_{2\text{thermal}}$ and $\Delta p$CO$_{2\text{non-thermal}}$ ($T - B$) or the ratio of $\Delta p$CO$_{2\text{thermal}}$ to $\Delta p$CO$_{2\text{non-thermal}}$ ($T/B$). In estuarine regions where thermal effects on surface water $p$CO$_2$ 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 $p$CO$_2$ 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 $\Delta p$CO$_{2\text{thermal}}$ and $\Delta p$CO$_{2\text{non-thermal}}$ decreased (Table 4). The decrease in $\Delta p$CO$_{2\text{thermal}}$ 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 ($15 \leq S \leq 25$) (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 $\Delta$DIC 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 contribution 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 fluxes in the urban river and turbidity maximum zone, respectively (Fig. 9). Presumably, the higher river-borne to 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 (Fig. 4B and 5A). This is consistent with the observed low $pCO_2$

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 were highest in the urban river (87.8 to 255.4 μmol $L^{-1}$) and smallest 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 $CO_2$ 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 $CO_2$ signals were negative in the mid- and lower bay zones and reached as much as eight folds greater than total river $CO_2$ inputs, ranging from -22.9 to -100.4 μmol $L^{-1}$ (Fig. 10). Thus, the majority of river $CO_2$ input was heavily compensated by the biological removal of $CO_2$ in the bay waters. In addition, during spring season (March) high $CO_2$ consumption was also observed in the upper bay with internal estuarine $CO_2$ signals (-30.7 μmol $L^{-1}$) exceeding total river $CO_2$ contribution (25.7 μmol $L^{-1}$) (Fig. 10). Depending on river discharge rates, the freshwater residence time in the Delaware Estuary ranges from about 40-90 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 $CO_2$ 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 $CO_2$ removal (Sharp, 1983).

**4.4 Assumptions and limitations**

While this study serves as the first air-water $CO_2$ 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 $p$CO$_2$ distributions in shallow waters 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 $pCO_2$ may vary from within the main channel to the perimeters of the estuary. Jiang et al., (2008a) found that surface water $pCO_2$ and air-water $CO_2$ flux in the marine-dominated Sapelo and Doboy sounds paralleled seasonal temperature changes and net $CO_2$ 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 $CO_2$ 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 $pCO_2$ and $CO_2$ flux dynamics may not be as influential in the Delaware Bay except near the shorelines where tides regularly flush marsh boundaries. Studies conducted by Culberson et al., (1987) and Lebo et al., (1990) performed several cross bay transects sampled at various depths, over diel cycles, within tributaries, and periodically offshore. Results showed that cross-bay gradients were inconsistent and relatively small, except in shallow waters near the shoreline when total suspended sediment and chlorophyll concentrations were frequently elevated (Culberson et al., 1987; Lebo et al., 1990; Sharp et al., 2009). Thus, the impact from marsh input of DIC to the Delaware Bay on overall $pCO_2$ distributions and associated $CO_2$ degassing fluxes are most likely small. During December 2014, $pCO_2$ measurements were not only collected in the main channel, but also near the Delaware and New Jersey perimeters of the bay (Fig. 6I). While slight variability was observed across the bay, $pCO_2$ values from the lower to upper bay regions remained within about 150 µatm (Fig. 6I and Table 2).

In addition to the lack of cross bay transects, there is a pressing need to conduct more winter and early spring surveys to fully cover seasonal ranges in key properties such as temperature and river discharge rates. Moreover, cruises or moored sensor studies at or around large discharge events are needed. Recent study by Voynova and Sharp (2012) found that in the past century there have been a recorded 54 extreme discharges (defined by the average daily discharge as recorded in Trenton, NJ from 1 Oct 1912 to 30 Sept 2011 plus 10 standard deviations); 46% of these occurring in the past decade (Voynova and Sharp, 2012). With increasing evidence suggesting that extreme

weather events will occur more frequently with climate change, it is important to maintain routine seasonal surveys to learn how such subsequent conditions (i.e. increased summer stratification, riverine $CO_2$ fluxes, removal of oxygen in bottom waters) impact various coastal environments (Allan and Soden, 2008; Yoana and Sharp, 2012). Furthermore, more research is needed in the urban and upper river sections of the estuary to better understand $CO_2$ dynamics throughout the whole estuarine gradient. The lack of inorganic carbon data in these upper regions limits syntheses of regional $CO_2$ fluxes and generalizations to underlying mechanisms. Routine sampling along small tributaries and river systems could provide crucial insight to the biogeochemistry in the upper tidal river.

There are also several limitations to the temperature-normalized and end-member mixing models that need to be addressed. First, knowing the extensively complex nature of estuarine systems, it is important to note that derived variances in temperature-normalized $p$CO$_2$ provide only a relatively simple analysis of seasonal $p$CO$_2$ 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 $p$CO$_2$ 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 to various physical and biological controlling mechanisms behind $p$CO$_2$ distributions that geographic boundaries may not. Unfortunately, due to the lack of winter surveys and unusually high $p$CO$_2$ values in December, interpolated temperature-normalized $p$CO$_2$ during cooler months may be biased and slightly overestimated. Moreover, the temperature derived constants ($\partial \ln p$CO$_2/\partial$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 two 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 $CO_2$ 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 $CO_2$ concentrations. In the chemical model of the CO2SYS, $NH_3$, $NH_4^+$, 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ than observed $CO_2$ 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 $CO_2$ flux estimates (Trabalka and Reichle, 2013) although due to the 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 $pCO_2$ throughout the Delaware Estuary, but these effects are partially compensated 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 sub-sections of the estuary (the urban river and turbidity maximum zone). 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 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 (~ 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. On the other hand, 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 on orders of magnitude more productive than smaller marine-dominated estuaries).

The continuation of research cruises on estuarine and coastal margins can provide crucial insight to the physical and biological changes in the past, present, and future ocean systems. Such extensive surveys, collection of carbonate parameters, and comparison of carbonate parameters over time, 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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Table 1. Averaged temperature coefficients [$(\partial \ln p\mathrm{CO}_2/\partial \mathrm{T})/p\mathrm{CO}_2$] for each salinity bin. Simulated surface water $p\mathrm{CO}_2$ values at varying salinities were computed using river and ocean end-member TA and DIC values of 900 and 960 µmol kg-1 and 2300 and 2000, respectively.

| Salinity | Coefficient |
|----------|-------------|
| 0 – 5    | 0.0332      |
| 5 – 10   | 0.0382      |
| 10 – 15  | 0.0411      |
| 15 – 20  | 0.0417      |
| 20 – 25  | 0.0417      |
| 25 – 30  | 0.0415      |
| 30 – 35  | 0.0420      |

Table 2. Area-averaged, standard deviation, and range of $pCO_2$ and $CO_2$ flux ($F_{CO2}$) in five of the six zones in the Delaware Estuary during each cruise.

| | | Mar 2014 | Jun 2013 | Jul 2014[*] | Aug 2013[*] | Aug 2014 | Oct 2013[*] | Oct 2014 | Nov 2013 | Dec 2014[*] | Annual Average |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Average $pCO_2$ (µatm)** | | | | | | | | | | | |
| Lower Bay | Mean ± SD | 230 ± 23 | 477 ± 11 | 473 ± 52 | 384 ± 42 | 315 ± 59 | 421 ± 6 | 405 ± 8 | 387 ± 3 | 596 ± 11 | 410 |
| | Range | 194 – 267 | 456 – 528 | 397 – 648 | 317 – 491 | 243 – 432 | 413 – 437 | 395 – 419 | 380 – 393 | 570 – 627 | |
| Mid-Bay | Mean ± SD | 198 ± 8 | 540 ± 66 | 559 ± 97 | 530 ± 36 | 250 ± 16 | 465 ± 22 | 422 ± 2 | 390 ± 8 | 590 ± 21 | 438 |
| | Range | 187 - 232 | 464 – 759 | 402 – 777 | 464 – 607 | 223 – 310 | 429 – 516 | 417 – 431 | 378 – 415 | 566 – 654 | |
| Upper Bay | Mean ± SD | 289 ± 47 | 919 ± 192 | 917 ± 97 | 680 ± 58 | 470 ± 98 | 566 ± 39 | 463 ± 19 | 434 ± 11 | 658 ± 26 | 599 |
| | Range | 225 - 401 | 645 – 1374 | 768 – 1149 | 594 – 846 | 312 – 697 | 508 – 651 | 428 - 483 | 411 – 461 | 597 – 744 | |
| Turbidity Maximum Zone | Mean ± SD | 595 ± 121 | 2087 ± 499 | 1473 ± 162 | 1237 ± 139 | 1102 ± 317 | 726 ± 34 | 575 ± 79 | 542 ± 61 | 786 ± 39 | 1014 |
| | Range | 397 - 854 | 1327 – 2981 | 1141 – 1680 | 837 – 1370 | 689 – 1866 | 645 – 754 | 481 – 737 | 457 – 709 | 711 – 1000 | |
| Urban River | Mean ± SD | 868 ± 48 | 3287 ± 163 | 2994 ± N/A | 2542 ± N/A | 2310 ± 589 | 1199 ± N/A | 816 ± 133 | 880 ± 179 | 878 ± N/A | 1753 |
| | Range | 762 – 945 | 3007 – 3600 | N/A | N/A | 1822 – 4000 | N/A | 640 – 1330 | 615 – 1450 | N/A | |
| **Average $F_{CO2}$ (mmol m$^{-2}$ d$^{-1}$)** | | | | | | | | | | | |
| Lower Bay | Mean ± SD | -15.4 ± 2.3 | 3.8 ± 0.5 | 4.4 ± 2.5 | 3.8 ± 1.9 | -3.0 ± 2.7 | 1.6 ± 0.4 | 0.8 ± 0.6 | -1.2 ± 0.3 | 13.5 ± 1.0 | 0.9 |
| | Range | -19.4 - (-12.0) | 2.8 – 6.2 | 0.5 – 13.1 | 0.8 – 8.5 | -6.4 – 2.5 | 1.1 – 2.6 | 0.1 – 1.8 | -1.9 – (-0.7) | 11.6 – 15.7 | |
| Mid-Bay | Mean ± SD | -20.0 ± 0.6 | 6.8 ± 3.2 | 11.1 ± 6.8 | 10.2 ± 1.6 | -6.7 ± 0.7 | 4.8 ± 1.8 | 2.0 ± 0.1 | -1.1 ± 0.7 | 13.5 ± 2.0 | 2.3 |
| | Range | -21.0 - (-17.8) | 3.2 – 17.4 | 0.8 – 27.8 | 7.3 – 13.6 | -8.0 – (-3.9) | 2.1 – 9.0 | 1.6 – 2.7 | -2.1 – 1.3 | 11.2 – 19.3 | |
| Upper Bay | Mean ± SD | -12.1 ± 4.9 | 25.3 ± 9.5 | 39.5 ± 7.3 | 16.8 ± 2.6 | 5.7 ± 6.0 | 13.0 ± 2.9 | 5.0 ± 1.4 | 3.4 ± 1.2 | 19.7 ± 2.0 | 12.9 |
| | Range | -18.4 – (-0.5) | 11.8 – 48.0 | 26.9 – 54.7 | 13.0 – 24.3 | -3.8 – 19.0 | 8.4 – 18.6 | 2.5 – 6.5 | 0.9 – 5.9 | 14.2 – 25.1 | |
| Turbidity Maximum Zone | Mean ± SD | 15.9 ± 9.6 | 83.9 ± 25.2 | 63.5 ± 2.9 | 42.2 ± 6.9 | 37.1 ± 13.9 | 21.1 ± 0.9 | 12.3 ± 5.1 | 10.1 ± 3.0 | 26.7 ± 1.9 | 34.8 |
| | Range | -0.9 – 36.9 | 45.6 – 129.1 | 54.3 – 65.5 | 23.9 – 47.6 | 18.6 – 71.9 | 18.3 – 21.7 | 6.3 – 23.6 | 5.6 – 19.7 | 23.3 – 44.8 | |
| Urban River | Mean ± SD | 38.3 ± 4.3 | 144.8 ± 8.1 | 131.0 ± N/A | 109.8 ± N/A | 98.9 ± 25.9 | 52.1 ± N/A | 30.2 ± 8.6 | 31.0 ± 8.1 | 32.1 ± N/A | 74.2 |
| | Range | 33.6 – 45.5 | 130.4 – 160.0 | N/A | N/A | 83.0 – 175.4 | N/A | 17.8 – 64.1 | 20.9 – 66.4 | N/A | |

[*]Months when surveys did not extend into Urban River. Area averaged was estimated by linearly regressing data from adjacent months with sample measurements. Standard deviation and range not available.

Table 3. Flushing time in five of the six zones in the Delaware Estuary during each cruise.

| | Mar 2014 | Jun 2013 | Jul 2014 | Aug 2013 | Aug 2014 | Oct 2013 | Oct 2014 | Nov 2013 | Dec 2014 | Annual Average |
|---|---|---|---|---|---|---|---|---|---|---|
| Flushing Time (day) | | | | | | | | | | |
| Lower Bay | 14.5 | 11.7 | 26.5 | 23.8 | 36.2 | 21.9 | 18.5 | 21.9 | 16.1 | 21.2 |
| Mid-Bay | 29.9 | 22.9 | 54.5 | 38.1 | 64.1 | 41.3 | 30.9 | 40.0 | 28.3 | 38.9 |
| Upper Bay | 15.1 | 13.3 | 26.6 | 23.9 | 32.8 | 25.5 | 27.6 | 27.2 | 16.6 | 23.2 |
| Turbidity Maximum Zone | 7.6 | 7.5 | 11.9 | 13.3 | 18.5 | 19.9 | 16.1 | 16.9 | 11.3 | 13.7 |
| Urban River | 2.5 | 2.3 | 3.7 | 6.1 | 6.9 | 6.5 | 6.5 | 6.5 | 5.9 | 5.2 |

Table 4. Calculated $\Delta pCO_{2thermal}$, $\Delta pCO_{2non\text{-}thermal}$, $T - B$, and $T/B$ values for each salinity interval in the Delaware Estuary.

|  | 0-5 | 5-10 | 10-15 | 15-20 | 20-25 | 25-30 |
|---|---|---|---|---|---|---|
| $\Delta pCO_{2thermal}$ (µatm) | 1005 | 800 | 635 | 514 | 417 | 431 |
| $\Delta pCO_{2non\text{-}thermal}$ (µatm) | 773 | 477 | 615 | 635 | 604 | 473 |
| $T - B$ (µatm) | 232 | 323 | 20 | -121 | -187 | -42 |
| $T/B$ | 1.30 | 1.68 | 1.03 | 0.80 | 0.69 | 0.91 |

Figure 1. Map of the Delaware Estuary divided into six zones from the head of the tide in Trenton, NJ to the mouth of the bay as defined in Sharp et al. (2009). The gray diamonds indicate the position of four NOAA buoys (LWSD1, CMAN4, SJSN4, and DELD1). The white star shows the location of the USGS gauging station (#01463500).

Figure 2. Simulated surface water $pCO_2$ against salinity grouped by temperature bins. Surface water $pCO_2$ values were calculated using river and ocean end-member TA and DIC values of 900 and 960 $\mu$mol kg$^{-1}$ and 2300 and 2000 $\mu$mol kg$^{-1}$, respectively.

Figure 3. Concentrations of (A) DIC, (B) TA, and (C) dissolved $CO_2$ in the Delaware Estuary during March 2014. Open circles represent in situ concentrations. Solid lines represent values after the ocean end-member is diluted by freshwater with a concentration of zero units. Dotted lines represent concentration after mixing of river and ocean end-members. CO2SYS was used to calculate $pCO_2$ from measured DIC and TA.

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/.

Figure 6. Spatial distributions of surface water $pCO_2$ in the Delaware Estuary measured during each sampling month. Black and red arrows show surface water $pCO_2$ values at the Chesapeake-Delaware Canal and the northern end member of each survey, respectively. The map was designed with the ODV software by R. Schlitzer (Ocean Data View software, 2015, http://odv.awi.de/.

Figure 7. Measured surface water $pCO_2$ against the salinity gradient during each sampling month in the Delaware Estuary.

Figure 8. Salinity-binned intervals of temperature-normalized observed $pCO_2$ values at 13.3 ºC, annual mean, area-averaged $pCO_2$ values at in situ temperature, and observed $pCO_2$ values in the Delaware Estuary over the year. Red arrows indicate increases in $pCO_2$ and blue arrows indicate decreases in $pCO_2$. The symbol T represents changes in $pCO_2$ due to thermal processes and the symbol B represents fluctuations in $pCO_2$ due to non-thermal processes. Error bars represent one standard deviation of the mean value for each month.

Figure 9: Air-water $CO_2$ fluxes against river-borne $CO_2$ fluxes in the urban river and turbidity maximum zone of the Delaware Estuary. Note the different axes used for the urban river and turbidity maximum zone.

Figure 10: Dissolved $CO_2$ concentrations (normalized to 13.3 ºC, area averaged) due to river inputs and internal estuarine sources in each region of the Delaware Estuary. Note the different axes used across all regions of the estuary. Error bars represent one standard deviation of the mean value for each month.