Interannual variability of air-water CO_2 flux in a large eutrophic estuary

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Abstract

Air-water CO_2 fluxes in estuarine environments are characterized by high interannual variability, in part due to hydrological variability that alters estuarine carbonate chemistry through multiple physical and biogeochemical processes. To understand the relative contributions of these varied controls on interannual air-water CO_2 fluxes in the mainstem Chesapeake Bay, we implemented both hindcast and scenario simulations using a coupled physical-biogeochemical model. Significant spatiotemporal variability in bay-wide fluxes was found over a 10-year period (1996-2005), where the mainstem Bay was primarily a net CO_2 sink, except in drought periods. Sensitivity scenario results suggested substantial effects of riverine nutrient and organic matter (OM) inputs to CO_2 flux variations. The high correlations between riverine inputs and upper-Bay fluxes were due to elevated respiration under increased OM inputs. The interannual flux variations in the lower Bay was mostly regulated by the nutrient inputs. Both nutrient and OM inputs contributed to the flux variability in the mid Bay. It is found that the interannual CO_2 flux of the mainstem was most sensitive to riverine nutrient inputs associated with the hydrological changes. For each hindcast simulation we computed the ratio of organic carbon turnover time to water residence time (λ), a proxy for CO_2 efflux potential, and found that the wetter periods had a relatively lower λ. The variability of mainstem CO_2 fluxes can be well represented using a generic function of λ. The model results showed that higher river flows would lead to enhanced CO_2 sinks into a large eutrophic estuary by promoting net autotrophy.

Keyword: CO_2 flux, hydrological effects, the Chesapeake Bay, numerical modelling, interannual variability.

1. Introduction

Estuarine CO_2 fluxes represent an important part of the global carbon budget. The total CO_2 degassing from estuaries has been estimated to balance the CO_2 uptake from the entire continental shelf, although the estuarine surface area equates to only 0.3% of the oceans and continental shelves (Cai et al., 2011; Borges et al., 2005). Estuaries are biogeochemically active areas that connect terrestrial, riverine, oceanic and atmospheric carbon cycling, and air-water CO_2 exchanges in estuaries are influenced by varying and complex physical, biological and chemical processes, displaying large spatial and temporal variations (Abril & Borges, 2005; Regnier et al., 2013; Gypens et al., 2009). Hence, estimates of CO_2 fluxes in estuarine environments often have high variability in magnitude and direction, and the underlying mechanisms in controlling CO_2 exchanges are not fully understood yet. Small, river-dominated, and anthropogenically impacted estuarine systems worldwide generally show significant heterotrophy, and are primarily strong CO_2 sources to the atmosphere (Caffrey, 2004; Laruelle et al., 2010; Cai and Wang, 1998). Unlike small systems, limited studies in large estuaries implied that large estuarine systems are often high in primary production, and mostly act as weak CO_2 sources or net sinks, such as the Guanabara Bay (Cotovicz et al., 2015), the Chesapeake Bay (Chen et al., 2020; Herrmann et al., 2020; Li et al., 2023), the Delaware Bay (Joesoef et al., 2015, 2017), and the St. Lawrence Estuary (Dinauer and Mucci, 2017).

River flows play an important and complex role in regulating carbonate chemistry and air-water CO_2 exchanges in estuarine environments with competing effects (Yao et al., 2020; Pacheco et al., 2015). Organic matter (OM) and nutrient inputs from surrounding tributaries could vary significantly between dry and wet periods. Riverine OM inputs could increase estuarine respiration, therefore elevating water column pCO_2 and promoting CO_2 efflux to the atmosphere (Rosentreter et al., 2018; Xiao et al., 2020). In contrast, elevated freshwater inflow delivers more nutrients to estuaries and subsequently enhances autotrophic production and increases CO_2 influx (Shen et al., 2019a; Zhong et al., 2021). River flows may also affect the riverine-estuarine mixing and water residence time, both of which would greatly influence the estuarine CO_2 exchanges (Van Dam et al., 2018; Crosswell et al., 2012; Jiang et al., 2008).

Riverine waters are generally high in pCO_2 (i.e., supersaturation condition), and the extensive riverine mixing during high-flow years would strengthen the net CO_2 efflux, particularly in regions closer to freshwater input locations. Estuaries with long water residence times may retain more dissolved inorganic carbon (DIC) generated from oxidation of autochthonous and allochthonous organic matter, and the enriched DIC is most likely released to the atmosphere rather than exported to the coastal regions (Joesoef et al., 2017; Borges & Abril, 2011).

Increasing efforts have been made in recent years to understand inorganic carbon cycling and CO_2 fluxes in Chesapeake Bay, and the diversity of reported results highlights the underlying variability in CO_2 fluxes. Chen et al. (2020) reported the first bay-wide, annual-scale observations of air-water CO_2 fluxes along the mainstem, and concluded that the Bay was a weak CO_2 source during the dry hydrological year 2016. Simulations using process-based models suggested the Chesapeake Bay as a whole was a net CO_2 sink, despite the significant spatiotemporal heterogeneity in bay-wide CO_2 fluxes (St-Laurent et al., 2020; Shen et al., 2019a). Because Chesapeake Bay is a larger (~320 km) system, it includes low-salinity and heterotrophic upper reaches that are net CO_2 sources, and high-salinity and nutrient-enriched lower regions that are CO_2 sinks. The Chesapeake Bay's drainage basin is particularly large, and more than 150 major rivers and streams flow into the Bay through a subset of larger tributary rivers. The variability of tributary inflows over a dry-wet cycle would inevitably alter bay-wide biogeochemical cycling and the CO_2 flux. Herrmann et al. (2020) calculated long-term (1998-2018) CO_2 fluxes of the mainstem Bay based on historical water quality data, indicating the mainstem was a weak CO_2 source to the atmosphere and the high CO_2 effluxes were mostly related to high bay-wide salinity (i.e., relatively low streamflow conditions). Thus, it is still challenging to separate and distinguish the effects of multiple factors (e.g., nutrient and OM inputs, riverine mixing) associated with hydrological conditions in different years on air-water exchanges in diverse estuaries, despite the need to better quantify these rates to understand the role of estuaries in the global carbon cycle.

The goal of this study is to explore the hydrological controls on air-water CO_2 fluxes in the mainstem Chesapeake Bay. The Chesapeake Bay is an ideal system within which to conduct

this study, given its diversity of physical and chemical environments over which to quantify CO_2 fluxes in response to riverine inputs. We used a well-calibrated, coupled physical-biogeochemical model to examine the spatiotemporal variability of CO_2 chemistry and the annual CO_2 flux in the mainstem over a 10-year period (1996-2005) with a changing hydrological regime (i.e., dry-wet cycles). Experimental scenarios were designed, and sensitivity simulations were conducted to isolate the physical (mixing, input) versus biological (nutrient-induced productivity and respiration of OM inputs) factors associated with the hydrological cycles in regulating the air-water CO_2 flux.

2. Materials and methods

2.1. Study site

The Chesapeake Bay, located in the United States mid-Atlantic coastal region, is the largest estuary in the United States and drains approximately 168,000 km^2 of watershed from the states of Maryland, Virginia, New York, Delaware, West Virginia, Pennsylvania, and the District of Columbia. The mainstem Bay is approximately 320 km long from the northern Susquehanna River to its southern mouth in the Atlantic Ocean (Fig. 1). The average depth is 6.5 m and a relatively deep central channel (20–35 m) runs the length of the middle region of the Bay. Water circulation in the mainstem is a typical two-layer pattern, consisting of the seaward movement of freshwater from the north and bottom intrusion of seawater from the south (Li et al., 2005). The water residence time of Chesapeake Bay was estimated in a range of 110 to 264 days, with an average of 180 days (Du & Shen, 2016). The Susquehanna River, among the major tributaries (Fig. 1) including the Potomac, James and York Rivers, is the largest tributary draining the watershed. It provides ~90% of the freshwater flow to the upper Bay and ~60% of the freshwaters to the entire mainstem, and is the only tributary that drains directly into the mainstem of Chesapeake Bay. Tributary inflows in Chesapeake Bay watersheds show clear seasonal and interannual variations. The annual freshwater inflows from tributaries into the Bay could reach 3000 $m^3 s^{-1}$ in high-flow wet years, but only 1000 $m^3 s^{-1}$ in dry years. We divided the mainstem into three regions to explore the spatial variability in CO_2

fluxes: upper Bay (north of 38.6° N), mid Bay (between 37.6° and 38.6° N) and lower Bay (south of 37.6° N) following Magnuson et al. (2004, Fig. 1) with a transition from freshwater to the ocean. The upper and lower Bay are freshwater-dominated and ocean-dominated regions, respectively, and the mid Bay is a mixture of the two.

2.2. Physical-Biogeochemical model

A three-dimensional physical-biogeochemical model (ROMS-RCA-CC) was used to explore the hydrological controls on CO_2 fluxes of the mainstem Chesapeake Bay. The coupled biophysical model has been well validated and applied in Chesapeake Bay to explore the interactions among physical, biological and chemical processes. In particular, the coupled model includes a physical Regional Ocean Modelling System (ROMS) configured for Chesapeake Bay (Li et al., 2005), a water quality model, Row Column Aesop (RCA), simulating variable forms (e.g., inorganic and organic, dissolved and particulate) of carbon, nitrogen, phosphorus and phytoplankton, DO in both the water column and sediments (Testa et al., 2014), and a carbonate chemistry (CC) module tracking key state variables of carbonate chemistry including DIC, total alkalinity (TA), pH and pCO_2 (Shen et al., 2019a; Li et al., 2020, 2023). The model mesh grid is 80×120 cells with ~1 km width (Fig. 1), and the time step for the biogeochemical model is 5 min to ensure a high spatiotemporal resolution for this study. The model adopts the sigma coordinate system in the vertical direction and is set up with 20 layers uniformly. A detailed description of the biogeochemical model configuration (e.g., the boundary forcing, simulation performances) and validation can be found in the supplemental material. The schematic diagram of the major state variables and transformation process in RCA-CC is presented in Fig. S1.

Air-water CO_2 exchanges were calculated as a function of transfer velocity, solubility and the pCO_2 difference between surface water and the air (Eq. 1).

$$F = v \times K \times (pC \quad , \ r - \ pC \quad ,w \ ter) \tag{1}$$

where K is the solubility of CO_2 from Weiss (1974), $pC \quad , \ r$ is the atmospheric CO_2 partial pressure, and v is the gas transfer velocity from Wanninkhof (2014),

$$v = 0.251 \times u_{10}\sqrt{\frac{660}{S}} \quad (2)$$

In Eq. 2, v has units of cm hr^{-1}, u_{10} is the 10-m height wind speed in m s^{-1}, which is measured at the Patuxent River Naval Air Station (KNHK, 38.5N, 76.7W), and Sc is the temperature-dependent Schmidt number. A positive flux from our calculation represents CO_2 release to the atmosphere or efflux, while a negative value represents CO_2 uptake by the water side or influx. Air-water CO_2 fluxes at each mesh grid in a year were added together, then divided by the total area of different regions to obtain the area-weight means. Atmospheric pCO_2 has been measured with an increase of 1.8 ppm each year due to continuous anthropogenic carbon emissions. As we focused on the impacts of river flows on interannual CO_2 fluxes in this study, we used a constant atmospheric pCO_2 between 1996-2005 to remove flux variations resulted from the increasing CO_2 levels in the air (i.e., 370 ppm measured at the Mauna Loa Observatory in year 2000, (https://gml.noaa.gov/ccgg/trends/). Given that the variability in water pCO_2 is much greater than this small air pCO_2 increase, this approach will not affect the results.

2.3. Model experiments

A control simulation was conducted to represent a 10-year period from January 1996 to December 2005, incorporating realistic riverine inputs (e.g., nutrient and OM loading, tributary discharges), coastal open boundary and meteorological forcing (e.g., tides, wind speed, shortwave radiation). The 10-year period (1996-2005) was chosen for this study, as it contains years with varying hydrological conditions (Fig. 2), including dry (1999, 2000, 2001, 25% more inflow than the average during 1986-2020), wet (1996, 2003, 2004, 25% less inflow than the average) and normal (1998) years. In addition, the coupled physical-biogeochemical model has been sufficiently validated in Chesapeake Bay for these 10 years from perspectives of physical advection and mixing (Li et al., 2005), nutrient and DO cycling (Testa et al., 2014; Li et al., 2016; Ni et al., 2020), and bay-wide variability of carbonate chemistry (Shen et al., 2019b, 2020).

The control simulation (Control) was compared to the results of two sensitivity scenarios in order to evaluate the relative impacts of riverine discharges on air-water CO_2 exchanges in the mainstem Bay. The dry-wet cycles would significantly change the nutrient and OM inputs from incoming rivers, therefore altering primary production/respiration and air-water CO_2 fluxes. In one experimental scenario, we applied an annually-constant nutrient loading from the Susquehanna River (RiverN) over the 10-year period. Specifically, the annually averaged inorganic nitrogen (including NO_2^-, NO_3^-, NH_4^+) loading was calculated, and we decreased/increased the riverine concentrations of inorganic nitrogen for each year, but keeping the freshwater discharge the same, to obtain a constant nitrogen loading for the study period (Fig. S2, e.g., the N concentrations were reduced in wet years, but increased in dry years.). To quantify the relative impacts of riverine OM loading (DOC and POC loading only), a set of riverine dissolved organic carbon (DOC) and particulate organic carbon (POC) experiments (RiverC) was conducted (Fig. S2). Similarly, these included increasing/decreasing the riverine organic carbon concentrations to remove the interannual variability in OM loading from the Susquehanna River. Model configurations including the impacts of CDOM and TSS on the light attenuation coefficient K_d and sinking velocity were not modeled to dynamically respond to riverine loading in the scenario model runs, although the time and space-varying impacts of TSS and CDOM on K_d values in the control run were included based on observational data (Testa et al. 2014). Both these two scenario experiments were run over the 10-year period, and compared with the control experiments.

3. Results

3.1. Control simulations – spatiotemporal variability of mainstem CO_2 fluxes

Results from control simulations showed large seasonal (-0.15 ± 0.92 molC m^{-2} yr^{-1}) and interannual (-0.15 ± 0.24 molC m^{-2} yr^{-1}) variations in the air-water CO_2 fluxes (Fig. 2). The mainstem Bay was typically estimated to be a net CO_2 sink to the atmosphere during spring and winter when tributary inflows were high, and it shifted to a net CO_2 source in summer and fall. The CO_2 fluxes were comparably less variable on the annual scale, and their magnitude and

direction were highly related to the hydrological dry-wet condition. In the dry years (e.g., 1999-2002), the mainstem was estimated a weak CO_2 source or neutral to the atmosphere (with an average efflux of 0.073 molC m^{-2} yr^{-1}), which is lower than the efflux derived from bay-wide cruises in the dry 2016 (i.e., 0.73 molC m^{-2} yr^{-1}, Chen et al., 2020). In contrast, the mainstem Bay turned into a net CO_2 sink (with an average influx of -0.28 molC m^{-2} yr^{-1}) in wet years (e.g., 1996-1997, 2004-2005). Overall, the mainstem was a net CO_2 sink (with an annual average of -0.15 ± 0.24 molC m^{-2} yr^{-1}) when averaged over 1996-2005.

The CO_2 fluxes showed clear spatial heterogeneity along the mainstem Bay (Fig. 3a). The upper Bay was consistently a strong CO_2 source during the 10-year period, and the efflux was even larger during the wet years, reaching 2.92 molC m^{-2} yr^{-1}. In contrast, there were consistent CO_2 influxes in the mid Bay on annual scales, and the average influx was estimated as -0.32 molC m^{-2} yr^{-1}. The lower Bay simulations showed high interannual variability, where the direction of CO_2 fluxes (i.e., sinks/sources) was greatly influenced by the wet-dry cycles, and this region was primarily a weak CO_2 source in dry years but switched to a net CO_2 sink in wet years.

We compared the Susquehanna River flow and CO_2 fluxes in the mainstem Bay to examine their relationships (Fig. 3b). High correlations were found between the two metrics ($r = 0.91$, $p < 0.01$) in the upper Bay, where elevated tributary inflows promoted elevated efflux of CO_2 to the atmosphere. The correlation in the lower Bay was also significant ($r = -0.80$, $p < 0.01$), as the CO_2 flux transitioned from a weak source at low flows (i.e., dry years) to a sink at high flows (i.e., wet years).

Discharge-CO_2 flux correlations for the mid and entire mainstem Bay were not Bay were not as strong as those in the upper and lower Bay (Fig. 3), and were not statistically significant. The inflow-flux correlation in the mid Bay was relatively modest ($r = 0.59$, $p = 0.07$), because the flux and its flow-related trend at this region are complicated due to its interactions with both the upper and lower Bay, which exhibited contrasting air-water CO_2 flux-flow relationships. The relations between the river inflows and CO_2 fluxes in the mainstem mainly resembled the

pattern of the lower Bay, but with a milder trend, displaying a weak source in drought periods and shifting to a net sink during wetter periods.

To illustrate dry-wet differences in the CO_2 fluxes, we compared the surface water pCO_2 of the mainstem in different seasons between the hydrological dry (year 1999) and wet (year 2004) years. The Susquehanna River inflows in 2004 were much higher in all seasons except during winter, when freshwater inputs were comparable between these two years (Fig. 4a). The spatial patterns of surface water pCO_2 in both dry and wet years were generally consistent with previous field observations and model simulations (Chen et al., 2020; Friedman et al., 2020; Shen et al., 2019a). Specifically, the upper Bay was primarily supersaturated in pCO_2, with its values in the very upper reaching over 1000 ppm (Fig. 4b-c). The pCO_2 level in the mid Bay was mostly below the atmospheric level (i.e., 370 ppm), and the lower Bay was nearly balanced with the atmosphere. Compared with the dry year (1999), the upper Bay was much higher in surface water pCO_2 in the wet year (2004). pCO_2 in mid Bay was relatively lower in 2004, and this low pCO_2 area was observed expanding from the mid Bay to the lower Bay. The differences of surface water pCO_2 between the two hydrological years were particularly obvious in summer and fall, when tributary inflows varied substantially.

3.2. Control simulations – CO_2 flux and trophic status

We examined the variability of net ecosystem metabolism (NEM, i.e., the difference between primary production and total respiration) in the mainstem, and analyzed the correlations between NEM and air-water CO_2 fluxes. Despite the consistent CO_2 effluxes modeled in the upper Bay, our model identified the upper Bay as heterotrophic (i.e., primary production < total respiration) in wet years but autotrophic (primary production > total respiration) in dry years (Fig. 5a). The upper-Bay NEM in wet years was highly heterotrophic, reaching -10.95 molC m^{-2} yr^{-1}. The annual NEM of mid Bay was consistently positive (with an average estimate of 3.65 molC m^{-2} yr^{-1}) over the 10-year period, displaying an autotrophic status. The trophic status of the lower Bay was exactly opposite of the upper Bay through time, being autotrophic in wet years, but heterotrophic in dry years.

The correlations between NEM and air-water fluxes were extremely high in the upper ($r = -0.99$, $p < 0.01$) and lower Bay ($r = -0.93$, $p < 0.01$). The efflux in the upper Bay decreased along with the increase of NEM. In other words, the trophic dynamics with transitions from heterotrophy to autotrophy would reduce CO_2 effluxes in the upper Bay (Fig. 5b). Similarly, the increase of NEM in the lower Bay would promote CO_2 influxes, or reverse the direction from effluxes to influxes of lower-Bay estuarine waters. The mid Bay was principally identified with CO_2 influxes and autotrophy, but no clear correlations were observed between these two metrics in the mid Bay. Overall, an intensified autotrophic status would increase the CO_2 influx in the mainstem Chesapeake Bay.

3.3. Sensitivity simulations - impacts of nutrient and OM loading

We examined the relationships between tributary influxes and air-water CO_2 fluxes for different scenarios to distinguish the impacts of riverine nutrient and OM inputs from those of riverine CO_2 inputs and physical mixing processes. CO_2 fluxes between the Control and RiverN (i.e., constant riverine nutrient inputs) scenarios did not differ much in the upper Bay (Fig. 6a), indicating that nutrient input variations associated with the hydrological conditions have little impacts on CO_2 fluxes of the upper Bay. Results of the RiverC (i.e., constant riverine OM inputs) scenario were much different, and the CO_2 fluxes of RiverC scenario did not co-vary significantly with tributary inflows when OM inputs were constant (Fig. 6), indicating that interannual variations in OM inputs regulate variability of upper-Bay CO_2 fluxes. A Comparison between the three scenarios in the lower Bay showed exactly the opposite impacts of riverine nutrient and OM loading as those in the upper Bay (Fig. 6c). The fluxes between the Control and RiverC scenarios in different hydrological years were approximately identical, demonstrating tributary OM loading did not affect the CO_2 flux in the lower Bay. However, the best fit line for RiverN scenario indicated that the CO_2 flux became much less dependent on riverine flows when nutrient inputs did not vary, suggesting that variability of CO_2 fluxes in the lower Bay was more associated with the changes of nutrient inputs.

294 Unlike the upper and lower Bay, both riverine nutrient and OM inputs were found to alter
295 mid-Bay CO_2 fluxes significantly (Fig. 6b). For the RiverN scenario, increases of tributary
296 inflows also lead to reduced influx like the Control Run, however, the air-water flux became
297 more sensitive to the changes of tributary inflows. For RiverC scenario, the trend became
298 different in that higher flows would result in more influxes into the mid Bay. Both riverine
299 nutrient-enhanced production and OM-enhanced respiration were important in the mid Bay,
300 and the best fit lines for CO_2 flux trends suggested overall higher impacts of nutrient inputs (as
301 revealed from the slope differences). Similar to the mid Bay, nutrient and OM inputs both had
302 large impacts on fluxes of mainstem as a whole. Assuming a constant nutrient loading (i.e.,
303 RiverN), the influx magnitude decreased quickly with the increasing of riverine flows, which is
304 opposite to the Control Run (Fig. 6d). The slope change ($0.75*10^{-3}$) of fit lines between Control
305 and RiverN scenarios was larger than that ($0.41*10^{-3}$) between Control and RiverC scenario,
306 indicating a more important role of nutrient inputs than OM inputs to mainstem CO_2 flux
307 variations in dry-wet cycles.
308
309 **4. Discussions**
310 **4.1. Spatial variability of air-water CO_2 fluxes**
311 Our results showed distinct features of air-water fluxes for different regions of the
312 mainstem Bay. The upper-Bay surface water was high in pCO_2, and was identified as a net CO_2
313 source to the atmosphere. The overall pCO_2 was below the atmospheric level for mid-Bay
314 waters, and CO_2 sinks during the study period were consistently observed in this region. The
315 lower Bay, however, primarily displayed a neutral condition with shift between sinks and
316 sources associated with hydrological variations. The Susquehanna River water has high pCO_2
317 year-round (supersaturated in most time, Shen et al., 2020), and the riverine freshwater flushes
318 into the upper Bay, where riverine waters directly mix with the upper-Bay estuarine water. In
319 addition to physical mixing, primary production in the upper Bay is largely inhibited due to
320 high turbidity (Xu et al., 2005). Both water column and sediment respiration are fueled by
321 riverine organic supplies (Kemp et al., 1997), leading to substantial DIC generation and CO_2

emissions to the air. Water clarity increases significantly in the mid Bay (Testa et al., 2019), and the associated relaxation of light limitation of phytoplankton photosynthesis in the mid Bay leads to autotrophy. The mid Bay is generally higher than the lower or upper Bay in terms of *Chl-a* and productivity, particularly during spring and summer (Harding et al., 2002), which assimilates large amount of DIC and reduces surface water pCO_2 (Xiao et al., 2022). The lower Bay is primarily nutrient limited, and primary production is relatively modest (Zhang et al., 2021; Acker et al., 2005), resulting in a nearly neutral metabolism. Meanwhile, the lower Bay is primarily ocean-dominated, and is influenced by the intrusion of coastal waters with pCO_2 close to the atmospheric level. Our study showed the mainstem Bay as a whole displayed a neutral/weak sink condition, close to the lower Bay. This is because the lower Bay occupies ~53% of the total mainstem area (11% and 36% for upper and mid Bay), and the efflux of upper Bay counterbalanced the influx of mid Bay to some extent.

Borges and Abril (2011) summarized estuarine CO_2 flux on global scale. Most estuaries in their synthesis have a strong CO_2 efflux to the atmosphere, and are heterotrophic. The global mean CO_2 efflux is ~26 molC m^{-2} yr^{-1}. We note that CO_2 effluxes in large estuaries such as the Chesapeake Bay (Herrmann et al., 2020) and Delaware Bay (Joeseof et al., 2015) are orders of magnitude lower. While it is not clear whether adding large estuaries will change the global mean estuarine CO_2 efflux, we suggest this new knowledge need be considered in global estuarine CO_2 flux synthesis. We also wish to point out the bimodal nature of CO_2 flux in large estuaries. Taking the Chesapeake Bay as an example, it is clear the Bay is neither river-dominated nor ocean-dominated. Interestingly, the upper Bay has all the physical, biogeochemical, and CO_2 chemistry features of small river-dominated estuaries reported in the European (Borges et al. 2006; Borges and Abril 2011) and the southeast U.S. (Cai and Wang, 1998; Jiang et al. 2008). In contrast, the lower Bay acts as an ocean-dominated estuary in its physical, biogeochemical, and CO_2 chemistry features.

4.2. Impacts of hydrological variations on CO_2 fluxes

The hydrological conditions had clear effects on the mainstem air-water CO_2 exchanges during 1996-2005. The magnitude of CO_2 efflux and influx in the upper and mid Bay varied notably between different hydrological years, and the CO_2 flux in the lower Bay even changed the direction during the dry-wet cycles (Fig. 3). During high-flow years, the Susquehanna River dominates the circulation in the upper Bay with its tidal reaches extending into the upper region of mid Bay in some seasons (e.g., spring, Li and Zhong, 2009). Correspondingly, the upper-Bay pCO_2 would be extensively regulated by the riverine-estuarine-water mixing, and displaying a strong CO_2 source in wet years, as revealed from our simulations (Figs. 3-4).

The high inflows in wet years are often associated with high nutrient and OM inputs, however, the external nutrient and OM inputs generally lead to opposing effects on inorganic carbon dynamics and air-water CO_2 fluxes. Enhanced photosynthesis/respiration due to external nutrient/OM loading would absorb/release more DIC, thereby decreasing/increasing surface water pCO_2. One may view the inorganic nutrient input as autotrophic loading and the OM input as heterotrophic loading (Cai et al., 2011). Our sensitivity scenarios suggested that riverine OM inputs are the primary driver of CO_2 efflux in the upper Bay (Fig. 6a), indicating that reductions in OM loading would lead to a reduced estuarine CO_2 efflux, and that respiration would be enhanced in wet years. This region is less sensitive to nutrient inputs because the upper Bay is consistently light limited and thus primary production is low, especially in years of high flow when turbidity is much higher. The impacts of riverine nutrient and OM inputs on lower-Bay fluxes were the opposite, where OM inputs from the Susquehanna River were oxidized before reaching the lower Bay, and had little impacts on the total respiration of the lower Bay. In contrast, because high flows transport more nutrients to the lower Bay to stimulate the primary production, the flow-CO_2 flux relationship was weaker in the simulations where nutrient loads were effectively muted with higher flows. Both remotely-sensed and field data revealed a much higher phytoplankton biomass in the lower Bay during high flow years (Acker et al., 2005; Harding et al., 2016), although some of the phytoplankton biomass in the lower Bay might be advected from the productive mid-Bay region rather than locally produced. The mid Bay connects the upper and lower Bay, and

variations of nutrient and organic inputs both altered the CO_2 flux. In dry years, the impacts of elevating nutrient loading to a 10-year average level (as revealed from the differences among three scenarios in low-flow dry years, Fig. 6b) would exceed those due to the OM increase, indicating the productive mid Bay is nutrient limited in dry periods. Unlike the dry years, CO_2 fluxes in wet years were not sensitive to nutrient load variations, and riverine OM has more influence on the CO_2 flux. From a perspective of 10-year period, the nutrient loading, rather than OM loading, along with tributary inflows was the dominant factor in altering the mid-Bay flux during the hydrological cycle. Similarly, it is the nutrient inputs that contributed to the high correlations between the riverine discharges and air-water CO_2 flux, though OM loading was also an important factor. This is primarily consistent with other large estuarine systems like the Pearl River Estuary (Dai et al., 2008), the Yangtze River Estuary (Chen et al., 2012), and the Mississippi River plume and northern Gulf of Mexico (Huang et al. 2015) that increases of nutrients inputs associated with high flows would increase the influx or shifts from a net source of CO_2 to a net sink of atmospheric CO_2.

4.3. Incorporation of estuarine hydrology in CO_2 flux estimates

The CO_2 fluxes showed much variability for the mainstem during the 10 years with large dry-wet cycles. The annual efflux ranged from 0.55 to 2.74 molC m^{-2} yr^{-1} in the upper Bay, from -0.71 to 0.09 molC m^{-2} yr^{-1} in the mid Bay and -1.35 to 0.53 molC m^{-2} yr^{-1} in the lower Bay. The mainstem was estimated to have an annual flux between -0.53 and 0.20 molC m^{-2} yr^{-1}. The hydrological impacts on estuarine CO_2 fluxes are mainly associated with the variability in freshwater-estuarine water mixing and estuarine ecosystem metabolism. Borges et al. (2006) implied that a positive NEM is often associated to the CO_2 influx for estuarine waters while a negative NEM is related to an efflux of CO_2, but there is a quantitative disagreement between the intensity of NEM and air-water CO_2 fluxes. The disagreement is probably related to the water residence time. Systems with short water residence time (e.g., the Palma Bay, Spain; the Altamaha Sound, USA) would flush water mass rapidly and the biological activity will have very limited effects on air-water exchanges, however, long water residence systems (e.g., the

Scheldt estuary, Belgium-Netherlands; the York River, USA) would accumulate large amounts of DIC through multiple biogeochemical processes and the ventilation of riverine CO_2 has been estimated to contribute to a low portion of overall CO_2 emissions (Jiang et al., 2008; Gazeau et al., 2005). Here we introduced a non-dimensional number (λ), which is the ratio of organic carbon turnover time to the water residence time for the mainstem Chesapeake Bay. The residence time was estimated using the empirical equation from Du and Shen (2016), which relates the water residence time with the mean annual flow of the Susquehanna River. The organic carbon turnover time was calculated with the water-column organic carbon pool divided by NEM from our model. Our study suggested that the wetter periods were characterized by lower λ (Fig. 7), and the variability of mainstem CO_2 fluxes can be well represented using a generic function of λ as confirmed from the high linear correlation ($r = 0.82$) between the two metrics. Water residence time decreased in wet years, however, the reduction of organic carbon turnover time was even faster (due to high NEM), leading to a lower λ and enhanced CO_2 influx for the mainstem Chesapeake Bay. The correlations between λ and air-water exchanges also indicated that nutrient loading is more important in regulating the mainstem CO_2 fluxes compared with the organic matter inputs and ventilation of riverine CO_2.

Estuaries and coastal regions are important systems worldwide influencing regional and global carbon cycling. Attempts to assess estuarine and coastal carbon fluxes requires a full incorporation of estuarine hydrology, which brings much uncertainty to air-water exchanges as revealed in this study. Although the controlling mechanism of estuarine CO_2 fluxes associated with the hydrological cycle has not been thoroughly explored, the hydrological impacts has been frequently observed. The four-year dataset over various hydrological conditions in subtropical estuaries of Gulf of Mexico revealed as much as 2-10 times increase in air-water fluxes driven by floods compared with dry periods (Yao et al., 2022). Similarly, CO_2 emissions from the Pearl River Estuary in wet periods was estimated as ~6 times of that in dry periods (Guo et al., 2009). The New River Estuary in the East Coast of U.S. was highly impacted from freshwater inflows that the estuarine system was estimated to be a weak CO_2 sink in a dry year, but shifted to a moderate source in the consecutive wet year (Crosswell et al., 2017). Hence, the

global carbon budget estimates need to fully consider the interannual variability of air-water fluxes, particularly in estuarine and coastal environments, where short-term estimates of air-water fluxes could be highly biased, and should be carefully used to interpolate into much larger spatiotemporal scales.

4.4. Other factors that influence interannual CO_2 fluxes

In this study, we examined the hydrological controls on estuarine CO_2 flux by investigating the variability of CO_2 flux due to riverine nutrient and OM inputs, which have very different impacts on CO_2 cycling and are tightly associated with hydrological conditions. However, there are other factors that relate to the hydrological conditions and may also alter air-water fluxes significantly and could be the focus of future studies. For example, high tributary inflows generally lead to elevated suspended sediments in estuarine waters, either by directly increasing external loading of riverine particles or by enhancing scouring of bottom sediments with comparably higher near-bottom currents. Historical data suggested that high flow generally produced very turbid conditions (with high light attenuation coefficients) in the upper Bay (Harding et al., 1994). The changes of light conditions in different hydrological years would inevitably alter bay-wide primary production and affect the air-water exchanges. The Chesapeake Bay is experiencing rapid climate change, and the surface water temperature in the Bay increased at the rate of 0.05 to 0.10 °C yr^{-1} during the past 30 years (Ni et al., 2020). Although no significant correlations between tributary inflows and bay-wide surface water temperature were observed, the interannual variability of surface water temperature is evident (0.7 °C) between 1996 - 2005. The water temperature variations would directly affect the air-water CO_2 exchanges by regulating CO_2 solubility, surface water pCO_2, and the other important biogeochemical processes.

5. Conclusions

In this study, we investigated the hydrological controls on CO_2 fluxes in the mainstem Chesapeake Bay using a coupled physical-biogeochemical model. Our model revealed

significant spatiotemporal variability in bay-wide fluxes over the 10-year period. The upper Bay was consistently a net CO_2 source on the annual scale, and the mid Bay was a net sink. The lower Bay shifted from a net source in dry years to a net sink in wet years. The entire mainstem was identified a net sink mostly with exceptions in drought periods, when the mainstem was a net source. Sensitivity scenario results suggested substantial effects of riverine nutrient and OM inputs to CO_2 flux variations. The high correlations between tributary inputs and upper-Bay fluxes were due to enhanced respiration under increased OM inputs. The interannual flux variation in the lower Bay was mostly regulated by nutrient inputs and associated stimulation of primary productivity. Both nutrient and OM inputs contributed to the flux variability in the mid Bay. Our results revealed that the CO_2 flux of the mainstem was more sensitive to tributary nutrient inputs associated with hydrological changes, rather than the import of organic matter or high-pCO_2 freshwater.

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Conflict of Interest

The authors declare no competing financial interest.

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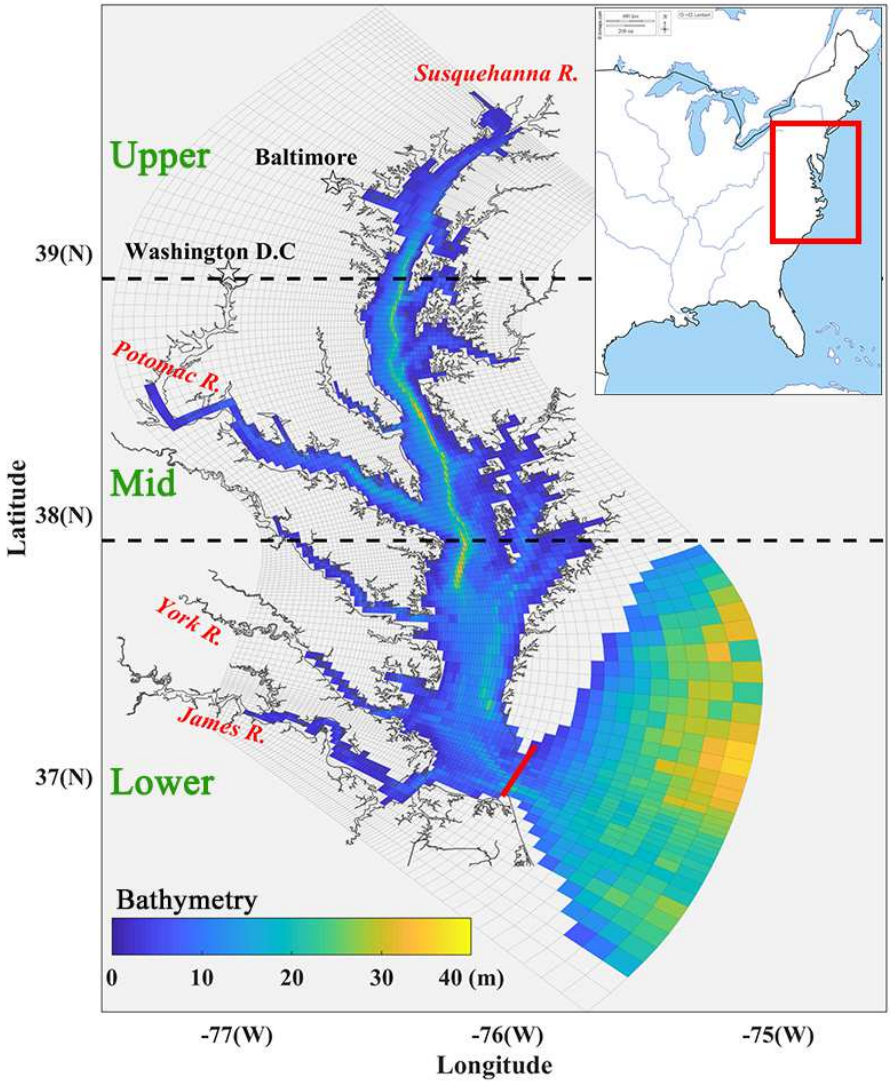

Fig. 1. Map of the Chesapeake Bay, including its regional location, key geographic features, major tributary rivers, the bathymetry, the boundaries between upper, mid and lower Bay, and the mesh grids for model simulations.

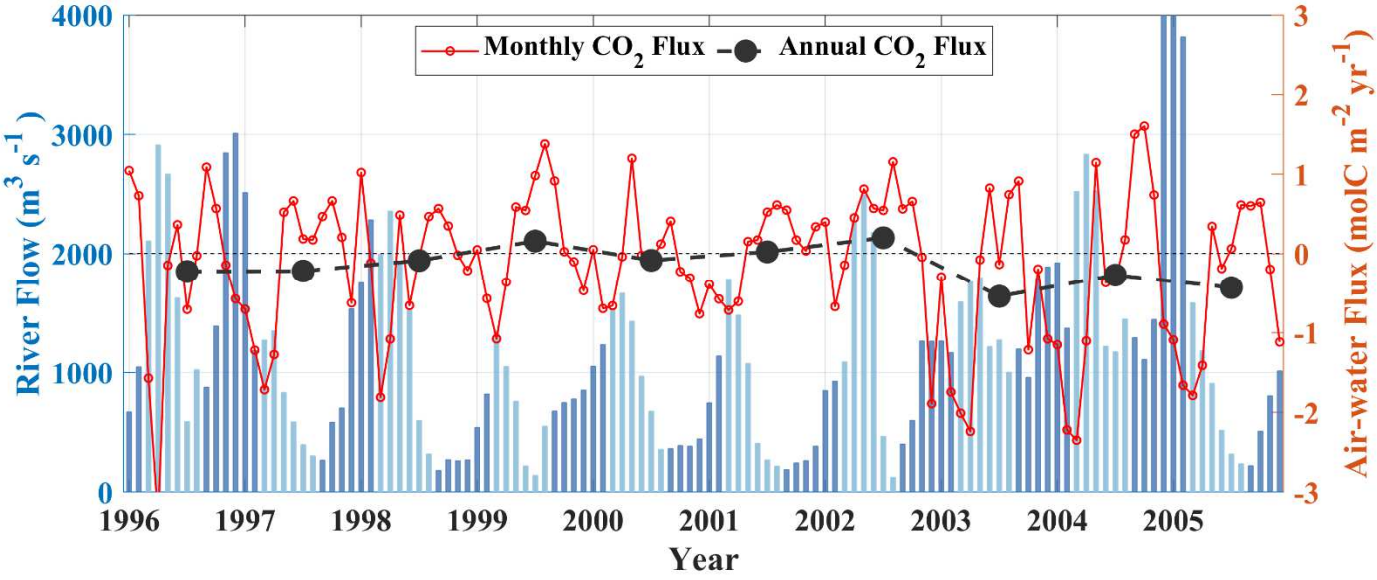

Fig. 2. (Left axis) monthly discharges of the Susquehanna River during 1996-2005. Dark blue represents the winter-spring period, and light blue represents the summer-fall period. (right axis) monthly (red line) and annual (black line) mean CO_2 fluxes of the mainstem Chesapeake Bay during 1996-2005. Positive fluxes (+) represent efflux, and negative fluxes (-) represent influx.

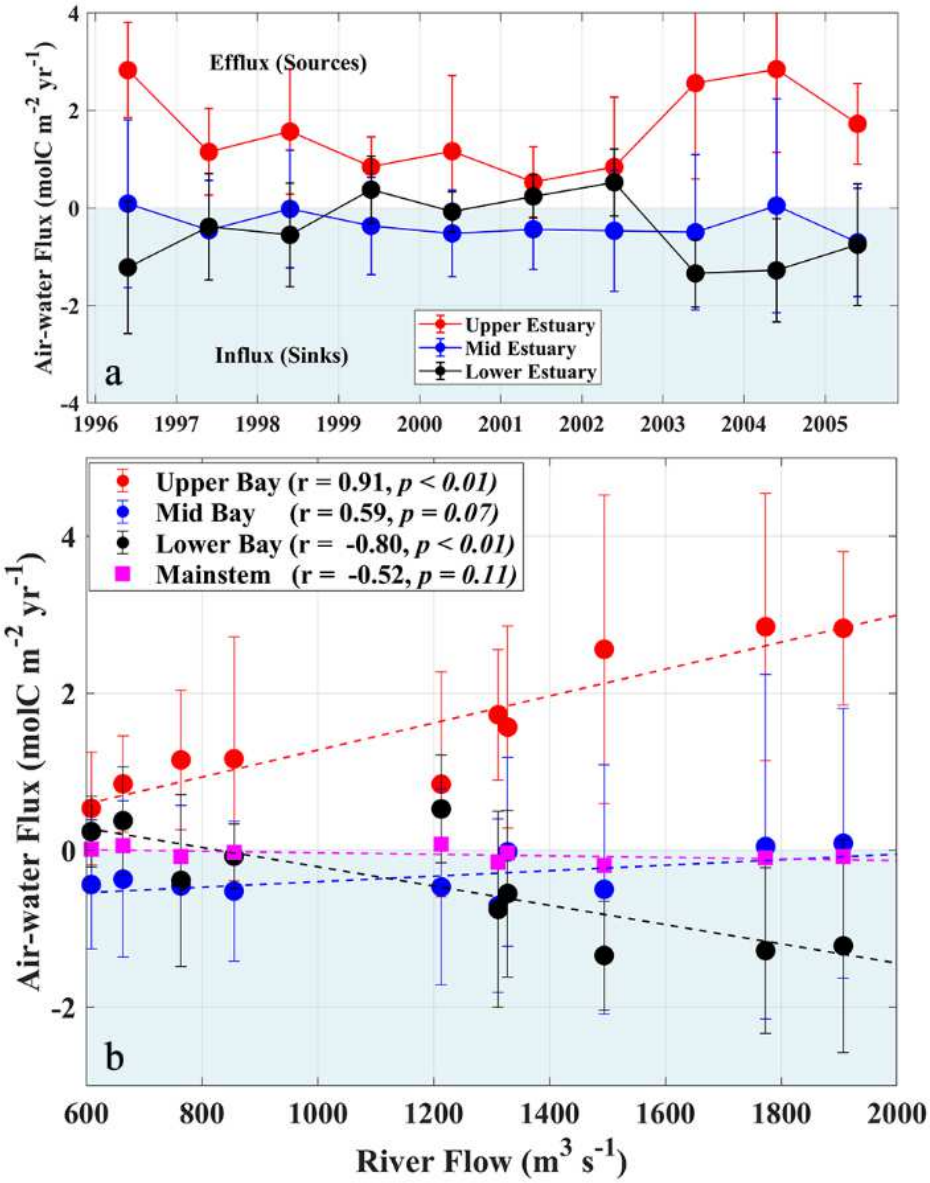

Fig. 3. (a) Model estimated CO_2 fluxes in the upper, mid and lower Bay from 1996 to 2005; (b) comparisons between annual inflows of the Susquehanna River and CO_2 fluxes in the mainstem during the study period. Positive fluxes (+) represent efflux, and negative fluxes (-) represent influx.

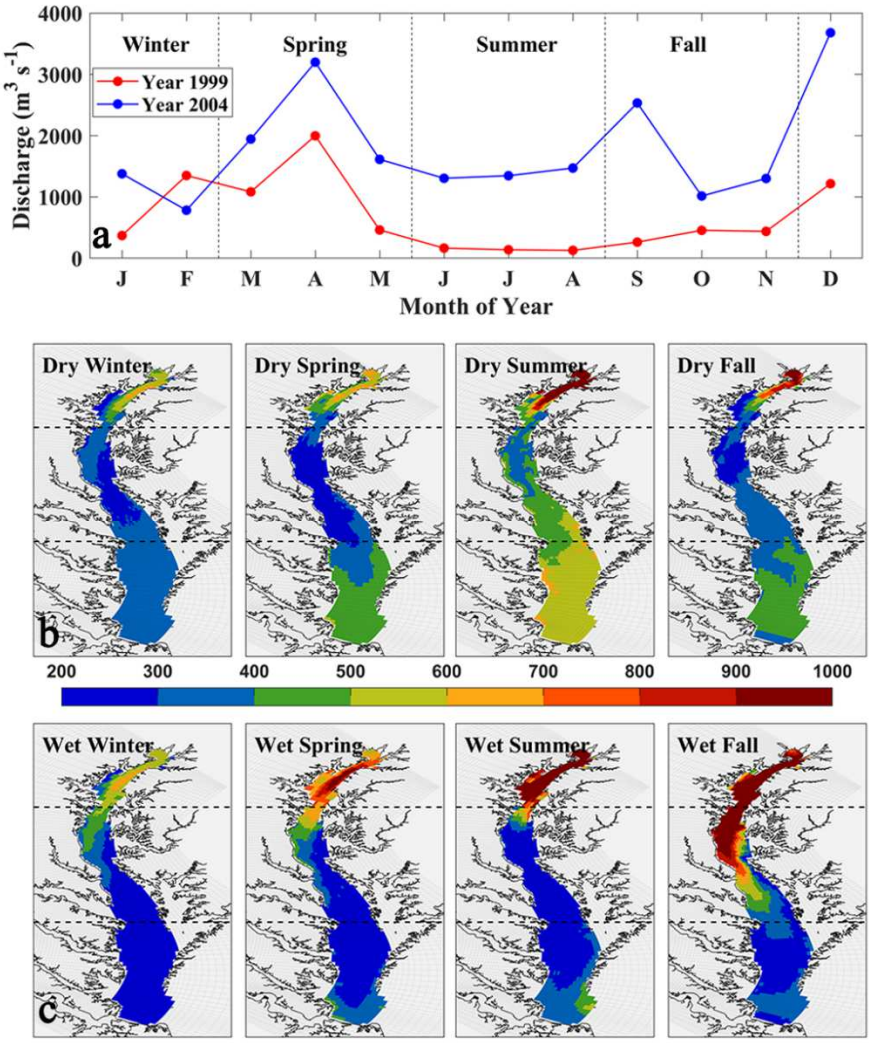

Fig. 4. (a) Monthly Susquehanna River inflows during the dry (1999) and wet (2004) year; seasonally averaged surface water pCO_2 (uatm) during the (b) dry and (c) wet years. The dashed lines are the boundaries of upper, mid and lower Bay.

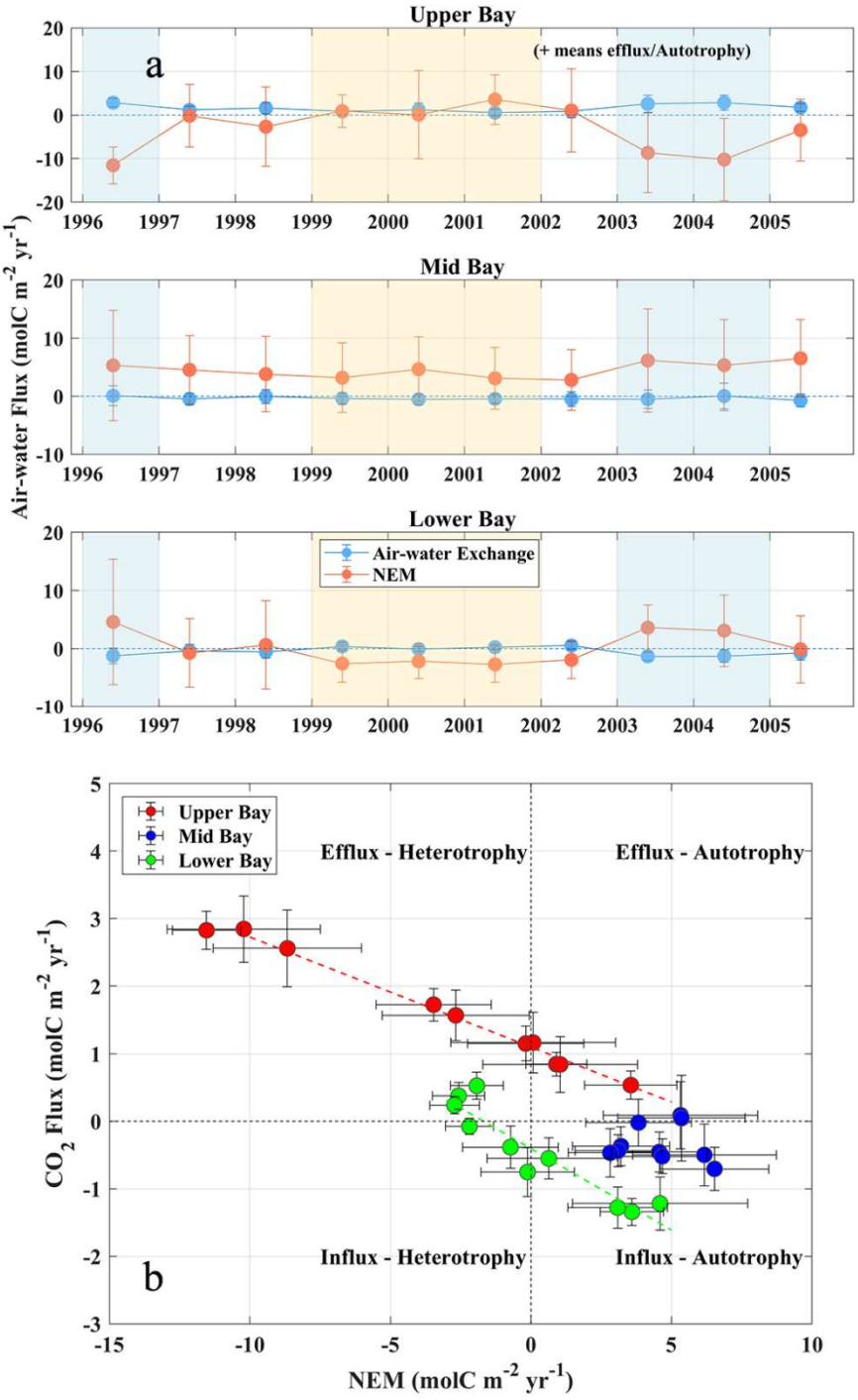

Fig. 5. (a) Comparisons between the annual net ecosystem metabolism (NEM) and CO_2 fluxes in upper, mid and lower Bay during 1996-2005 (light-blue shadow represents wet years, and light-yellow shadow represents dry years.); (b) correlations between NEM and air-water fluxes. The dashed lines are the best fit lines.

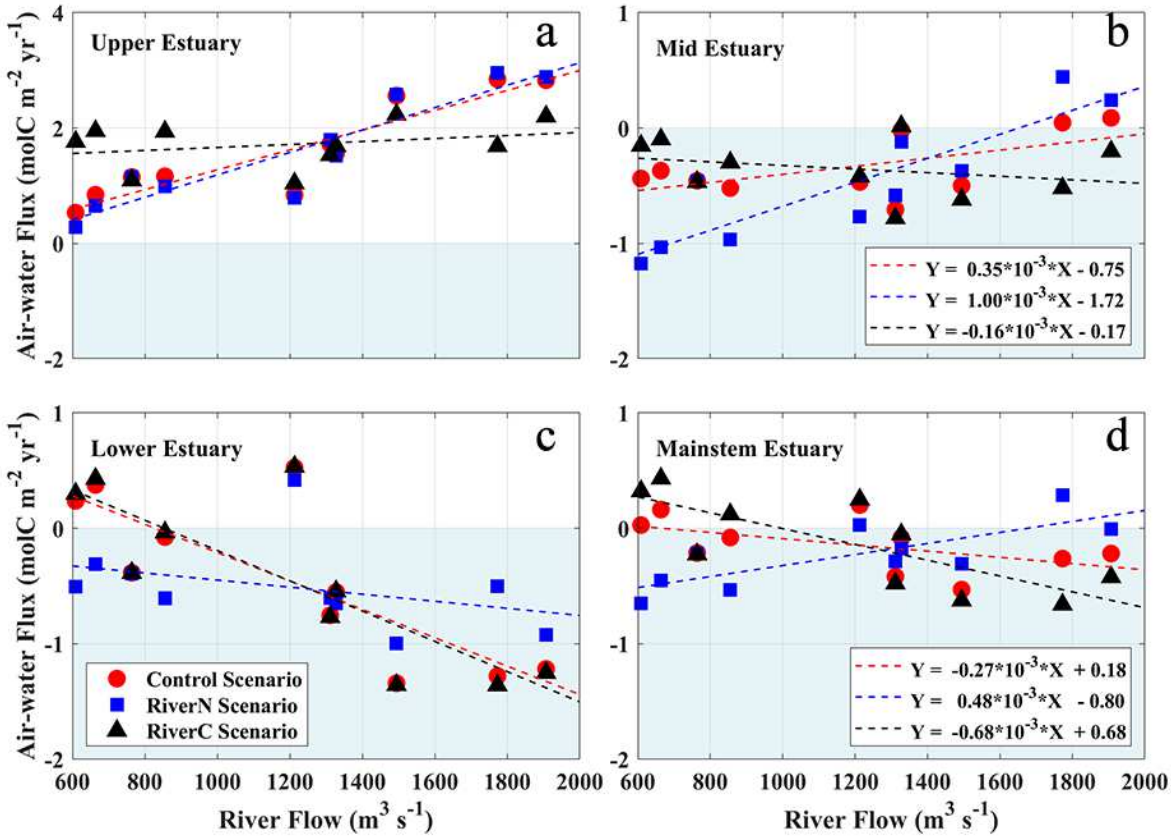

Fig. 6. Comparison between tributary inflows and CO_2 exchanges in the (a) upper, (b) mid, (c) lower and (d) the mainstem Bay for different sensitivity scenarios. Dashed lines are the best fit lines.

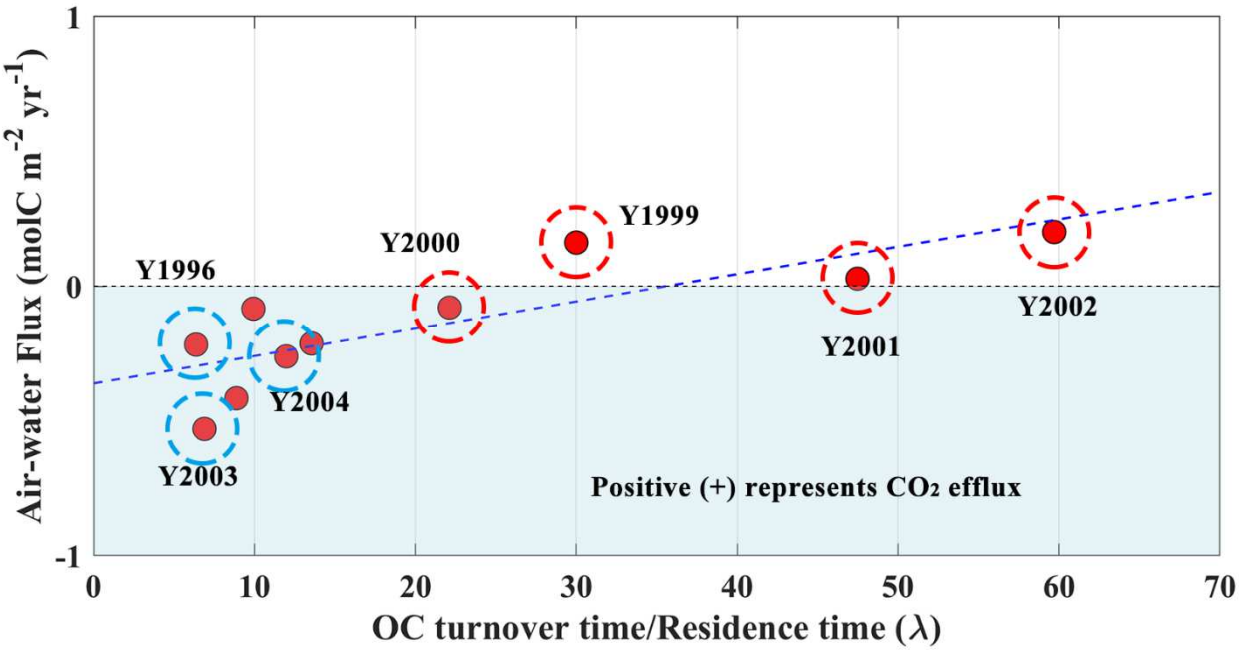

Fig. 7. Comparison between annually averaged air-water fluxes and λ (the ratio of organic carbon turnover time to water residence time) in the mainstem Bay. The dashed line is the best fit line. Red circles represent the dry years, and blue circles represent the wet years.

Graphic Abstract