Referee # 2

Major Comments

I found the introduction particularly unbalanced. Specifically, I think that the first paragraph of the introduction (p. 2, l. 7-24) can be shortened, whereas the second and third sections may be extended. As the main research area is an estuary, I'd expect discussions of carbon cycling on both the freshwater and marine sides, whereas here, only the freshwater side is discussed. I also miss a description of how waters from both sides interact and mix in the estuary, i.e. a section on (seasonality in) C cycling in estuaries.

Response: Good point. We have shorten the first paragraph of the introduction and added more discussion on carbon cycling in estuaries, specifically on the marine sides. Please see below.

"As carbon is transported horizontally along the land and ocean continuum, various environmental processes impact the total carbon fluxes between reservoirs. Recent studies suggest that on average 10% of CO_2 *emitted in estuaries is sustained by freshwater inputs while 90% of the* CO_2 *released is from local net heterotrophy, with the majority of organic carbon inputs stemming from adjacent salt marsh and mangrove ecosystems (Regnier et al., 2013). These systems are supported by inputs from various autochtonous and allochtonous organic carbon sources,* CO_2 *enriched pore waters during ebbing, and high concentrations of dissolved inorganic carbon from inter-tidal and sub-tidal benthic communities (Cai et al., 2003; Neubauer and Anderson, 2003; Wang and Cai, 2004; Ferrón et al., 2007; Chen and Borges, 2009). Terrestrial OC that is transported by large and fast-transit river systems generally bypasses decomposition in estuaries and contributes to respiration along coastal ocean margins (Cai, 2011). Consequently, rapid increases in atmospheric* CO_2 *concentrations reduce the amount of* CO_2 *released along ocean margin systems, especially in low latitude zones where a majority of the terrestrial OC is delivered (Cai, 2011)."*

The authors do not clearly explain in the manuscript why increases in both DIC and TA indicate inputs of HCO_3^-, whereas an increase in DIC only must mean an input of CO_2. This may not be common knowledge to everyone and should be mentioned in the introduction.

Response: We agree that this is unclear and may not be common knowledge. In turn, we should define and expand on these terms in the introduction. We have added the following text to paragraph two of the introduction.

"Total alkalinity (TA) is defined as $TAlk = [HCO_3^-] + 2[CO_3^{2-}]$ *plus all other weak bases that can accept* H^+ *when titrated to the carbonic acid endpoint. Comparably, dissolved inorganic carbon (DIC) is expressed as the sum of all inorganic carbon species (*$[CO_2]$, $[HCO_3^-]$, $[CO_3^{2-}]$*). In terrestrial aquatic systems, there are three sources of dissolved inorganic carbon. The most important sources are the carbonate and silicate weathering processes as described below:*

$CaCO3 + CO2 \rightarrow 2HCO3- + Ca2+$
$CaSiO3 + 2CO2 + 3H2O \rightarrow 2HCO3- + Ca2+ + H4SiO4$

In both cases, the amounts of DIC and TA production are equal. Here, CO_2 may come from soil organic matter respiration but ultimately it is linked to the atmospheric CO_2. Respiration of soil and aquatic organic carbon is another source of CO_2, but it does not contribute to TA. Since alkalinity of natural waters is mainly comprised of $[HCO_3^-]$ and $[CO_3^{2-}]$ ions and all other species are generally insignificant, DIC to TA ratios can provide broad insight into the sources of carbon, aquatic pH dynamics and regional carbonate buffering capacity."

p.6, l.29 - p.7, l.1: I miss some methodological details here. In case surveys were longer than 1 day, was the average discharge for the whole cruise period taken? (this also applies to l.18-20). Plus, I understand that on an annual scale it is valid to assume that discharge at the seawater endmember is the same as riverine discharge, but is this valid at the time scale of separate surveys (as presented in Table 3) as well? There is another point in the manuscript where these different temporal scales come into play and that is in the context of calculating NEP in section 4.5. If I'm not mistaken, here annual averages for the import and export fluxes are used, whereas it is convincingly shown for at least the import fluxes that there is considerable temporal variability. If the authors did take this into account in their calculations for Fig.9, they should write this more clearly. If they didn't take this into account, I have my doubts about the calculated NEP values.

Response: Yes, we used the average discharge for the whole cruise period to estimate input fluxes during this time. We have added this detail to our flux calculation descriptions. You bring up an interesting point in our export flux calculations about how it is valid to assume that seawater endmember discharge is equivalent to riverine discharge on an annual time scale, but it may not be for the time scales of separate surveys. We did take this into account and used average discharge for the entire cruise period plus discharges recorded 10 days prior to the survey. We agree that this approach must have substantial uncertainty but feel it is probably a good first order approximation given largely linear distribution of DIC at high salinity.

Section 4.1: Please discuss the reliability and quality of the long-term monitoring data. Such data are often known to display unrealistic trends due to e.g. methodological changes. Also, I do not believe that Fig. 6b displays a real trend as the y-axis variable highly depends on the x-axis variable (as is also shown in Fig. 6d).

Response: Agreed. Often, the methodology of scientific methods change over time, especially with advancements in technology. We have added some discussion investigating these changes to section '4.3 Historical trends in river alkalinity'. Please see our response to Referee #1.

Section 4.2, p.9, l-10-13: Don't the authors have enough data available to make a simple linear mixing model at the point where the Schuylkill and Delaware rivers meet near Philadelphia, to actually test and quantify the hypothesis postulated here?

Response: Agreed. In fact, we did use a simple three end-member mixing model to estimate the composite river DIC and TA concentrations at the confluence of the Delaware and Schuylkill river (C_m^*), and then using this value determined the composite concentrations at the confluence of the Delaware and Christina rivers (C_{m2}^*) as well. We multiplied (C_{m2}^*) by total river discharge

(Q_T) to compute riverine input fluxes. We agree that these steps were missing in the manuscript and should be added to avoid any confusion as shown below:

"Water mixing from multiple tributaries can complicate two end-member mixing models (Officer, 1979; Cai et al., 2004). In this case, from Trenton, NJ to the mouth of the Delaware Bay, two external sources of water, the Schuylkill and Christina River, discharge into the Delaware River. Thus, additional input from these tributaries contribute to effective end-member concentrations. Past studies have shown that a composite river end-member can be estimated for a set of tributaries given their respective discharge rates (Cai et al., 2004; Guo et al., 2008). In turn, a simple three end-member mixing model can be generated where C_1, C_2, and C_s represent the end-member concentrations at the Delaware River, the Schuylkill River, and the ocean side, respectively. Assuming that only mixing occurs between the two river end-members, we can estimate a new effective concentration (C_m^*) as follows:

$$C_m^* = \frac{C_1 x\, Q_1 + C_2 x\, Q_2}{Q_1 + Q_2}, \tag{1}$$

where Q_1 and Q_2 represent discharge rates for rivers 1 and 2, respectively. The linear mixing line for $C_{1\text{-}s}$ is estimated as follows:

$$C_{1\text{-}s} = C_1 + \frac{C_s - C_1}{S_s} S, \tag{2}$$

Linear mixing equations for $C_{2\text{-}s}$ are similar. Likewise, C_m is a linear combination of $C_{1\text{-}s}$ and $C_{2\text{-}s}$ and is estimated as follows:

$$C_m = C_m^* + \frac{C_s - C_m^*}{S_s} S, \tag{3}$$

Through this simple three end-member mixing model, we estimate a composite river end-member at the confluence of the Delaware and Schuylkill River (approximately 150km from the mouth of the Delaware Bay). The chemical fluxes for each tributary can be calculated as follows:

$$F_i = C_i \; x \; Q_i, \tag{4}$$

Thus, the total flux at the confluence of the Schuylkill and Delaware River is estimated as:

$$F^T = C_m^* \; x \; Q^T = F_1 + F_2, \tag{5}$$

With C_m^* as a new upstream end-member value, we can further estimate the composite river end-member (C_{m2}^*) at the confluence of the Delaware and Christina River (approximately 110km from the mouth of the bay) using end-member concentrations and discharge rates for the Christina River and the previous equations above. To compute the total river input flux, we add estimated flux from the Christina River (C_3 x Q_3) to the results obtained from Eq. 5 as shown below:

$$F^T = C_m^* \; x \; Q^T + (C_3 \; x \; Q_3) = F_1 + F_2 + F_3, \tag{6}$$

or $F^T = C_{m2}^* \times Q^T$ *where* C_{m2}^* *is calculated from Eq. 1 with* C_m^* *and* C_3 *being the two river end-members,* Q_1 *being the sum of the Delaware and Schuylkill River discharge, and* Q_2 *being the discharge rate for the Christina River."*

Section 4.3: The authors discuss long-term trends in alkalinity, but as riverine TA export is the product of concentration and discharge, it would be interesting to discuss long term trends in discharge patterns as well. With the high-resolution data available, the authors can focus not only on long-term trends in discharge, but also on changes in the numbers and intensity of episodic events. Also, the authors disregard the fact that these historical riverine TA data have been previously published and discussed (Kaushal et al., 2013). They should at least refer to this work, and I feel that this manuscript can benefit from the (quantitative) way that work explored possible drivers for the long-term trends. In what has been discussed by the authors, I miss a discussion of the role of increased temperature, which can enhance weathering but has not been shown to the primary driver of weathering in the Baltic Sea catchment (Sun et al., 2017).

Response:

1) Agreed. With such high-resolution data, it would be informative to examine long-term trends in discharge in addition to long-term trends in river alkalinity. We have added additional figures plotting daily mean discharge recorded in the Delaware and Schuylkill rivers from 1940 to 2015. We further highlight the intensity of episodic discharge events at these locations (defined by the average daily discharge plus 10 standard deviations). We also added the following section '4.4 Long-term trends in river discharge' to the discussion portion of the paper as shown below.

"To investigate long-term trends in discharge for the Delaware and Schuylkill rivers, we plot daily discharge from 1940 – 2015 at Trenton, NJ and Philadelphia, PA. Further, we follow similar methods as discussed in Voynova and Sharp (2012) to examine the intensity of episodic discharge events (defined by the average daily discharge plus 10 standard deviations) with time (Fig. 8). Unlike historical trends in river alkalinity, there has been minimal to no increase in mean discharge over time in the Delaware and Schuylkill rivers suggesting that increased alkalinity flux is due to increased alkalinity concentrations and weathering rates. While there was no long-term increase in mean river discharge, the frequency of episodic events with time has significantly increased. Over the past 70 years, 29 extreme discharges have been recorded in the Schuylkill River (from 1 Jan 1940 to 31 Dec 2015) with 48% of these occurring in the past two decades. Similarly, recent study by Voynova and Sharp (2012) showed that in the past century 54 extreme discharges have been recorded in the Delaware River (from 1 Oct 1912 to 30 Sept 2011). Of the 54 extreme discharges, 46% of these occurred during the past decade. Bauer et al., 2013 suggest that episodic discharge events (large flooding/heavy rains) can carry a disproportionately large part of the annul flux of organic carbon from a certain drainage basin. Our work suggests that this mechanism may also apply to riverine TA flux. Thus, with recent evidence indicating a shift towards more frequent episodic weather events, it is important to consider how such anomalies impact biogeochemical patterns among coastal systems (i.e. prolonged summer stratification, freshwater residence times, riverine bicarbonate concentrations, estuarine CO_2 *fluxes) (Allan and Soden, 2008; Yoana and Sharp, 2012)."*

2) We agree that we should refer to previous work done by Kaushal et al., 2013 as this would greatly enhance and support our discussion on increasing trends in riverine alkalinity. In addition, we also should refer to previous work done by Stets et al., 2014 as they conducted a similar study investigating long-term alkalinity trends in river systems throughout the U. S. We have revised and expanded on this section to incorporate the following:

"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, it was suggested that 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."

p.11, l.12-17: It could be me but this sentence reads like: "Because of X, we assume X". But, more importantly, the authors do not discuss the validity of their assumption of upscale not only the discharge but also the import fluxes. How valid is it to assume that the remaining 30% of discharge has DIC and TA concentrations equal to the weighted average of the three major rivers?

Response: Good point. We have acknowledged this problem. We also changed "estimate" to "assume". Yes, you are correct in that we should discuss the validity of our assumptions and highlight the possible errors in to our calculations. However we must point out as such upscaling applies to both input (river flux) and export (estuarine flux to the offshore), it doesn't affect our conclusion on the DIC source and sink balance. We have added the following explanation to the DIC mass balance discussion section.

"Since approximately 70% of the freshwater inflow to the estuary comes from the Delaware, Schuylkill, and Christina rivers, and the remaining percentage comes from small rivers and nonpoint source runoff, we estimate that the Delaware, Schuylkill, and Christina rivers provide the estuary with about 70% (annual mean discharge of these rivers together was 387 $m^3 s^{-1}$ from 2013-2015) of its total freshwater input. Thus, by upward scaling, we obtain an annual mean discharge of 553 $m^3 s^{-1}$ and a final DIC input flux of $15.7 \pm 8.2 \times 10^9$ mol C yr^{-1} and export flux of $16.5 \pm 10.6 \times 10^9$ mol C yr^{-1}. It is important to note that these final flux values are 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 impact on final flux values. However, since extensive research and data is needed, here we assume that the mineralogy and drainage basins of the remaining small rivers yield similar carbonate concentrations as Delaware's three major river systems."

p.12, l.3: "small riverine systems" No, as these have already been taken into account by upscaling the riverine discharge. I would also suggest to specify groundwater discharge as an additional source here, rather than pooling it into the various external sources.

Responses: Good catch. After upscaling the riverine discharge, we eliminated additional input from small riverine systems (i.e. creeks). We also removed this variable from our DIC mass balance equation and specified benthic recycle and ground water discharge as an additional source. The following section now reads as follows:

"Thus, a DIC mass balance for the estuary is formed as follows:

River input flux (15.7×10^9 mol C yr^{-1})
+ Internal estuarine production (?)
+ Inputs from surrounding salt marshes (?)
+ Inputs form benthic recycling (?)
= Estuarine output flux (16.5×10^9 mol C yr^{-1})
+ Atmospheric flux (4.3×10^9 mol C yr^{-1})

The total sum of the unknown internal DIC production terms is therefore estimated as 5.1×10^9 mol C yr^{-1}. This total internal DIC production includes respiration in the water column and benthos, CO_2 addition from intertidal marsh waters, wastewater effluents, ground water discharge, and other various external sources. If we pool water column and benthic respiration into one term and ignore additional input from wastewater effluents and ground water discharge, DIC fluxes can be viewed as a measure of net ecosystem production (NEP)."

Section 4.5: I feel that the estimate of NEP can be discussed a bit more in the context of previous work in the estuary. For example, earlier measurements of production and respiration in the estuary also pointed at the latter exceeding the former (Preen and Kirchman, 2004). I am sure there is more relevant work done, perhaps also on the role of salt marshes and groundwater discharge in this system. Also, on p.12, l.27 marshes are mentioned as a possible source of CO_2 into the bay, whereas on p.10, l.24-29 it is discussed that the export of DIC from salt marshes is small. So can they really be a substantial CO_2 source?

Conclusions: p.13, l. 28-30: The manuscript does not quantify how important seasonal changes in NEP are relative to variations in river discharge and mixing on the same time scale. This ties in with one of my earlier comments on time scales, but would it be possible to show how the relative contribution of NEP versus river discharge changes over the course of the year?

Responses:

1) Agreed. Additional comparisons to previous work done in the estuary would significantly strengthen the paper's discussion. We have expanded the section to discuss more about previous studies that have investigated respiration, production, and net ecosystem production within the estuary as 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 pCO_2 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)."

2) In regards to additional CO_2 input from surrounding marsh systems, we agree that intertidal marshes can have drastic impacts to estuarine CO_2 dynamics, particularly in small estuarine systems. However, previous work found that in general cross-bay gradients were erratic and comparatively small (Culberson et al., 1987; Lebo et al., 1990; Sharp et al., 2009), consistent with our main channel bay study that found marsh impact to be small. In our case, significantly more research and data are needed especially near the perimeters of the estuary to accurately ascertain the impact from marsh systems. Thus, we caution the audience in jumping to conclusions as it is unclear whether the organic matter respiration occurs in the main channel of the estuary or from nearby internal marshes with the resulting CO_2 flushed into the bay.

3) Yes, it is important to examine the relationship between NEP and variations in seasonal discharge. We have added additional discussion comparing the two variables to section 4.5 as *shown below. We also added an additional figure comparing seasonal discharge, NEP, and air-water* CO_2 *fluxes.*

"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 CO_2 *fluxes. When the estuary acted as a source of* CO_2*, negative NEP was observed. In comparison, when the system served as a* CO_2 *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."*

Minor Comments

p.1, l.17: define HCO_3^- before using it.
p.1, l.19: same here for CO_2
p.1, l.19-21: this sentence is not very clear. I would at least suggest writing "additional DIC input in the form of CO_2" instead of "additional CO_2 input", and perhaps do some more rephrasing.

Response: We agree. We have defined HCO_3^- *and* CO_2 *and rephrased the sentence as follows, "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 (*CO_2*), most likely from organic matter decomposition rather than from other bicarbonate (*HCO_3^-*) inputs due to drainage basin weathering processes."*

p.1, l.27: "CO_2 flux" should be termed "net DIC production" or, as used later in the manuscript, "net ecosystem production".
p.1, l.27: replace "inclusive of" with "including".
p.1, l.27 - p.2, l.3: It is the small difference between riverine input and export that suggests that most of the DIC produced in situ is lost within the atmosphere, not the fact that in situ production is small to the riverine input. Please rephrase this.

Response: Good points. We have rephrased the sentences as follows, "Annual DIC input flux to the estuary and export flux to the ocean are estimated to be $15.7 \pm 8.2 \times 10^9$ *mol C* yr^{-1} *and* $16.5 \pm 10.6 \times 10^9$ *mol C* yr^{-1}*, respectively, while net DIC production within the estuary including inputs from intertidal marshes is estimated to be* 5.1×10^9 *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."*

p.2, l.22: add in which form of DIC is transported here (HCO_3^- or CO_2) and whether this depends on silicate versus carbonate weathering.

Response: We agree. We should be more specific here. We have added the weathering reactions in the introduction and modified the sentence to, "The weathering of carbonate and silicate minerals consumes atmospheric CO_2 and transports HCO_3^- ions and subsequent cation and anion products into oceanic systems. Eventually, CO_2 is released back into the atmosphere via oceanic carbonate sedimentation and volcanic activity (Lerman et al., 2004; Regnier et al., 2013)."

p.2, l.25: supply of DIC by rivers…add "to estuaries".

Response: Added. Now read as, "Typically, the supply of inorganic carbon by rivers to estuaries is governed by river discharge, weathering intensity, and the geology of the drainage basin (White and Blum, 1995; White, 2003; Guo et al., 2008)."

p.4, l.13: I miss some basic information here: how many stations were measured each cruise, and what were the coordinates of these stations? The trajectory and stations can easily (and should) be added to Fig. 1.

Response: Unfortunately, most of the research cruises were conducted on ships of opportunity (i.e. funding was supported by other lab groups). Thus, the number of sampling stations and cruise path varied throughout surveys. In turn, for our study we collected surface water CTD and underway samples across the salinity gradient. Since stations were different for each cruise, it is difficult for us to label their locations in Fig. 1 and we have clarified this in the text as shown below:

"DIC, TA, and pH were measured along the salinity gradient of the Delaware Estuary on eight cruises: 8-10 June 2013, 17-22 November 2013, 23-24 March 2014, 2-3 July 2014, 27 August to 1 September 2014, 30 October to 2 November 2014, 5 December 2014, and 6 April 2015. However, because stations were different for each cruise, we do not label them in Fig. 1."

p.4, l.20: Add a reference to Fig.1 here.
p.4, l.22: Add a reference to Fig.2 at the end of the sentence.

Response: References have been added.

p.4, l.28: "preserved at". Also, how long were the samples stored before analysis?

Response: Corrected. Now reads as, "DIC and TA samples were filtered through a cellulose acetate filter (0.45 µm) into 250 ml borosilicate bottles, fixed with 100 µl of saturated mercury chloride solution, preserved at 4°C, and analyzed within two weeks of sample collection (Cai and Wang, 1998; Jiang et al., 2008)."

p.5, l.7: What are the accuracy & precision of the pH measurements? What is the potential error with the NBS scale in the more saline waters?

(related to the previous question) p.5, l.18: Here, pH is suddenly mentioned with 3 significant digits, whereas in l.15 and Table 1 only 2 significant digits are given. Please be careful and consistent here.

Response: We agree. We should be consistent when reporting measurement values. In this study, pH values were measured to within 0.005 units however the expected accuracy is probably not better than 0.01 units. We have changed all pH values to two significant figures. In addition, our methods now read as, "For pH measurements, water samples were collected in glass bottles with a narrow mouth and left in a thermal bath (at 25°) for about 30-60 minutes. pH was then determined onboard using an Orion 3-Star Plus pH Benchtop Meter with a Ross pH electrode (Thermo Fisher Scientific Inc. Beverly, MA, USA) and calibrated using three National Bureau Standard (NBS) pH buffers of 4.01, 7.00, and 10.01. Note that the narrow mouth of the glass bottle is only slightly larger than the outer diameter of the pH electrode thus preventing CO_2 *degassing during the analysis. While the analytical precision is ± 0.005 units, the expected accuracy is probably not better than ± 0.01 pH units."*

p.5, l.20: A comma is used here as thousand separator, which is not done in other parts of the manuscript. Please be consistent here.

Response: Yes. Consistency is key and we have removed this accordingly.

p.5, l.28-30: I feel this is part of the discussion.

Response: We agree and have moved these sentences to section '4.1 Influence of river discharge and weathering intensity'.

p.6, l.4-6: What do the authors exactly mean with "TA" in l.5? The average concentration of riverine TA? Please clarify.

Good point. We have clarified on this description. Now reads as, "Despite mixing from multiple end-members, such differences in discharge indicate that average riverine TA is predominantly governed by carbonate concentrations in the Delaware River."

p.6, l.23: "varied linearly…" add "with salinity".

Added.

p.7, l.29: not only respiration from soil OM, but also imbalances between production and respiration along the aquatic continuum can impact DIC:TA ratios.

Agreed. The sentence now read as follows, "On the other hand, CO_2 *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)."*

p.9, l.19: This section should be termed "Historical trends in riverine alkalinity", not "estuarine alkalinity".

Changed.

p.10, l.9-11: These deviations from conservative mixing for a specific month are really difficult to see in Fig.3.

Yes, perhaps there is a better way to display this variation. Plotting separate months may be better to see individual trends, however we would lose the group comparison gained when plotting all months together.

p.11, l.6 ff.: I'd say that this is a DIC mass balance, not a CO_2 mass balance. Please change this throughout the manuscript.

Good point. We have changed this throughout the manuscript.

Table 1: Add that pH is at 25 degrees and on the NBS scale.

We have added that pH was measured at 25 degrees on the NBS scale.

Figure 1: do the arrows point at the exact sampling locations of the rivers? It would be clearer to add symbols indicating the exact locations in the plot. Also, as said before, I miss an indication of the trajectory and/or the exact sampling locations within the estuary in this plot. What is the C&D canal?

Good points. We now describe what the black arrows mean (river names) in Fig.1. As mentioned earlier, most of the research cruises were conducted on ships of opportunity. Thus, the number of sampling stations and cruise path varied throughout surveys and would be difficult to plot in the figure. In turn, for our study we collected surface water CTD and underway samples across the salinity gradient. We have removed C&D canal as it is not necessary.

Figure 2: add in the caption what the diamond symbols and green lines indicate.

Yes, we now describe that the red diamonds indicate exact sampling dates and the green lines are when river waters were frozen.

Figure 5: I find it confusing that this plot should be read in the reverse direction as Fig. 3 and suggest that the x-axis be reverted.

Good idea. We have reverted the axis direction so that it is more comparable to our previous plots.

Figure 6: as discussed above, I suggest removing Fig. 6b (and merge 6d with 6c), as I don't believe it to display a real trend. In the figure caption, change "data measured in our lab" to "our data". I would also suggest using "our data" in the legends of Figs. 6 and 7, rather than the corresponding author's last name.

Interesting point. As TA flux is defined as concentration multiplied by discharge, one would expect a solid correlation between the two variables. We have removed Fig. 6b and merged 6c and 6d. In the figure caption, we changed ‘data measured in our lab’ to ‘our data’. Yes, for the legend description we have changed the name to ‘This Study’ instead of ‘Cai’ in Fig. 6 and 7.