

Referee # 3

Major Comments

One newer idea presented in the paper is that the authors draw a distinction between the carbon cycle behavior of larger estuaries compared to the smaller ones that have received more attention in the literature, highlighting the role of different types of habitats (e.g. intertidal wetlands vs. open estuarine water column) in driving the overall carbon balance of the estuary system. This may benefit from a conceptual diagram if the authors want to argue this is a generalizable phenomenon they are describing – to show the relative influence of different biogeochemical processes and pathways.

Response: Good point. We have expanded on the comparison and discussion of NEP and DIC mass balances between various estuarine systems. We now compare our results to previous studies that investigated respiration and production rates throughout the Delaware Estuary. Further, we have expanded on the impact of discharge on seasonal variations in NEP and discuss how different physical features can affect overall DIC production within estuarine systems. The following revised/modified parts of discussion section 4.6 ‘DIC mass balance’ are shown below:

“While this study estimates overall NEP of the Delaware Estuary, other studies have explored NEP across the estuarine gradient (Sharp et al., 1982; Lipschultz et al., 1986; Hoch and Kirchman, 1993; Preen and Kirchman, 2004). Significant depletion of dissolved oxygen and supersaturation of pCO₂ levels in freshwaters (salinity < 10), suggests that the upper estuary is heterotrophic while the lower estuary is autotrophic (Sharp et al., 1982). More recent studies have found that respiration often exceeds primary production in the upper Delaware River (Hoch and Kirchman, 1993; Preen and Kirchman, 2004). Comparably, Culberson (1988) used inorganic carbon and dissolved oxygen measurements to estimate apparent carbon production and oxygen utilization throughout the Delaware Estuary. Similar to our spring NEP results, Culberson (1988) found that during the months of March to May from 1978 to 1985, most of the estuary (6 < S < 30) suffered a net inorganic carbon loss. Presumably, this loss occurred during the spring phytoplankton bloom, a period of intense inorganic carbon uptake by phytoplankton. While respiration rates often outweigh primary production in the upper tidal river, generally net community production increases down the estuary, transitioning to a near balanced to autotrophic system in the mid- to lower bay regions (Hoch and Kirchman, 1993; Preen and Kirchman, 2004).”

“Riverine input and estuarine export fluxes show considerable temporal variability and are largely governed by seasonal discharge patterns (Table 2 and 3). The highest fluxes occurred during spring when discharge was high while the lowest values occurred in the fall and winter when discharge was low. However, seasonal changes in NEP did not reflect variations in river discharge. Discharge values decreased throughout the year while NEP rates fluctuated across seasons. On the other hand, NEP trends largely mirrored seasonal variations in air-water CO₂ fluxes. When the estuary acted as a source of CO₂, negative NEP was observed. In comparison, when the system served as a CO₂ sink, NEP was positive. From the annual mass balance model, the small difference between riverine input and export flux suggests that the majority of DIC

produced within the estuary is exchanged with the atmosphere rather than exported to the ocean. It is important to note that such conclusions were estimated based on surveys conducted during different months from different years. More research and data is needed to accurately ascertain seasonal variations in estuarine fluxes and NEP.”

“Unlike in most previously studied estuaries, freshwater residence times in the Scheldt Estuary and Delaware Bay are generally long ranging from about one to a few months (Gay and O’Donnell, 2009; Borges and Abril, 2011). In contrast, the smaller stratified Randers Fjord has a much shorter residence time (few days) (Nielsen et al., 2001). In the smaller Randers Fjord, CO₂ emission to the atmosphere is lower than net community production (NCP) in the mixed layer or much less significant (Gazeau et al., 2005). This occurrence is partly due to the decoupling in ecosystem production caused by water stratification. As organic matter is produced in the surface waters, its degradation occurs in the bottom waters, and ultimately delaying CO₂ exchange with the atmosphere (Borges and Abril, 2011). Further, total DIC export to the Baltic Sea is higher than riverine DIC inputs to the Randers Fjord, suggesting that, due to the shorter freshwater residence times of systems, much of the DIC produced by net respiration is exported rather than removed to the atmosphere (Gazeau et al., 2005). Comparably, the Rhine exhibits extremely rapid freshwater residence time (~2 days) due to intense freshwater discharge (~2200 m³ s⁻¹): Such rapid turnover time, leads to reduced emission of methane (CH₄) to the atmosphere by bacterial oxidation and smaller internal DIC production due to net heterotrophy (Borges and Abril, 2011). However, lateral inputs from intertidal marsh systems in small estuaries can enhance accumulation and degradation of organic matter in surface waters, resulting in high CO₂ degassing fluxes (Dai and Wiegert, 1996; Cai and Wang, 1998; Neubauer and Anderson, 2003). Due to the broad geographic size of the Delaware Bay, the effect from the production and decomposition of marsh plants on CO₂ flux dynamics in the system may not be as influential as in smaller estuaries except near the coastlines where tides regularly flush marsh boundaries (Joeseof et al., 2015). In the macrotidal Scheldt Estuary, long freshwater residence time typically leads to DIC accumulation in the water column (Abril et al., 2000; Borges et al., 2006). In addition, in both the Delaware and Scheldt estuaries, small differences between riverine input and export flux suggests that the majority of DIC produced within the estuary is exchanged with the atmosphere rather than exported to the ocean. While similar NEP values may be observed, the enrichment of DIC in estuarine waters and resulting CO₂ exchange with the atmosphere will be more intense in estuarine systems with long residence times versus estuaries with short residence times (Borges and Abril, 2011). Thus, we suspect that in estuaries with long freshwater residence times (i.e. the Delaware Estuary), much of the DIC produced by NEP is most likely removed to the atmosphere rather than exported to the sea.”

While the title is clear and appropriate and the paper is generally well-structured, there are quite a few places where the language is not as clear as it could be. In particular, the abstract could use a fairly substantial rewrite in that the authors’ wording is often vague. For example, they say “Our data further suggest that DIC in the Schuylkill River can be substantially different from DIC in the Delaware River, and thus in any river system, tributary contributions must be considered when addressing DIC inputs to the estuary” – the second half of this sentence is so broad as to be essentially meaningless. I’m not sure they ever made a really compelling argument for why this might be important. I am sure there are several reasons why it could be important, but the authors should articulate their reasons for believing this to be important.

Response: We agree that certain points in the abstract are rather vague and need further clarification. Specifically here if the tributary contribution is not recognized, the high TA and DIC observed in this section of the estuary would be mistakenly attributed to an internal source (rather is from a tributary with high TA and DIC). Thus, we have revised and modified several sections of the abstract. We expand on why it is important to consider tributary contributions when addressing input fluxes, clarify the significance of changes in DIC to TA ratio, and elucidate on the importance of river input and export fluxes to the DIC mass balance model. The following sections of the abstract now read as:

“The ratio of DIC to TA, an understudied but important property, is high (1.11) during high discharge and low (0.94) during low discharge, reflecting additional DIC input in the form of carbon dioxide (CO₂), most likely from organic matter decomposition rather than from other bicarbonate (HCO₃⁻) inputs due to drainage basin weathering processes. Our data further suggest that TA and DIC in the Schuylkill River can be substantially different than TA and DIC values in the Delaware River. Thus, tributary contributions must be considered when attributing estuarine DIC sources to internal carbon cycle vs. external processes such as drainage basin mineralogy, weathering intensity, and discharge patterns. Long-term records of increasing alkalinity in the Delaware and Schuylkill river support global shifts toward higher alkalinity in estuarine waters over time. Annual DIC input flux to the estuary and export flux to the ocean are estimated to be $15.7 \pm 8.2 \times 10^9 \text{ mol C yr}^{-1}$ and $16.5 \pm 10.6 \times 10^9 \text{ mol C yr}^{-1}$, respectively, while net DIC production within the estuary including inputs from intertidal marshes is estimated to be $5.1 \times 10^9 \text{ mol C yr}^{-1}$. The small difference between riverine input and export flux suggest that, in the case of the Delaware Estuary and perhaps other large coastal systems with long freshwater residence times, the majority of the DIC produced by biological processes is exchanged with the atmosphere rather than exported to the sea. Based on a DIC mass balance model, we concluded that annually the Delaware Estuary is a weak heterotrophic system ($-1.3 \pm 3.8 \text{ mol C m}^{-2} \text{ yr}^{-1}$), which is in contrast to many highly heterotrophic smaller estuaries.”

One part of the interpretation of the data that was never really explained to my satisfaction was why DIC and TA wouldn't both be diluted under higher discharge and thus why the DIC:TA ratio would change with discharge. I suspect that there's a role of temperature in biotic production of CO₂ in soils that has a different slope than the temperature dependence of weathering, or something along these lines. The authors' could do a more complete job of illuminating readers on the various factors contributing to the seasonal changes of DIC vs. TA to create a fuller picture and narrative about why they observe a changing DIC:TA ratio through the seasons. The importance of temperature in driving these changes is critical if this work is to have any bearing on predictive studies under future climate change.

Response: We agree the temperature dependence is likely different in respiratory CO₂ production and in weathering production of DIC, but it will be hard to argue only from this point as such differences will also be enhanced or depressed during the wet and dry cycle. We believe our proposed simple mechanism --a hydrodynamic control--provides a more fundamental first order control. That is during the rainy season more stored CO₂ from organic matter respiration is flushed out of the drainage basin and less time is permitted for CO₂ degassing from creeks and rivers before entering the estuary. We first add an explanation in the Introduction about the

source of DIC (organic carbon respiration and weathering) and Alkalinity (weathering reactions only). Then we explain the hydrodynamic control more clearly in the Discussion.

We further agree that temperature and moisture may also play a role in seasonal changes in DIC vs. TA, particularly regarding the role of temperature and moisture on biotic production of CO₂ in soils. We have added a few sentences discussing the impact that temperature and moisture may have on DIC:TA ratios as shown below. With a shift towards increasing temperatures and frequency of episodic weathering events, it is critical that we continue to explore such issues to help understand the impact of future climate changes.

“If only influenced by the weathering of carbonate and silicate minerals, the ratio of DIC to TA remains close to unity (Cai et al., 2004). On the other hand, CO₂ production from soil organic matter respiration and imbalances between production and respiration along the aquatic continuum can increase DIC to TA ratios (Mayorga et al., 2005). Presumably, during the wet season and high discharge periods, more CO₂ from soil organic matter respiration stored in the drainage basin is brought along the river system while less CO₂ is lost to the atmosphere due to a faster transport. Additionally, extensive research has shown positive correlations between temperature and soil respiration (Singh and Gupta, 1977; Reich and Schlesinger, 1992). While more research is needed, we suggest that changes in the DIC to TA ratio at the freshwater end-member may reflect inputs of soil organic matter respiration due to seasonal variations in discharge, temperature, and moisture content. As the ratio of DIC to TA determines aquatic pH and the buffer capacity (Eggleston et al., 2010), our observations indicate that variation of this ratio should be considered in future global carbon cycle models, in particular regarding how wet and drought cycles in future climate scenarios would affect coastal water acidification and how coastal waters will respond to a changing terrestrial carbon export (Reginer et al., 2013; Bauer et al., 2013).”

The discussion of the lithology in the watersheds of each of the study rivers was a bit more detailed than needed, so some of this could be placed into supplemental material, or the text could just be shortened, with the same references. I don't think the detail adds anything to the understanding that one part of the watershed and its tributary contain more carbonate rocks than other parts. Again, why does this matter? (I'm not saying it doesn't, but tell us why you find it important.)

Response: Agreed. This section is perhaps too detailed and could be significantly shortened. We have substantially revised section 4.2 'Influence of tributary mixing', shortening in certain areas, and expanding on the importance that drainage basin mineralogy has on the carbonate chemistry of regional watersheds. The section now reads as follows:

“River TA collected at the Schuylkill River was much higher than TA in the Delaware River near the Philadelphia region (Fig. 5). A compilation of historical data collected at two USGS stations in Philadelphia from 1940 to the present show that not only was alkalinity in the Schuylkill River negatively correlated with river discharge, but that during periods of low river discharge markedly high alkalinity was observed (Fig. 7A). Further, historical records agreed remarkably well with our alkalinity measurements. Over the past two decades, after low river discharge (<

$100 \text{ m}^3 \text{ s}^{-1}$) alkalinity reached from 1300 to 2500 $\mu\text{mol kg}^{-1}$, nearly two-fold greater than alkalinity values observed at the Trenton end-member (Fig. 7B).

The mineralogy of the Schuylkill River drainage basin may have a significant impact on TA patterns throughout the Delaware estuarine system. Geographically, the lower Schuylkill drainage basin extends through the Piedmont province, underlain by a mixture of limestone, shale, gneiss, schist, and dolomite, before discharging into the Coastal Plain province and the Delaware River (Stamer et al., 1985). Within this region, the Schuylkill River flows through the Valley Creek basin in which 68% of the region is comprised of carbonate rocks (Sloto, 1990). The center of the basin, otherwise known as Chester Valley, is primarily underlain by easily eroded limestone and dolomite bedrock with regional flow discharging into the Schuylkill River. Thus, it is likely that high riverine TA in the Schuylkill River is due to the weathering of carbonate rocks in the lower Schuylkill drainage basin. We suggest that elevated DIC and TA values exhibited in the Delaware River near Philadelphia are the result of the mixing of relatively high carbonate freshwater from the Schuylkill River, specifically due to the chemical weathering of limestone and dolomite bedrock across the lower Piedmont province. In turn, tributary contributions must be considered when addressing total riverine DIC and TA fluxes as differences in drainage basin mineralogy can have a substantial impact on the carbonate chemistry throughout regional watersheds. Influences from human activities such as wastewater discharge, agriculture, and acid mine drainage may also contribute to the high TA, an issue that deserves further study (Raymond and Cole, 2003; Raymond et al., 2008)."

Minor Comments

The language is fluent and mostly clear, save in a few places where the language becomes vague/imprecise. It may seem redundant to the writer, but there are numerous places where a few more words added would make the difference between vagueness and clarity.

P1, L7: "widely understudied" seems like a bit of a non sequitur/oxymoron.

Changed to 'understudied'.

P1, L26: You might want to say "flux to the coastal ocean" instead of just "flux to the ocean" as in coastal carbon cycle circles, we also discuss export from coastal oceans to the open ocean.

Good point. We have changed to 'flux to the coastal ocean'.

P2, L2: "majority of the DIC produced" – in the estuary, I presume? Clarify.

Changed to 'majority of the DIC produced in the estuary'.

P2, L10: land-to-ocean continuum?

Correct.

P2, L 25: "The supply of inorganic carbon by rivers: : :'" – to the coastal ocean?

Yes, we have changed to ‘The supply of inorganic carbon by rivers to the coastal ocean’.

P2, L 23-24: I thought it was just for carbonate minerals that the CO₂ is eventually released back to the atmosphere via oceanic carbonate sedimentation, stoichiometrically speaking. Please verify that this statement is correct.

Yes, the reviewer is correct. During CaCO₃ weathering, CO₂ is removed from the atmosphere while at sea this process is reversed during CaCO₃ precipitation. However, for silicate weathering CO₂ is removed from the atmosphere but this process cannot be reversed as diatoms precipitate opal minerals (no C in it). Only after a much slower process later (reverse weathering that converts CaCO₃ and opal minerals to silicate minerals) is the cycle completed. However, as that is beyond our research here, we do not mention it but only cite the Lerman paper. We have modified the sentence as follows:

“The weathering of carbonate and silicate minerals consumes atmospheric CO₂ and transports HCO₃⁻ ions and subsequent cation and anion products into oceanic systems. Eventually, CO₂ is released back into the atmosphere via oceanic carbonate sedimentation and volcanic activity (Lerman et al., 2004; Regnier et al., 2013).”

In several places, the authors use the word “impact” when “affect” would be more appropriate. “Impact” is often used to convey negative connotations.

Good point. We have changed accordingly.

P3, L3: “by weathering and decomposition”

Changed.

P3, L12: “more large bay systems” would be clearer

Agreed. We have changed to ‘an urgent need to expand global research to more large bay systems’.

P4, L 18: replace “ongoing” with “underway”

Replaced with ‘underway’.

P4, L27-28: does this method of filtering samples affect the DIC values? I presume the references given address this, but if not, it would be good for these authors to address whether filtering samples introduces any artifacts or bias. Filtering DIC samples is not typical (e.g., per the Dickson et al. 2007 SOPs for the CO₂ system), but can be done without introducing bias with adequate care (e.g. Bockmon and Dickson 2015? L&O).

Correct. We did not filter samples unless they were collected in the upper tidal river portion of the estuary which was heavily turbid. We have revised the sampling description.

P5, L4: Are you sure it's precision that is +/- 2 umol/kg? Vs. some overall uncertainty or average offset from CRMs?

Good point. It is the overall uncertainty of our measurements with respect to the CRMs. We have changed to, "All measurements were calibrated against certified reference material (provided by A.G. Dickson from Scripps Institution of Oceanography) with an uncertainty of $\pm 2 \mu\text{mol kg}^{-1}$ (Huang et al., 2012)."

P5, L 5-7: Need to state pH scale is NBS.

Agreed. Added pH scale in NBS.

P6, L 10: "northernmost"

Changed.

P6, L21-22: might be good to clarify that this is from the rivers where measurements were taken (vs. the scaled up estimate presented later on).

Good point. We now clarify and add the Delaware, Schuylkill, and Christina rivers to this description.

P6, L27-28: re-cite figure here? Here and just below, it seems like there are a few steps left out of your description of how you did the calculations.

We have re-cited the figure and have expanded on the description of our calculations as follows:

"The effective river end-member concentrations of DIC and TA were calculated by extrapolating the DIC and TA conservative mixing lines from the high salinity waters to zero salinity (Fig. 3) (Cai et al., 2004; Guo et al., 2008). The difference between the effective and actual concentrations at the river end-member indicates the amount of DIC and TA added or removed during mixing and therefore not transported to the ocean (Boyle et al., 1974; Cai and Wang, 1998; Liu et al., 2014). Using the effective concentrations and the combined river discharge for the Delaware, Schuylkill, and Christina rivers recorded in each cruise period plus the average discharges measured during the month prior to each survey, we estimate net DIC and TA export fluxes for each cruise (Table 3)."

P7, L5: Not enough info given about what this data set is and how the data compare to yours. Put in methods or otherwise describe.

Agreed. We now elaborate on the specific USGS alkalinity parameter codes used and compiled this information into a new table (Table 4). We also expand on the importance of historical USGS water quality data as shown below.

“The extensive and routine collection of water samples conducted by USGS allows us to explore long term trends (from the mid-20th to early 21st century) in alkalinity and discharge in the Delaware and Schuylkill rivers (USGS stations 01463500 and 01474500, respectively). For USGS alkalinity values, we use similar approaches as conducted in Stets et al., 2014. We combine 8 various parameter codes that include alkalinity, acid neutralizing capacity (ANC), or HCO₃⁻ (Table 4). Alkalinity and ANC follow identical electrometric procedures except that alkalinity samples are filtered while ANC samples are not.”

Table 4. USGS parameter codes used during analysis

| Parameter Code | Parameter Description | Total Count | Percentage of Total Count |
|----------------|---|-------------|---------------------------|
| 00410 | Acid neutralizing capacity, water, unfiltered, fixed endpoint titration, field | 920 | 28.5 |
| 00419 | Acid neutralizing capacity, water, unfiltered, inflection-point titration, field | 25 | 0.8 |
| 00440 | Bicarbonate, water, unfiltered, fixed endpoint titration, field | 1529 | 47.4 |
| 00450 | Bicarbonate, water, unfiltered, inflection-point titration, field | 25 | 0.8 |
| 00453 | Bicarbonate, water, filtered, inflection-point titration, field | 86 | 2.7 |
| 29801 | Alkalinity, water, filtered, fixed endpoint titration, laboratory | 133 | 4.1 |
| 39086 | Alkalinity, water, filtered, inflection-point titration, field | 283 | 8.8 |
| 90410 | Acid neutralizing capacity, water, unfiltered, fixed endpoint titration, laboratory | 224 | 6.9 |

P7, L7: This seasonality doesn’t agree with what you described above (summer+fall vs. spring+summer, etc.).

Good catch. We have corrected it to ‘TA was highest during low flow season (fall) and lowest during high flow season (spring)’.

P7, L16: “strong” correlations, not “high” (or “highly correlated”)

Changed to ‘strong’.

P7, L20: “dilution of weathering products” (vs. production)

Agreed. We have changed to ‘products’.

P8, L3: could be faster transport or lower surface area to volume ratio (i.e. deeper)

Good point. We have added this detail.

“Presumably, during the wet season and high discharge periods, more CO₂ from soil organic matter respiration stored in the drainage basin is brought along the river system while less CO₂ is lost to the atmosphere due to a faster transport and lower surface area to volume ratio (i.e. deeper water depths).”

P9, L1: I am not sure what you mean by “physiographic”

We have significantly modified and shortened this section as requested in your earlier comments and by others. This sentence has been removed and is no longer in the discussion.

P9, L7: not totally clear what “the historical record” refers to - all USGS data? Just a subset?

Yes, we agree that before this was unclear throughout the manuscript. We have added more detail to the exact USGS data used for our analysis and it is now described at the beginning of section 4.1 ‘Influence of river discharge and weathering intensity’ and in the addition of Table 4 as described in the above responses.

P9, L8: closer to 3 decades, at 26 years – maybe “over recent decades” is better?

Agreed. We have changed to ‘over recent decades’.

P9, L9-11: to facilitate reading the paper, it may be best to stick to river names rather than mixing in city names for those readers outside your region.

Yes, we now refer to the river names instead of city names.

P9, L 16-18: After too much detail on watershed lithology at the start of this section, a bunch of things are summarily mentioned without discussing how these processes might contribute to TA change sufficiently (e.g. would these processes individually increase or decrease TA, and how?).

We have significantly modified and shortened this section as requested in your earlier comments and by others. Please refer to the revised 4.2 section as described in our previous responses.

P9, 26-31: See previous – superficial treatment of these factors (also “can also have huge effects” on following page). Be more specific about the relative roles each of these factors would play if they are important.

Yes, we have expanded greatly on section 4.3 ‘Historical trends in riverine alkalinity’. Further, we now refer to several more comprehensive studies that have explored long term alkalinity records across various streams and watersheds throughout the U.S. (Kaushal et al., 2013; Stets et al., 2014). We also expand on how various factors effect long term alkalinity patterns as described below:

“A more comprehensive study conducted by Kaushal et al., 2013 examined long-term trends in river alkalinity at 97 different stream and river locations throughout the eastern U.S. They observed increasing alkalinity trends at 62 of the 97 river locations (64%). Moreover, of the remaining sites, none showed any statistically decreasing alkalinity trends. Various contributing factors can influence long-term trends in river alkalinity such as carbonate lithology, acid deposition, and topography in watersheds. Kaushal et al., 2013 suggests that increased acid deposition elevates riverine alkalinity by promoting weathering processes, particularly in watersheds with high carbonate lithology. Further, watershed elevation may be a good predictor for alkalization rates. Acid deposition may be greater at higher elevations, and such areas tend to have thinner soils and a weaker buffering capacity, increasing susceptibility to the effects of acid deposition. Recent studies show that human induced land-use changes such as deforestation, agricultural practices (Oh and Raymond, 2006), and mining activities (Brake et al., 2001; Raymond and Oh, 2009) have direct impacts on the buffering capacity of streams and rivers. Through chemical weathering processes, enhanced precipitation and local runoff can also have huge effects on increased alkalinity in coastal ecosystems (Raymond et al., 2008). For example, over the past century, total alkalinity export from the Mississippi River to the Gulf of Mexico has risen by nearly 50% due to widespread cropland expansion and increased precipitation in the watershed (Raymond and Cole, 2003; Raymond et al., 2008). Comparably, Stets et al., 2014 explored historical time series of alkalinity values in 23 different riverine systems throughout the U.S. They found increasing alkalinity trends at 14 of these locations with the majority occurring in the Northeastern, Midwestern, and Great Plains areas of the U.S. While most sites observed increasing alkalinity values with time, decreasing trends were found in the Santa Ana, Upper Colorado, and Brazos rivers. Factors contributing to decreasing trends at these locations include dilution by water from external sources outside the basin and retention of weathering products in storage reservoirs.”

P10, L18-20: this is very qualitative. Can you be more quantitative about this?

We have added the following quantitative details:

“In March and August 2014, $p\text{CO}_2$ was low (160 – 350 μatm) and CO_2 take was greatest (-21 – 2.5 $\text{mmol m}^{-2} \text{d}^{-1}$) throughout the mid- and lower bay regions, indicating biological CO_2 removal (Joesoef et al., 2015).”

P11, L12-17: This sentence seems circular to me – how are you defining the difference between input and inflow? If you mean to consider groundwater inputs too, you need to be more concrete and specific with your wording. (Also, there was the roughly 10% from wastewater treatment plants [WWTPs] from up top not mentioned here. Intentional?)

Yes, we meant to define as 70% of the freshwater ‘input’, not ‘inflow’ and have changed this. Although minor, we have added inputs from WWTPs to the remaining 30% percentage (from small rivers and nonpoint source runoff). We also acknowledge that bicarbonate concentrations from these remaining sources may not be the same as the three main Delaware river systems. However, since additional research and data is needed to accurately determine their contribution, we assume that the remaining 30% yield similar concentrations. We now acknowledge this uncertainty as follows:

It is important to note that these final flux values are strictly a rough estimate. We acknowledge that average riverine DIC and TA concentrations from remaining small rivers and nonpoint source runoff are not necessarily equivalent to the weighted DIC and TA averages for the Delaware, Schuylkill, and Christina rivers. As such uncertainties are most often neglected, it is imperative to consider their effect on final flux estimates. However, since additional research and data collection is needed, here we assume that the mineralogy and drainage basins of the remaining 30% yield similar carbonate concentrations as Delaware's three major river systems.

P11, L26: Do you mean water column/internal estuarine CO₂ production (per top of next page, I think you do)? Calling it “production” without further clarification of what is being produced gets confusing when primary/community production may also be involved.

Agreed. We have changed this to ‘internal estuarine CO₂ production’.

P12, L5: near the top, you had a figure for 30 m³/s from WWTPs – this seemed like not a trivial part of the total input.

We agree that inputs from WWTPs is important and can influence river carbonate concentrations and overall metabolic processes, especially in the upper tidal river. However, much more research is needed near waste water discharge locations and treatment plants to evaluate their impact on the Delaware river system. In turn, for simplicity we ignore WWTP contributions in our DIC mass balance model.

P12, L27: “intertidal” instead of “internal,” yes?

Correct. We have changed to ‘intertidal’.

P13, L9: “Here” – where are you referring to?

We have changed to ‘In these small river systems with rapid residence times’ to clarify what we are referring to.

P14, L1: “compared to total DIC input flux” – suggest adding “from rivers”

Agreed. The phrase now reads as ‘compared to total DIC input flux from rivers’.

P26: Seems to ignore interannual variability to list cruises by month w/o noting they occurred in different years. Do you have enough data on interannual variability to justify that this makes more sense than an alternative? (I don't feel strongly that this shouldn't be done but am curious about the choice to do it this way – would be nice to have some explanation – but doesn't need to be extensive).

This is an interesting thought and we have now pointed this issue out in section 4.6 to inform the audience. We have added the following sentences to clarify this issue:

“Discharge values decreased throughout the year while NEP rates fluctuated across seasons. On the other hand, NEP trends largely mirrored seasonal variations in air-water CO₂ fluxes. When the estuary acted as a source of CO₂, negative NEP was observed. In comparison, when the system served as a CO₂ sink, NEP was positive. From the annual mass balance model, the small difference between riverine input and export flux suggests that the majority of DIC produced within the estuary is exchanged with the atmosphere rather than exported to the ocean. It is important to note that such conclusions were estimated based on surveys conducted during different months from different years. More research and data is needed to accurately ascertain seasonal variations in estuarine fluxes and NEP.”