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Seasonal variability of the inorganic carbon system in a large coastal plain estuary

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Abstract. Carbonate geochemistry research in large estuarine systems is limited and widely understudied. Further, changes in land use activity have profoundly influenced watershed export of organic and inorganic carbon, acids, and nutrients to the coastal ocean. To investigate the seasonal variation of the inorganic carbon system in the Delaware Estuary, one of the largest estuaries along the U.S. east coast, dissolved inorganic carbon (DIC), total alkalinity (TA), and pH were measured down the estuary from June 2013 to April 2015. In addition, to explore how drainage basin mineralogy, weathering intensity, and tributary discharge impact total riverine DIC and TA fluxes to the estuary and export fluxes to the ocean, DIC, TA, and pH were periodically measured from March to October 2015 in the non-tidal freshwater Delaware, Schuylkill, and Christina rivers. Strong negative relationships between river TA and discharge support that changes in HCO_3^- concentrations reflect the dilution of the weathering derived products in the drainage basin. The ratio of DIC to TA, a rarely studied but important property, is high (1.11) during high discharge and low (0.94) during low discharge, reflecting additional CO_2 input most likely from land surface organic matter decomposition other than HCO_3^- input from the drainage basin weathering processes. 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. Long-term records of increasing alkalinity in the Delaware and Schuylkill river support global shifts toward higher alkalinity in estuarine waters with time. Annual DIC input flux to the estuary and export flux to the ocean are estimated to be $15.7 \pm 8.2 \times 10^9$ mol C yr^{-1} and $16.5 \pm 10.6 \times 10^9$ mol C yr^{-1}, respectively. CO_2 flux produced within the estuary inclusive of inputs from intertidal marshes is small (5.1×10^9 mol C yr^{-1}) when compared to total riverine flux. This finding suggests that, in

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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 CO_2 mass balance model, we concluded that annually the Delaware Estuary is a weak heterotrophic system (-1.3 ± 3.8 mol C m^{-2} yr^{-1}), which is in contrast to many highly heterotrophic smaller estuaries.

1 Introduction

The global carbon cycle involves dynamical processes of carbon exchange among the earth's atmosphere, land, vegetation, coastal zones, and oceans. Over the past century, human perturbations and land-use changes have significantly modified the transport of carbon across the land and ocean continuum and have resulted in imbalances to present-day carbon fluxes and storage reservoirs (Aumont et al., 2001; Cotrim da Cunha et al., 2007; Quinton et al., 2010; Bauer et al., 2013; Regnier et al., 2013). The total carbon input to freshwaters is estimated to be 2.7-2.9 Pg C yr^{-1} (Battin et al., 2009; Tranvik et al., 2009; Regnier et al., 2013). The majority of carbon fluxes in inland waters involve inputs from soil-derived carbon, chemical weathering of carbonate and silicate minerals, dissolved carbon in sewage waste, and organic carbon produced by phytoplankton in surface waters (Battin et al., 2009; Tranvik et al., 2009; Regnier et al., 2013). To balance the influx of carbon, a large fraction is returned to the atmosphere by organic carbon decomposition within inland waters (Cole et al., 1994; Butman et al., 2015). Additionally, carbon is transported to adjacent waters, buried in freshwater sediments, and in some cases released as methane (CH_4) gas (Downing et al., 2008; Bastviken et al., 2011). In the inorganic carbon cycle, the weathering of silicate and carbonate minerals consumes atmospheric CO_2 and transports dissolved inorganic carbon and subsequent cation and anion products into oceanic systems. Eventually, this CO_2 is released back into the atmosphere via oceanic carbonate sedimentation and volcanic activity (Lerman et al., 2004; Regnier et al., 2013).

The supply of inorganic carbon by rivers is typically governed by river discharge, weathering intensity, and the geology of the drainage basin (White and Blum, 1995; White, 2003; Guo et al., 2008). Large shifts in seasonal precipitation and weathering rates can significantly impact dissolved inorganic carbon (DIC) and total alkalinity (TA) concentrations (Probst et al., 1992; Cai, 2003; Guo et al., 2008). Guo et al., (2008) found that in the Pearl River estuary DIC and TA values were substantially lower during the wet season (~ 1000 and 700 µmol kg^{-1}, respectively) than

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during the dry season (> 2700 and > 2400 µmol kg^{-1}, respectively). They suggested that the much lower DIC and TA values in the wet season were a result of increased river discharge diluting overall production of DIC and TA by weathering. Similar results were found in the Mississippi and Changjiang where river HCO_3^- concentration and discharge are negatively correlated (Cai et al., 2008).

While there have been several inorganic carbon studies on rapidly transiting large river systems, globally carbonate chemistry research in estuaries remains limited (Ternon et al., 2000; Cai, 2003; Cai et al., 2004; Cooley et al., 2007; Cai et al., 2008; Liu et al., 2014). Further, the majority of past estuarine CO_2 studies have focused primarily on small estuarine systems, generally with short freshwater residence times (Chen and Borges, 2009; Cai, 2011; Borges and Abril, 2011). Thus, there is an absence of carbonate research in large estuaries and an urgent need to expand global research to more extensive bay systems. Through monthly sampling at the Delaware, Schuylkill, and Christina rivers and data collected from eight cruises (2013-2015), we examine how input from multiple tributaries, contrasting geographical settings, and physical mixing processes impact total riverine DIC and TA fluxes, internal net ecosystem production, and overall export flux in one of the largest estuaries along the U.S. east coast, the Delaware Estuary, exceeded only by the Chesapeake Bay, Long Island Sound, and the Albemarle/Pamlico Sounds (Frithsen, 1991; Sutton et al., 1996). Using historical and contemporary data collected along the Delaware and Schuylkill rivers, we explore how rapidly changing environments influence regional trends in riverine carbonate chemistry. In turn, recent and ongoing conclusions gained over this study provide broad implications and future insights to the biogeochemistry and health of estuarine systems.

2 Methods

2.1 Study area

The Delaware Estuary is a 215 km long coastal plain estuary that extends from the head of the tidal Delaware River at Trenton, New Jersey to the mouth of the Delaware Bay between Cape Henlopen and Cape May (Fig. 1). The Delaware River provides 50-60% of the total freshwater inflow to the estuary. Based on U.S. Geological Survey (USGS) stream gauging data, the annual mean discharge of the Delaware River at Trenton is 340 $m^3 s^{-1}$ (1950-2015). Of the many small rivers in New Jersey, Pennsylvania, and Delaware that flow into the estuary, the Schuylkill River is the largest with an annual mean discharge of 80 $m^3 s^{-1}$, whereas the Brandywine-Christina rivers

are the smallest gauged tributaries with a combined mean of 20 m^3 s^{-1}. Together, the Delaware, Schuylkill, and Brandywine-Christina rivers contribute ~ 70% of the total freshwater input to the estuary with the balance sourced mostly by smaller ungauged rivers. Freshwater input from municipal wastewater treatment plants is important as well with a discharge around 30 m^3 s^{-1}. As the tidal freshwater river passes through the industrial Philadelphia region, it transitions to an extensive river estuary and bay system surrounded by intertidal salt marshes. Depending on precipitation and discharge, freshwater residence times in the Delaware Estuary generally range from 40 to 90 days but may exceed 200 days during periods of drought. Circulation in the estuary is influenced by tides, wind, and dynamical interactions between freshwater runoff from the drainage basin and saltwater inflow from the Atlantic Ocean (Wong and Sommerfield, 2009; Sommerfield and Wong, 2011; Aristizáhal and Chant, 2015).

2.2 Field measurements

DIC, TA, and pH were measured along the axis 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. Water column samples were collected with a SeaBird Electronics 911 (SBE 911) plus CTD rosette system. Discrete underway samples were taken from the outlet of an onboard SeaBird thermosalinograph (SBE-45), which measured ongoing surface water temperature and salinity. In addition to the eight cruises, DIC, TA, and pH were periodically collected from March to October 2015 from the Delaware, Schuylkill, and Christina rivers (Fig. 2 and Table 1). Instantaneous water discharge data for the Delaware and Schuylkill rivers were available from gauging stations in Trenton, NJ and Philadelphia, PA, respectively (USGS gauges 01463500 and 01474500). Discharge data for the Christina River, Brandywine Creek, Red Clay Creek, and White Clay Creek were used to compute total freshwater discharge for the Christina River system (USGS gauges 01478000, 01481500, 01480015, and 01479000).

2.3 Analytical methods

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 bichloride solution, and preserved in 4°C for future analysis (Cai and Wang, 1998; Jiang et al., 2008). DIC was determined via acid extraction by quantifying the released CO_2 using an infrared gas analyzer (AS-C3, Apollo Scitech).

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TA was measured by Gran titration (Gran, 1952) using an open cell semi-automatic titration system (AS-ALK2, Apollo Scitech) (Cai et al., 2010; Huang et al., 2012). All measurements were calibrated against certified reference material (provided by A.G. Dickson from Scripps Institution of Oceanography) with a precision of ± 2 μmol kg^{-1} (Huang et al., 2012). The pH of water samples was determined onboard (at 25°) 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.

3 Results

3.1 Spatial distributions of DIC and TA

DIC and TA varied greatly in the estuary and with season (975-2015 and 915-2225 μmol kg^{-1}, respectively) (Fig. 3). DIC and TA were lowest near zero salinity in the spring and summer when river discharge was strong and were highest in the fall and winter when discharge was weak (Fig. 3). At the bay mouth (S > 30), DIC and TA concentrations remained fairly constant throughout all seasons (1920-1990 and 2095-2180 μmol kg^{-1}, respectively). During spring and summer, DIC was reduced while pH (8.0-8.5) was highest in waters with values 15-25 salinity, suggesting biological consumption of CO_2 in the mid- to lower bay (Fig. 3). In the fall and winter, DIC and TA generally varied linearly in relation to salinity, although the change in pH was small across the salinity gradient (Fig. 3). At salinity < 2.5, pH decreased greatly, reaching as low as 7.09 in June.

Depending on river discharge conditions, DIC concentrations typically range from about 300 to 1,200 μmol kg^{-1} at the head of the estuary at Trenton (Sharp et al., 2009). During the spring and summer surveys when discharge was high, DIC and TA concentrations were about 300 μmol kg^{-1} lower than concentrations in the fall when river discharge was low (Fig. 3). Following 5-day high discharge, TA on July 2, 2015 was an average of 410.4 μmol kg^{-1} (Table 1) about 600 μmol kg^{-1} lower than the high TA in the river at low discharge from March to October (Fig. 4 and Table 1). DIC followed similar patterns. TA also changed greatly at the Schuylkill River. Additionally, when average river discharge in the Schuylkill River was less than 50 m^3 s^{-1}, TA values exceeded 1500 μmol kg^{-1} (Fig. 4 and Table 1). Thus, it appears that variation in DIC and TA is mainly a result of seasonal shifts in river discharge. Such fluctuations in river DIC and TA are expected as they are primarily governed by the dilution of weathering products by rain (White and Blum, 1995; White, 2003; Cai et al., 2008).

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While TA in the Schuylkill River was nearly double than that for the Delaware River at Trenton, Delaware River discharge was nearly four-fold greater than the discharge for the Schuylkill River (Table 1). Moreover, the average discharge in the Delaware River was more than 10-fold greater than discharge of the Christina River (Table 1). Despite mixing from multiple end-members, such differences in river discharge indicate that TA is predominantly governed by carbonate concentrations in the Delaware River. However, during periods of low discharge, TA increased significantly at the Schuylkill River (Fig. 4 and Table 1). On September 29, 2015, TA values were as high as the oceanic values at the bay mouth exceeding 2100 µmol kg^{-1}. The mixing of high TA from the Schuylkill River may increase TA values at the confluence of the Delaware and Schuylkill River. Slight increases in TA values were observed at the northern most points (around 125-150 km upstream) of the August 2014, November 2013, and October 2014 cruises (Fig. 5).

3.2 DIC and TA riverine flux

We examined inputs of DIC and TA from the Delaware, Schuylkill, and Christina rivers from March to October 2015 (Fig. 2). As DIC and TA in the Delaware River and tributaries were only measured periodically, in order to estimate input fluxes precisely we first established a quantitative relationship between concentration and river discharge. We found that the observed DIC and TA concentrations in each tributary varied negatively with river discharge (Fig. 4). We then used these relationships to estimate DIC and TA in the tributaries from measured discharge for each cruise (Table 2), which were then combined with daily discharges recorded at each river from 2013 to 2015 to compute a more robust estimate. We estimate that the annual flux of DIC and TA from the rivers to the estuary was 11.0 ± 5.8 x 10^9 and 10.8 ± 5.1 x 10^9 mol C yr^{-1}, respectively.

3.3 DIC and TA export flux

DIC and TA values varied linearly near the ocean end-member value, suggesting no net addition or removal of DIC and TA beyond conservative mixing. 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 (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 combined river discharges for the Delaware, Schuylkill, and Christina rivers, we estimate net DIC

and TA export fluxes in each survey (Table 3). The estimated annual DIC and TA fluxes to the ocean are $11.5 \pm 7.4 \times 10^9$ and $13.0 \pm 9.0 \times 10^9$ mol C yr^{-1}.

4 Discussion

4.1 Influence of river discharge and weathering intensity

A compilation of historical USGS water quality data from 1940 to the present shows that TA for the Delaware River at Trenton was negatively correlated with river discharge (Fig. 6A). TA was highest during low flow seasons (summer and fall) and lowest during high flow seasons (spring and winter) (Fig. 6C). This negative correlation has been observed for other river systems such as the Mississippi, Changjiang, Pearl, Huanghe, Congo, and Indus (Probst et al., 1992; Karim and Veizer, 2000; Cai, 2003; Li and Zhang, 2003; Chen et al., 2008; Guo et al., 2008; Liu et al., 2014). While TA was negatively correlated with river discharge, TA export flux was positively correlated with discharge (Fig. 6B). The highest TA fluxes occurred during peak flow season (spring) and the lowest TA fluxes occurred during the lowest flow season (fall) (Fig. 6D). Similarly, Cai et al., (2008) observed strong correlations between TA flux and discharge in the Mississippi, Changjiang, Pearl, and Huanghe river basins as well (Cai 2003; Chen et al., 2008; Guo et al., 2008). While the correlations between TA flux and river discharge were high, it is important to note that flux is governed by both river discharge and concentration. In the case of an extreme weather event, TA fluxes may be twice as large as the average flux. Under the same conditions, if river discharge is four-fold higher, concentrations must be reduced in half to yield a two-fold increase in TA flux. Cai et al., (2008) suggested that dilution of weathering production by precipitation leads to lower concentrations in the wet season. Thus, during the wet season TA decreases while the drainage basin weathering rate and river TA flux increase.

Another interesting but rarely reported phenomenon is the seasonal variation of the DIC to TA ratio at the freshwater end-members. At Trenton, the ratios (1.02 – 1.11) were highest during high discharge periods (> 200 m^3 s^{-1}) and lowest (0.86 – 1.01) at low discharge periods (< 150 m^3 s^{-1}) (Table 1). Similar results were found in the Schuylkill River where DIC to TA ratios were highest (1.02 – 1.07) at high discharge (> 100 m^3 s^{-1}) and lowest (0.93 to 1.02) during low discharge (< 75 m^3 s^{-1}) (Table 1). If only influenced by the weathering of carbonate minerals, the ratio of DIC to TA remains close to unity (Cai et al., 2004). On the other hand, CO_2 production from soil organic matter respiration can increase DIC to TA ratios (Mayorga et al., 2005). Presumably, during the

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wet season and high discharge periods, more CO_2 from soil organic matter respiration stored in the drainage basin is brought along the river system while less CO_2 is lost to the atmosphere due to a faster transport. While not fully resolved, 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 river discharge. As the ratio of DIC to TA determines aquatic pH and the buffer capacity (Egleston 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).

4.2 Influence of tributary mixing

The mineralogy of the Schuylkill River drainage basin may have a significant impact on TA patterns throughout the Delaware estuarine system. Originating in the Valley and Ridge province of the Appalachians, the Schuylkill River flows southeast through the New England and Piedmont domains before discharging into the Coastal Plain province and the Delaware River (Stamer et al., 1985). The upper Blue Ridge Mountains of the Valley and Ridge province are primarily underlain by coal, sandstone, and shale while the Great Valley region is composed mostly of shale and carbonate rocks (Stamer et al., 1985). In comparison, the New England province is comprised mainly of dolomite and sandstone. Continuing southward, the Piedmont province is primarily underlain by a mixture of limestone, shale, gneiss, schist, and dolomite (Stamer et al., 1985). Within this region, the Schuylkill River flows through the Valley Creek basin in eastern Chester County, PA. Here, about 68% of the basin is underlain by carbonate rocks (Sloto, 1990). Moreover, 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.

The Delaware River originates in the Catskill Mountains of New York. The Appalachian Plateaus province is heavily forested with only about 3 percent of the basin population residing there (Fischer et al., 2004). Similar to the Schuylkill River, the upper Delaware River basin in New Jersey and Pennsylvania extends through the Appalachian Plateaus, underlain by glacial till, sedimentary sandstone, and shale bedrock, and southward into the Blue Ridge Mountains and Great Valley Provinces (Fischer et al., 2004). The lower region of the Delaware River basin briefly transects through the New England province before flowing into the Piedmont and Coastal Plain provinces.

While the Delaware and Schuylkill river basins consist of similar physiographic provinces, TA collected at the Schuylkill River was much higher than TA in the Delaware River near the Philadelphia region likely due to the weathering of carbonate rocks in the lower Schuylkill drainage basin. 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). Moreover, the historical records agreed remarkably well with our alkalinity measurements. Over the past two decades, after low river discharge (< 100 m^3 s^{-1}) alkalinity reached from 1300 to 2500 µmol kg^{-1}, nearly two-fold greater than alkalinity values observed at the Trenton end-member (Fig. 7B). Thus, 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 lower Schuylkill River drainage basin, 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).

4.3 Historical trends in estuarine alkalinity

Over the past century, changes in land use activity have significantly impacted the watershed export of organic and inorganic carbon, acids, and nutrients to the coastal ocean (Duarte et al., 2013). Long-term USGS records of river alkalinity in the Schuylkill River show that not only are alkalinity and river discharge negatively correlated, but that over decadal periods alkalinity values have increased with time (Fig. 7A). Although changes were not as great, a similar increasing trend in river alkalinity was also observed in the historical USGS dataset for the Delaware River (Fig. 7B). Moreover, long-term records of increasing alkalinity values in the Mississippi River (Raymond et al., 2008) and in the Swedish rivers (Duarte et al., 2013) have been reported suggesting a common shift towards increased alkalinity in estuarine waters. 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. In addition, through chemical weathering

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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).

4.4 Seasonal variation in estuarine DIC

DIC in the Delaware Estuary also shifted with the seasons. Generally, nonlinear concentration-salinity trends indicate an in situ addition or removal of chemical species (Cai and Wang, 1998). In spring (March 2014 and April 2015) and summer (July 2014 and August 2014), DIC deviated slightly from conservative mixing in mid-salinity waters (S ~ 15 to 25) while TA varied linearly with salinity, suggesting consumption of CO_2 in the water column (Fig. 3). During the same time, pH was highest over the entire year, further supporting the presence of a phytoplankton bloom in spring and late summer (Fig. 3). Nonlinear distributions were observed when plotting DIC against TA (Fig. 8). The curvature (concave upward trend at both ends) pattern indicates DIC removal in the mid-Delaware Bay during productive seasons. Joesoef et al., (2015) found that internal biological processes have significant impact on CO_2 dynamics within the Delaware Bay. In March, July, and August 2014, pCO_2 was low (160 – 350 µatm) throughout the mid- and lower bay regions, indicating biological CO_2 removal (Joesoef et al., 2015). Thus, while not as large as changes in weathering and precipitation rates on DIC variability, internal biological processes within the bay system can lead to seasonal shifts in DIC concentrations.

In addition, the flushing of intertidal marsh waters can influence DIC patterns in estuarine systems. For example, CO_2 degassing fluxes are high in the marine-dominated Sapelo and Doboy Sounds (Georgia, USA) due to the extensive accumulation, decomposition, and flushing of organic matter from surrounding salt marshes (Jiang et al., 2008). However, recent studies suggest that except near the shorelines, the flushing of intertidal marshes has a relatively small impact on overall surface water pCO_2 and CO_2 flux dynamics in the Delaware Bay system (Joesoef et al., 2015). Strong linear trends of TA with salinity across the estuarine mixing zone throughout all seasons suggest that the export of inorganic carbon from salt marshes to the main channel of the estuary is relatively small. If this was not the case, a two end-member conservative mixing line should generate both an upward concave TA and DIC salinity relationship (showing enrichment above the mixing line), as SO_4^{2-} reduction is an important organic matter decomposition pathway that

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would generate HCO_3^- in salt marshes (Cai and Wang, 1998; Jiang et al., 2008). Such concave upward distribution is not observed. Nonetheless, it is evident that more research in estuarine systems is needed to accurately depict the influence of salt marsh exports on the carbonate chemistry of estuarine waters, especially in larger bay systems with long freshwater residence times.

4.5 CO_2 mass balance

Here we present a CO_2 mass balance for the Delaware Estuary. Using freshwater discharge from the Delaware, Schuylkill, and Christina rivers (Table 1), DIC input fluxes to the estuary were computed for each cruise based on the linear relationships shown in Fig. 4. Combining total DIC fluxes for each river, we obtain an annual-averaged DIC input flux of 11.0 ± 5.8 x 10^9 mol C yr^{-1}. Using the effective concentrations extrapolated from the high salinity water, an annual-averaged DIC export flux to the ocean of 11.5 ± 7.4 × 10^9 mol C yr^{-1} was calculated. 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 assume 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 ± 8.2 × 10^9 mol C yr^{-1} and export flux of 16.5 ± 10.6 × 10^9 mol C yr^{-1}. Annual air-water CO_2 flux to the atmosphere from the Delaware Estuary has recently been estimated as 2.4 ± 4.8 mol C m^{-2} yr^{-1} (Joesoef et al., 2015). Using the annual air-water CO_2 flux and an estimated surface water area of 1773 km^2 for the estuarine system (Sutton et al., 1996), the total CO_2 flux to the air is estimated as 4.3 × 10^9 mol C yr^{-1}. Thus, a CO_2 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 marshes and creeks (?)
+ 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})

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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, small riverine systems, and other various external sources. If we pool water column and benthic respiration into one term and ignore additional input from river and wastewater effluents, DIC fluxes can be viewed as a measure of net ecosystem production (NEP). Using DIC input and export fluxes and air-water CO_2 fluxes from Joesoef et al. (2015), we estimate NEP during each cruise as described above (Fig. 9). In early spring, positive NEP indicates that the estuary is net autotrophic (10.3 ± 2.0 mmol C m^{-2} d^{-1}), and exports or stores an excess of organic carbon. A shift to negative NEP in the summer (-9.8 ± 11.6 mmol C m^{-2} d^{-1}) indicates a net heterotrophic system where ecosystem metabolism is sustained by external inputs of organic matter. In contrast, from fall to early winter season, the estuary fluctuates from a near balanced ecosystem to a net heterotrophic environment.

While CO_2 consumption was large during the spring and late summer, annually the Delaware Estuary is a weak source of DIC production with an NEP = -1.3 ± 3.8 mol C m^{-2} yr^{-1}, which is in great contrast to many smaller river estuaries that exhibit strong net heterotrophy (-17 ± 23 mol C m^{-2} yr^{-1}) (Borges and Abril, 2011). Of the 79 estuarine studies compiled in Borges and Abril (2011) that reported gross primary production (GPP), community respiration (CR), and NEP rates, overall only 12 estuaries are net autotrophic. Most estuaries are net heterotrophic probably because of high inputs of labile organic matter from tributaries that support CR while GPP is reduced due to limited light availability caused by elevated suspended matter (Smith and Hollibaugh, 1993; Heip et al., 1995; Gattuso et al., 1998; Gazeau et al., 2004; Borges and Abril, 2011). However, the relationship between NEP and GPP varies considerably across different estuaries depending on factors such as the degree of light limitation, the fraction of inorganic nutrient to organic carbon inputs, and the size of the estuarine system, with smaller estuaries showing increased heterotrophy over larger systems such as the Delaware Bay (Hopkinson, 1988; Heip et al., 1995; Kemp et al., 1997; Caffrey, 2004; Borges and Abril, 2011). In this study, 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. It is plausible that the main stem of the Delaware Estuary is still autotrophic with net CO_2 consumption, while the surrounding intertidal marshes export CO_2 to the main stem of the estuary.

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From the annual mass balance model, the CO_2 flux produced within the estuary is small (~32%) compared to the total riverine flux. Moreover, it appears that only a small percentage of the internally produced CO_2 is exported to the coastal ocean as most of it is lost to the atmosphere. Similar conclusions were observed for the macrotidal well-mixed Scheldt Estuary where much of the DIC produced by NEP is removed to the atmosphere rather than exported to the North Sea (Borges and Abril, 2011). 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 Randers Fjord and the Altamaha River have a much shorter residence time (few days) (Cai and Wang, 1998; Nielsen et al., 2001). Here, CO_2 emission to the atmosphere is lower than the NEP in the mixed layer or much less significant (Gazeau et al., 2005; Jiang et al., 2008). Furthermore, 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 such as the Randers Fjord and the Altamaha River, much of the DIC produced by net respiration is exported rather than removed to the atmosphere (Gazeau et al., 2005; Jiang et al., 2008). In the Scheldt estuary, long freshwater residence time typically leads to DIC accumulation in the water column and high CO_2 emissions (Abril et al., 2000; Borges et al., 2006). Thus, in the Scheldt Estuary and other systems 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.

5 Conclusion

Strong negative correlations between river TA and freshwater discharge in the non-tidal Delaware, Schuylkill, and Christina rivers suggest that changes in HCO_3^- concentrations reflect the dilution of the weathering derived products in the drainage basin. Elevated DIC and TA concentrations near the Philadelphia region in the upper Delaware Estuary are largely the result of the mixing of relatively high carbonate freshwater from the lower Schuylkill River drainage basin due to the chemical weathering of limestone and dolomite bedrock. Increased alkalinity in the Delaware and Schuylkill rivers over the past 70 years coincide with global trends toward higher alkalinity in river and estuarine waters over decadal timescales. In addition to strong variations in discharge and mixing from multiple end-members, seasonal changes in NEP within the estuary also contribute to shifts in DIC concentrations. Lastly, from the annual mass balance model, CO_2 flux produced within the estuary including inputs from the intertidal marshes is small (5.1×10^9 mol C yr^{-1}) when

compared to total DIC input flux. Thus, in the case of the Delaware Estuary and other estuarine systems with long freshwater residence times, much of the DIC produced by NEP or supplied from surrounding marshes is most likely emitted to the atmosphere rather than exported to the sea.

6 Acknowledgements

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Table 1. Sampling dates, average discharge, pH, DIC, TA, and DIC to TA ratio in the Delaware (Trenton), Schuylkill, and Christina rivers.

Location	Date	Discharge (m^3 s^{-1})	pH	DIC (µmol kg^{-1})	TA (µmol kg^{-1})	DIC to TA Ratio
Trenton	3/10/2015	182	8.8	973.4	1038.8	0.94
	4/21/2015	442	7.8	745.2	723.7	1.03
	5/7/2015	190	8.8	856.5	902.9	0.95
	5/21/2015	148	8.0	1025.5	1015.9	1.01
	6/9/2015	199	8.2	857.8	869.2	0.99
	6/23/2015	425	7.7	783.5	765.5	1.02
	7/2/2015	1127	7.2	454.2	410.4	1.11
	9/15/2015	183	8.2	945.8	936.7	1.01
	9/29/2015	98	8.7	945.8	1103.9	0.86
	10/12/2015	170	8.1	1095.2	1046.1	1.05
Schuylkill	4/16/2015	52	8.9	1421.2	1525.7	0.93
	5/21/2015	32	8.1	1682.9	1655.9	1.02
	6/9/2015	105	7.9	1400.1	1371.3	1.02
	7/2/2015	271	7.7	1095.3	1026.3	1.07
	9/15/2015	60	7.8	1506.1	1472.2	1.02
	9/29/2015	19	8.1	2071.3	2107.8	0.98
	10/12/2015	34	8.3	1869.3	1851.4	1.01
Christina	4/16/2015	14	7.7	1056.5	1015.1	1.04
	4/28/2015	15	7.5	1076.4	1018.6	1.06
	5/21/2015	11	7.7	1134.1	1072.8	1.06
	6/9/2015	32	7.5	1089.4	1004.0	1.08
	9/15/2015	6	7.9	1326.9	1210.6	1.10
	9/29/2015	7	8.0	1188.6	1165.4	1.02
	10/12/2015	7	8.0	1199.6	1168.0	1.03

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Table 2. Estimated TA and DIC in the Delaware (Trenton), Schuylkill, and Christina rivers, calculated by linear regression using discharge and their input fluxes to the Delaware Estuary.

Survey	Trenton		Schuylkill		Christina		TA	DIC
	TA (μmol kg^{-1})	DIC (μmol kg^{-1})	TA (μmol kg^{-1})	DIC (μmol kg^{-1})	TA (μmol kg^{-1})	DIC (μmol kg^{-1})	input flux (10^9 mol yr^{-1})	input flux (10^9 mol yr^{-1})
March 2014	700.3	721.5	1341.8	1366.8	935.3	1004.8	15.6	16.0
April 2015	609.1	647.6	1382.8	1404.3	1030.1	1093.7	16.7	17.6
June 2013	634.0	667.8	995.4	1050.5	870.7	944.2	21.3	22.5
July 2014	901.6	884.7	1565.3	1571.0	1050.7	1113.0	9.7	9.6
August 2014	1101.0	1046.4	1977.9	1947.8	1131.8	1188.9	5.4	5.2
October 2014	1147.2	1083.9	1860.7	1840.8	1123.1	1180.8	5.3	5.1
November 2013	1154.0	1089.4	1929.7	1903.7	1112.0	1170.3	5.0	4.8
December 2014	998.9	963.7	1548.0	1555.1	1057.9	1119.7	8.4	8.3
Annual Average	894.6	879.1	1568.2	1573.6	1044.4	1107.0	10.8	11.0

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Table 3: Effective TA and DIC as a function of salinity, calculated by linear regression using data from high salinity waters in the Delaware Estuary and their export fluxes to the ocean.

Survey	Effective TA ($\mu mol\ kg^{-1}$)			Effective DIC ($\mu mol\ kg^{-1}$)			Total discharge ($m^3\ s^{-1}$)	TA export flux ($10^9\ mol\ yr^{-1}$)	DIC export flux ($10^9\ mol\ yr^{-1}$)
	Slope	Intercept	R^2	Slope	Intercept	R^2			
Mar 2014	35.99	1034	0.97	35.59	889	0.97	597	19.5	16.7
Apr 2015	37.33	1071	0.99	40.73	714	0.99	740	25.0	16.7
Jun 2013	37.91	978	0.93	32.03	948	0.94	895	27.6	26.8
Jul 2014	51.05	532	0.96	46.21	514	0.90	297	5.0	4.8
Aug 2014	36.63	974	0.97	37.99	747	0.94	139	4.3	3.3
Oct 2014	37.45	954	0.98	28.69	1087	0.97	129	3.9	4.4
Nov 2013	28.48	1261	0.99	20.27	1360	0.98	124	4.9	5.3
Dec 2014	35.28	1119	0.99	25.16	1219	0.96	234	8.3	9.0
Annual Average							387	13.0	11.5

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Figure captions

Figure 1. Map of the Delaware Estuary and river tributaries. Gray stars indicate USGS gauging stations (1) 01463500, (2) 01474010, (3) 01474500, (4) 01481500, (5) 01480015, (6) 01479000, and (7) 01478000.

Figure 2. Daily discharge at the Delaware (Trenton), Schuylkill, and Christina rivers from March to October 2015. Note the different scales used for each river.

Figure 3. Salinity distributions of DIC, TA, and pH in the Delaware Estuary.

Figure 4. TA and DIC versus log discharge at the Delaware (Trenton), Schuylkill, and Christina rivers. Note the different scales used for each river.

Figure 5. Spatial distribution of TA, DIC, and pH in the Delaware Estuary from the mouth of the bay (0 km) to the head of the tide at Trenton, NJ (215 km).

Figure 6. (a) Relationship between alkalinity and Delaware River discharge at Trenton (1940 – 2015), (b) alkalinity flux versus river discharge for the same period, (c) seasonal river discharge and alkalinity, and (d) seasonal river discharge and alkalinity flux. In (a) and (b), black circles indicate data obtained from the USGS station while red circles indicate data measured in lab. In (c) and (d), errors bars represent one standard deviation of the mean value for each month.

Figure 7. (a) Time series of the Schuylkill River discharge at Philadelphia, PA and (b) the Delaware River discharge at Trenton, NJ against alkalinity from 1940 to 2016. Note the different scales used for each river.

Figure 8. DIC versus TA measured along the axis of the Delaware Estuary.

Figure 9. Seasonal variations of net ecosystem production in the Delaware Estuary.

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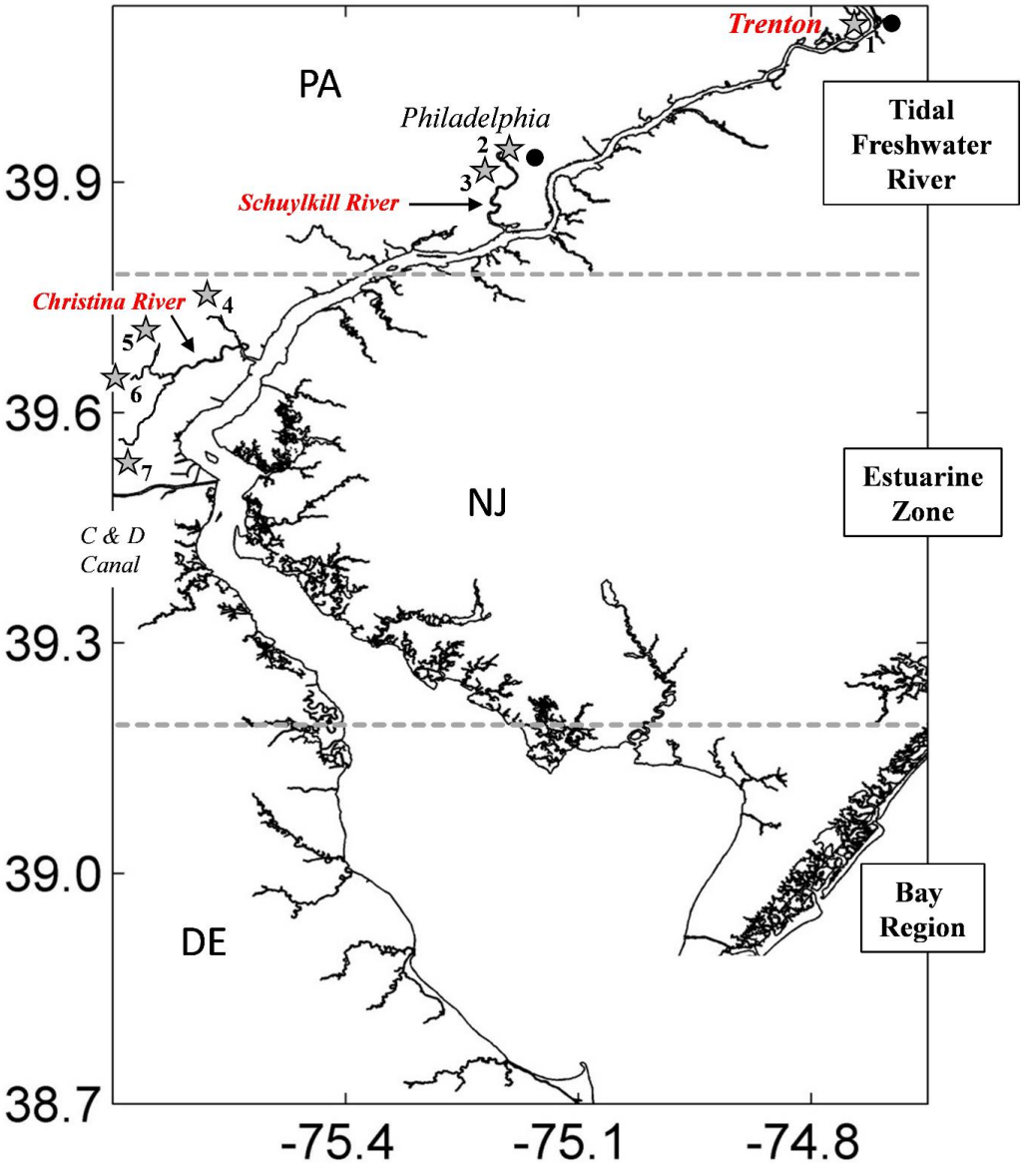

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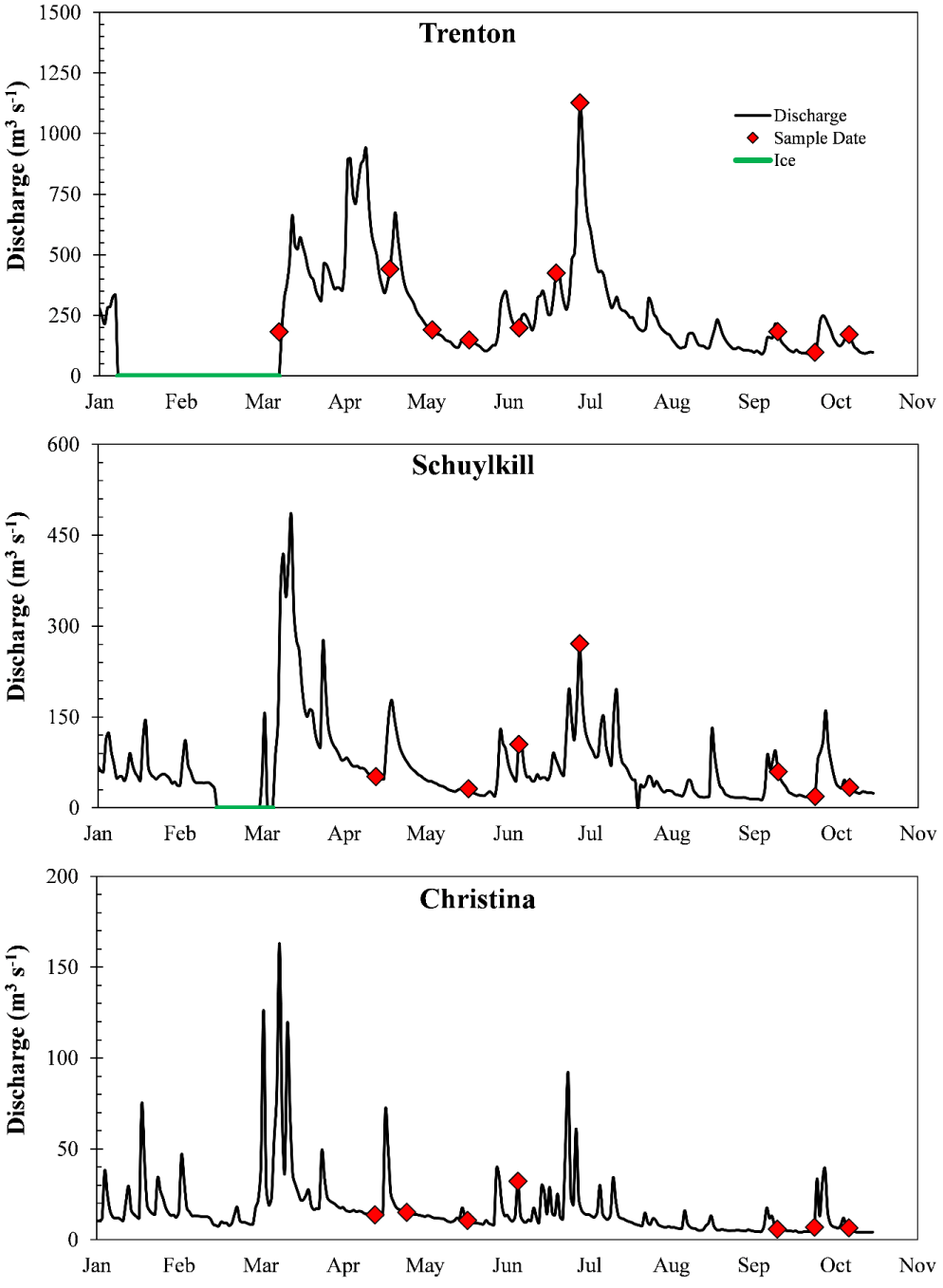

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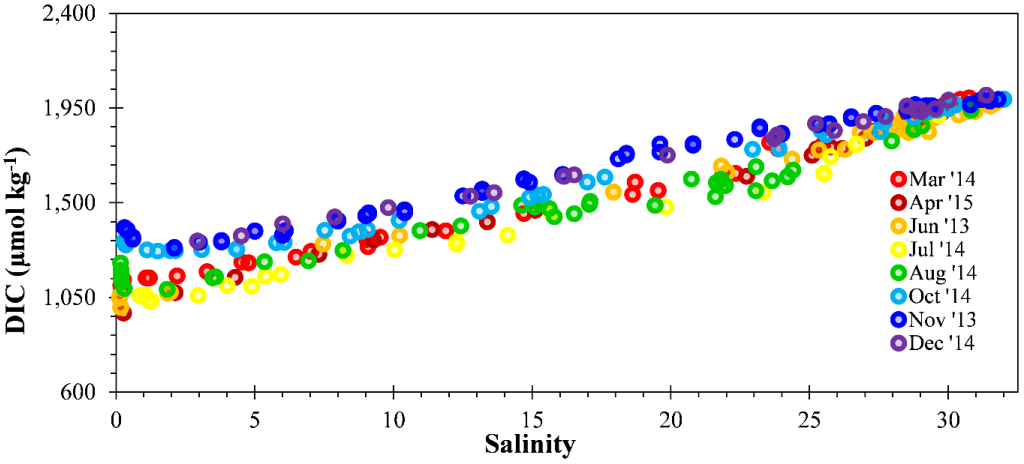

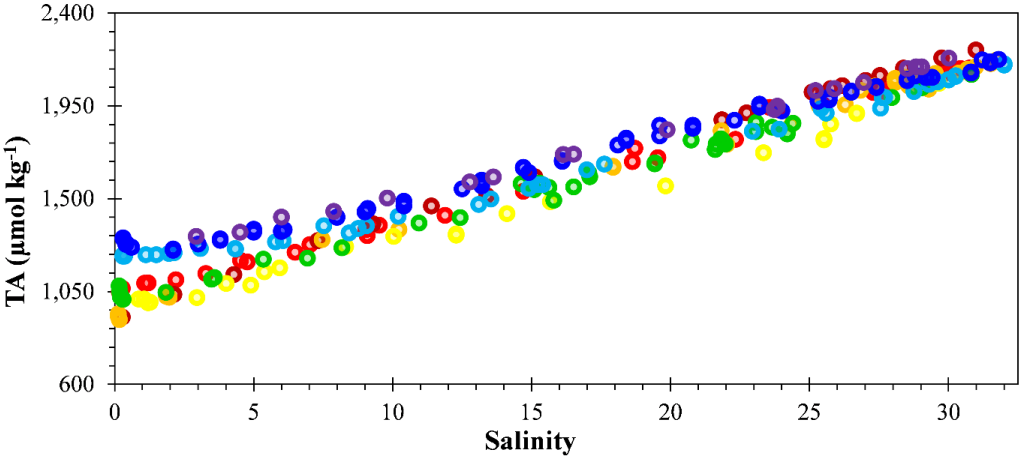

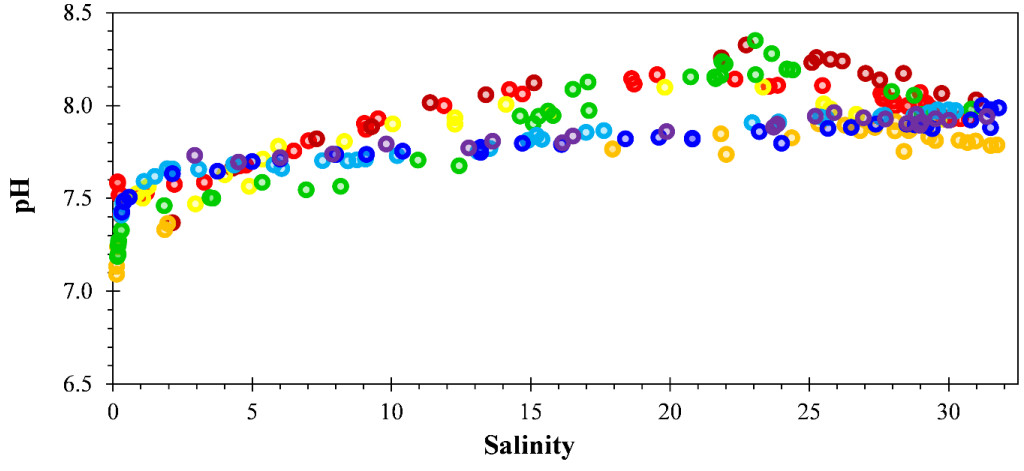

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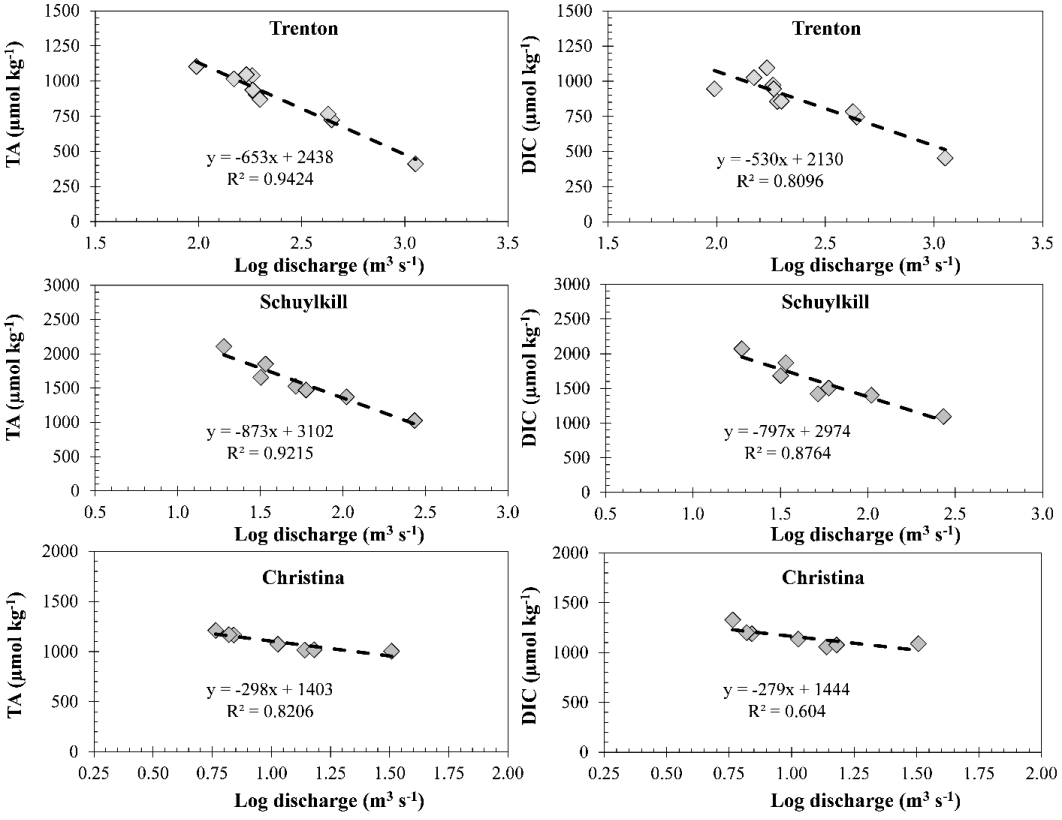

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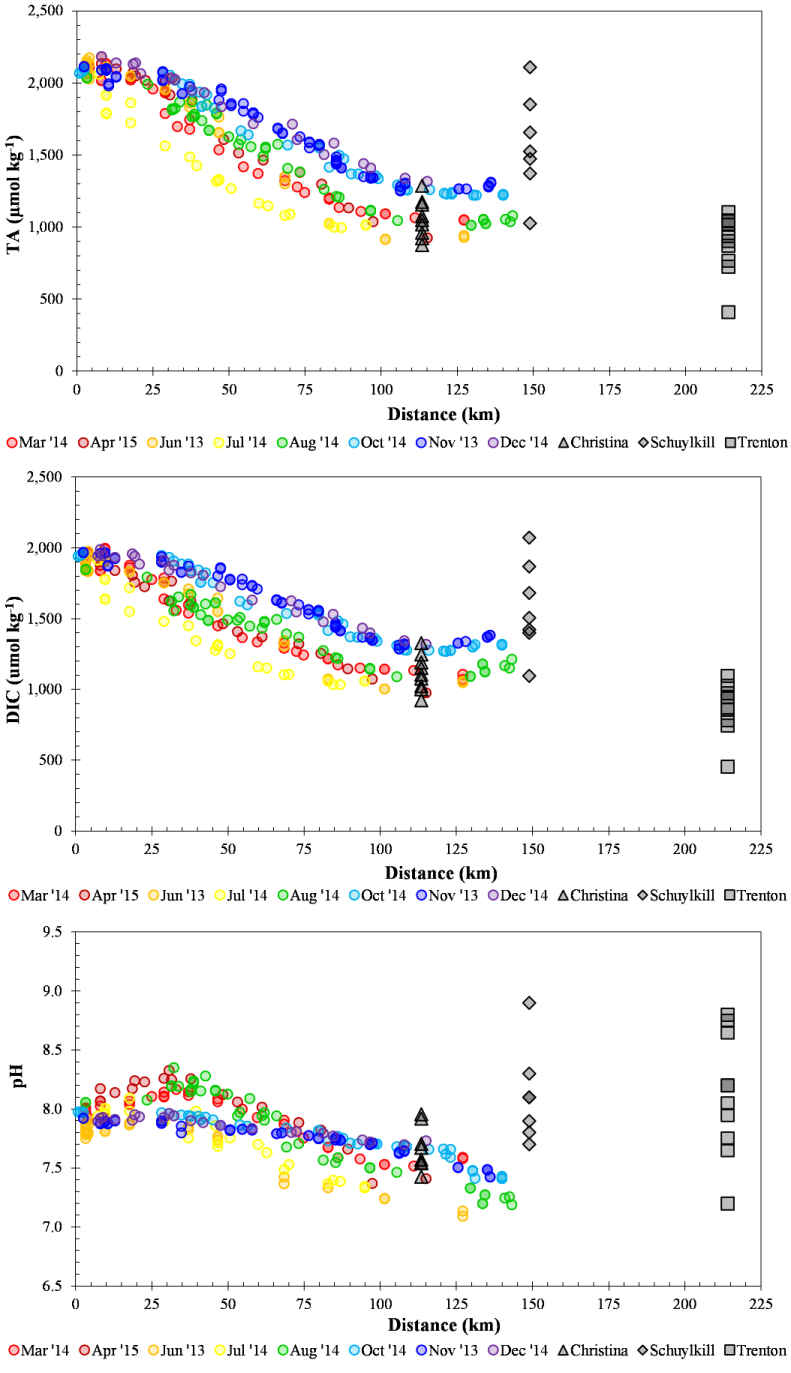

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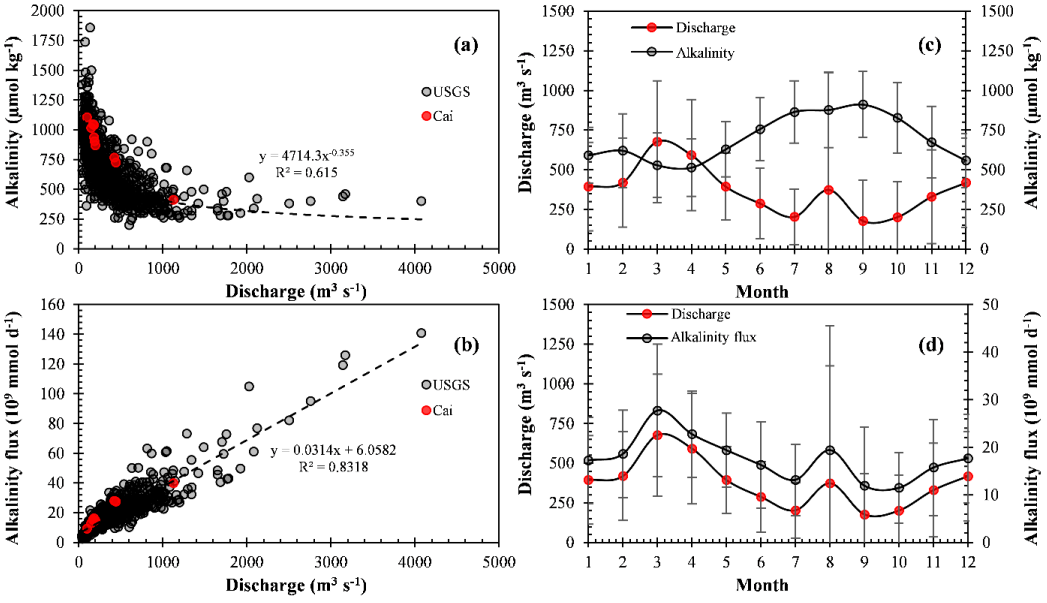

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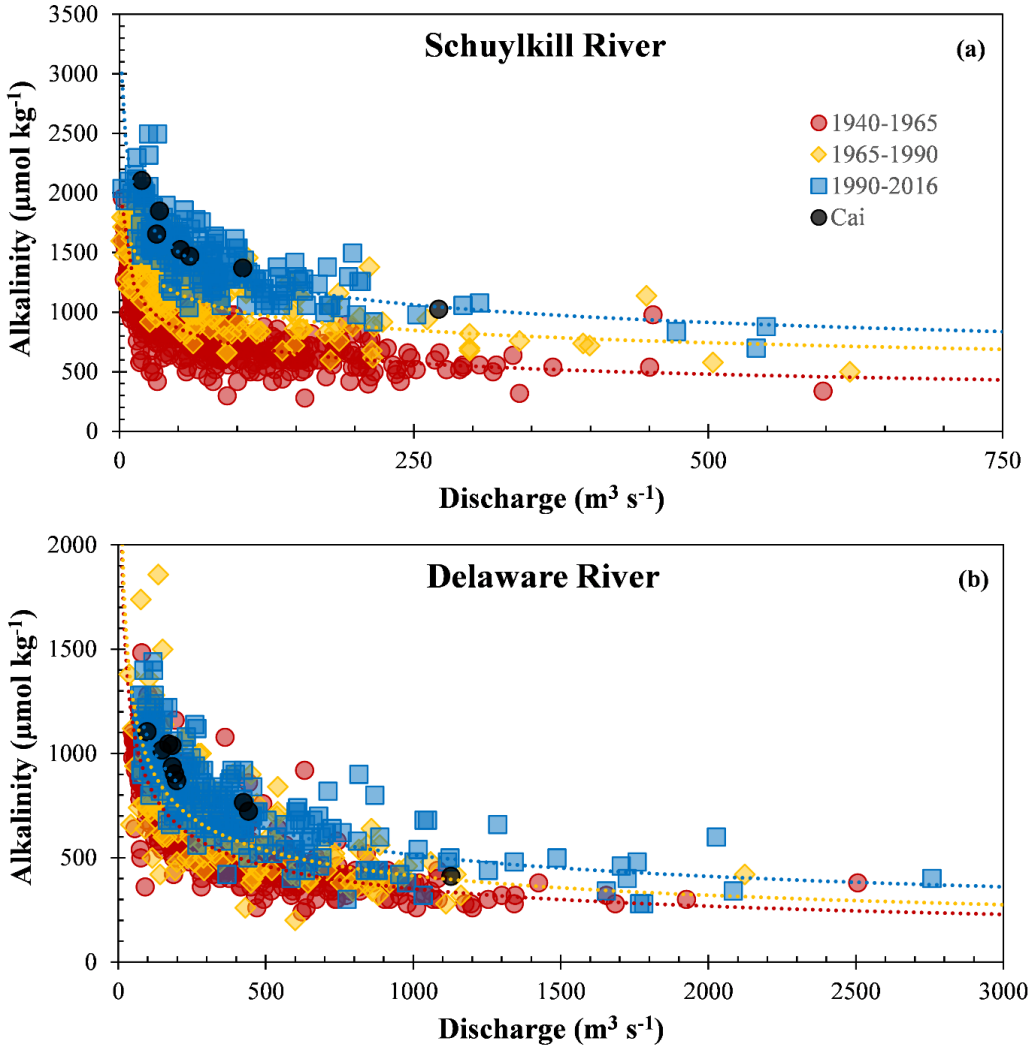

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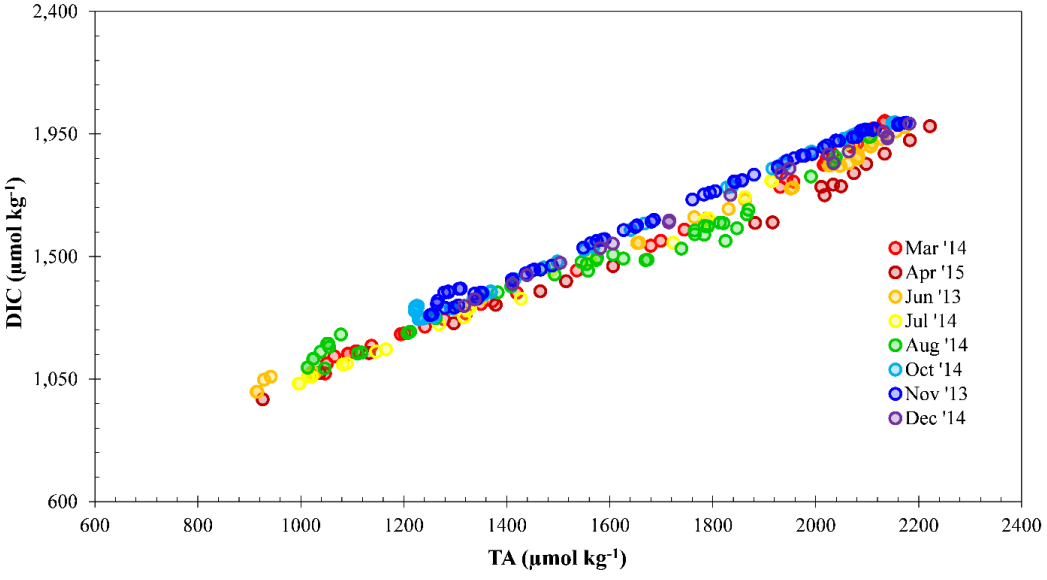

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