

Role of inter-annual variability in the magnitude of river discharge on CO₂ fluxes in the Godavari tidal river zone, India

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Abstract

Variations in the magnitude of river discharge may alter pH, $p\text{CO}_2$ of surface water, and flux of CO₂ to the atmosphere in the Tidal River Zone (TRZ). To test this hypothesis, a nearly decade-long time-series data of salinity, pH, and $p\text{CO}_2$ data were collected and analyzed in the TRZ of Godavari River. The higher freshwater discharge occurred in the TRZ during the wet period (June to December) compared to the dry period (January to May). An increase in annual mean discharge was noticed between 2008 and 2019 due to surplus rainfall and the expansion of the hydropower plant. The surface water pH and $p\text{CO}_2$ in the TRZ were controlled by the river discharge as evidenced by the linear positive and negative relationships with the rate of river discharge respectively. A strong relationship was observed between apparent oxygen utilization (AOU) and excess CO₂ indicating a strong influence of heterotrophic activity on $p\text{CO}_2$ levels in the TRZ. The respiration quotient (Rq) was above the aerobic respiration value of 1.35 indicating that terrestrial sources, such as sewage, and groundwater discharge, may have contributed to pH and $p\text{CO}_2$ levels in the TRZ. The CO₂ fluxes during the peak discharge period contribute to 48-88 % of annual mean fluxes followed by moderate (12-52 %) and dry periods (<4 %). The annual mean CO₂ emission amounted to 0.04 ± 0.05 TgC for the area of 36.9×10^6 m² and increased at the rate of 0.005 TgC y⁻¹ between 2008 and 2019 due to an increase in river discharge. The CO₂ flux from the Godavari TRZ (0.04 TgC y⁻¹) contributes to ~0.2% of global tropical estuaries (18 TgC y⁻¹). The CO₂ flux contributed to ~1.5 % of the total carbon (both particulate and dissolved) exported from the Godavari TRZ to the Bay of Bengal and it is lower than the global mean contribution of 16 %.

1. Introduction

The oceans and land biosphere are known to be important sinks for atmospheric CO₂, but a major uncertainty comes from the lack of knowledge on CO₂ fluxes in the land-sea margin, including estuaries and continental shelf (Laruelle et al., 2014; 2018; Roobaert et al., 2019; Dai et al., 2022). The CO₂ fluxes from the land-sea margin play a key role in the global carbon cycle. Despite estuaries occupying a small surface area (7-8 %), high CO₂ fluxes are noticed due to the high rate of primary production, remineralization, and the burial of organic carbon and calcium carbonate (Mackenzie et al., 2005; Cai, 2011; Bauer et al., 2013; Chen et al., 2013). Estuaries are known to be a strong source of CO₂ to the atmosphere due to dominant heterotrophy supported by terrestrial organic carbon inputs (Smith and Mackenzie, 1987; Amdt et al., 2013; Raymond et al., 2013). The estimated CO₂ fluxes from the global estuaries amounted to 0.27 ± 0.23 PgC y⁻¹ to the atmosphere (Laruelle et al., 2010). The mean CO₂ fluxes from the global estuaries contribute to 16 % of the total carbon (dissolved and particulate) fluxes to the ocean from rivers (1060 TgC y⁻¹; Li et al., 2017). These estimates carry significant uncertainties due to a lack of data with reference to space and time. In addition to this, estuaries are notorious for high temporal variability. The budget for CO₂ flux in the Asian estuaries was estimated based mostly on seasonal data (Zhai et al., 2005; Sarma et al., 2001; 2012; Mukhopadhyay et al., 2003; Bouillon et al., 2003; Borges et al., 2018; Nanya et al., 2021), therefore, these estimates may be either under or overestimated. The availability of CO₂ fluxes with high temporal and spatial coverage may decrease the uncertainty of the contribution of CO₂ fluxes to the atmosphere.

The tidal river zones (TRZ), which are influenced by bidirectional surface water oscillations due to tide and unidirectional freshwater discharge (Hoitink and Jay et al., 2016; Jones et al., 2020), play a significant role in controlling nutrients and carbon fluxes to the coastal region (Arndt et al., 2007; Mooney and McClelland, 2012; Knights et al., 2017). The TRZs are altered by the sea level rise, upstream hydrological controls (e.g. Dams), and coastal populations through a change in the balance between tide and hydrology (Destouni et al., 2008; Johnson, 2009; Neumann et al., 2015). The discharge of freshwater into the TRZ of the Indian rivers is mainly controlled by rainfall during summer (June to September) and dams. Hence the variability in freshwater discharge to the TRZ is strongly controlled by the variability in the intensity of monsoon over the Indian subcontinent (Acharyya et al., 2012; Sarma et al., 2011; 2012). Based on daily time-series observations, Sarma et al. (2011) reported that *p*CO₂ levels go to >30,000 μatm during summer (June to September) when peak river discharge occurs in the Godavari TRZ. The high *p*CO₂ levels in the Godavari TRZ were attributed to the injection of porewater *p*CO₂, and the decomposition of soil/terrestrial organic matter

(Sarma et al., 2010; 2011). Perennial dominance of heterotrophy was observed in the Godavari TRZ with a mean P: R ratio of 0.14 ± 0.02 (Sarma et al. 2009). The terrestrial organic matter brought by the river discharge supports 40-99 % of the heterotrophic carbon demand in the TRZ and, therefore, any modifications in the discharge may significantly influence estuarine biogeochemical cycling of material and trace gas fluxes (Sarma et al., 2009; 2012; Rao and Sarma, 2013; 2016). Recently Praveen et al. (2020) reported a declining trend in annual rainfall in the Indian subcontinent, in contrast, an increase was observed during summer (June to September) in central India (Maharashtra, Telangana and Andhra Pradesh states), where the Godavari River flows. In addition to this, a decline in rainfall due to atmospheric extreme conditions, such as El Niño and the Indian Ocean Dipole (IOD), resulted in a decrease in river discharge reported in the Godavari TRZ (Sarma et al., 2015). Therefore, it is hypothesized that the variability in the magnitude of rainfall modifies the river discharge to TRZ resulting in alterations in $p\text{CO}_2$ levels and fluxes to the atmosphere. To test the above hypothesis, near decade-long monthly time-series data were analyzed in this study to evaluate the role of discharge on $p\text{CO}_2$ levels and their fluxes to the atmosphere in the TRZ of Godavari River.

2. Material and methods

2.1. Study Region

The Godavari River system is the largest monsoonal river in the Indian subcontinent and ranks 34th and 32nd in the world with reference to catchment area, and water discharges, respectively. The Godavari River originates in western India at Nasik and flows through eastern India, and opens to the Bay of Bengal at Bhairawapalem (central east coast of India) covering an area of $\sim 330,000 \text{ km}^2$ and a length of 1465 km. Nearly 350 major and medium dams and barrages were constructed in the river basin and the number of dams constructed on the Godavari is the highest among all the river basins in India. The last dam in eastern India, close to the TRZ, was constructed at Dowleiswaram, which is ~ 80 km west of the mouth (Fig. 1). With the onset of rainfall during June, the dam reservoirs are first filled and the surplus water is released to the TRZ (Fig. 1). After the Dowleiswaram dam, the Godavari River is bifurcated into Gautami, and Vasishta with the former being wider than the latter. The daily river discharge data were obtained from Dam authorities at Dowleiswaram. The monthly mean rainfall data over south and central India was obtained from the Ministry of Earth Sciences (<https://data.gov.in/>).

2.2. Sampling

The monthly time-series observations were conducted between 2008 and 2019 in the Gautami branch of Godavari at three locations, representing upper, middle, and lower regions of TRZ, covering the salinity gradient of 0 to 33 (Figure 1). Due to some logistic problems, sampling was not carried out

between 2013 and the middle of 2015. The mean depth of the estuary is 5 m (varies between 3 and 8 m). Surface water (0.5m depth) was sampled using a 5 L Niskin bottle using a mechanized boat starting from the upper to the lower TRZ. The sampling of the entire TRZ was covered within 6-8 hours.

2.3. Measurements

Water column temperature and conductivity were measured using a CTD system (Sea-Bird Electronics, SBE 19 plus, USA). The measured conductivity was converted to salinity following Fofonoff and Millard (1983). The subsampling for dissolved oxygen (DO), pH, and total alkalinity (TA) was carried out using a tube connected to a Niskin bottle into a 100 ml pre-acid washed glass bottle and care was taken to avoid trapping gas bubbles. Dissolved oxygen was measured using the Winkler titration method using potentiometric detection (Carritt and Carpenter, 1966). The pH and TA were measured by the potentiometric method (Metrohm, Switzerland) following Gran titration methods (DOE, 1998). The pH electrodes (Metrohm) were calibrated with NBS buffers and home-made phthalate buffer (Bates, 1973). The temperature corrections were made following Fuhrmann and Zirino (1988) and Perez and Fraga (1987). The precision for pH and TA were 0.002, and $2.0 \mu\text{mol l}^{-1}$ respectively through repeated measurement of samples 20 times. The error in $p\text{CO}_2$ estimation is $<4\%$ based on $\text{CO}_{2\text{sys}}$ version 3.0 (Pierrot et al., 2021).

Dissolved organic carbon (DOC) was measured following High-Temperature Catalytic Oxidation (HTCO) technique using a TOC analyzer (Isotoc, Isoprime, Germany). Samples were collected into pre-acid cleaned glass bottles and acidified using HCl to bring pH to 3. Samples were sparged with high-purity (99.9999 %) helium to remove inorganic carbon before measurements. A detailed description of measurements is given in Kumar et al. (2022).

2.4. Computations

2.4.1. $p\text{CO}_2$ estimations and errors

The $p\text{CO}_2$ was computed using pH and TA using dissociation constants given by Millero et al. (2006) for 0 to 40 salinity ranges using the CO_2 sys program (Pierrot et al., 2021). Since TA measurements include organic alkalinity, the computed $p\text{CO}_2$ may carry some errors. Abril et al. (2015) estimated the influence of organic alkalinity on estimated $p\text{CO}_2$ at different ranges of pH, TA, and DOC concentrations. The pH of the TRZ was mostly >7 (7.2 to 7.8), except in the upper estuary for a few months, during the wet period whereas 8 to 8.3 during the dry period. TA in the Godavari TRZ was close to $1000 \mu\text{M}$ during the wet period and $>2000 \mu\text{M}$ during the dry period. The concentration of DOC was $<200 \mu\text{M}$ during the dry period and between 200 and $500 \mu\text{M}$ during the wet period (Kumar et al., 2022). Based on the Abril et al (2015) computations, the median error on $p\text{CO}_2$ computation due

to organic alkalinity comes to -2 to 5 % during the dry and wet periods except for October and November months when it amounts up to 54 % due to high DOC concentration (>400 μM). These corrections were applied to remove the influence of organic alkalinity. The estimated $p\text{CO}_2$ carries an error of <4 % due to errors in measurements of TA, pH, salinity, temperature, and dissociation constants.

2.4.2. Estimation of Apparent oxygen utilization and excess CO_2

Apparent Oxygen Utilization (AOU; μM) rates were estimated as a product of oxygen concentration (μM) at *in situ* temperature ($^\circ\text{C}$) and salinity ($c(\text{O}_2)_{\text{sat}}$; μM) following Garcia and Gordon, 1992) and measured dissolved oxygen ($c(\text{O}_2)_{\text{meas}}$; μM) as

$$\text{AOU} = c(\text{O}_2)_{\text{sat}} - c(\text{O}_2)_{\text{meas}} \quad \text{-- (1)}$$

The riverine respiratory quotient (R_q) was derived from Richey et al. (1988) to determine the ratio of CO_2 excess (μM) to oxygen depletion (μM) as

$$[\text{CO}_2]_{\text{excess}} = [\text{CO}_2]_{\text{meas}} - [\text{CO}_2]_{\text{eq}} \quad \text{-- (2)}$$

Where $[\text{CO}_2]_{\text{meas}}$ and $[\text{CO}_2]_{\text{eq}}$ represents CO_2 measured and at the equilibrium respectively

$$R_q = -[\text{CO}_2]_{\text{excess}} / (c(\text{O}_2)_{\text{meas}} - c(\text{O}_2)_{\text{sat}}) \quad \text{-- (3)}$$

2.4.3. Estimation of CO_2 fluxes at the water-air interface

The gas transfer velocity (k) is a crucial estimate to obtain the flux of CO_2 at the water-air interface. The different methods are used to parameterize k using wind speed, current velocity, water depth, turbidity, etc. We estimated k following 6 different formulations of k , such as Raymond and Cole (2001), Borges et al. (2004), Wanninkhof (1992, 2014), Jiang et al. (2008), and Ho et al. (2006) and compared the estimated fluxes. The Schmidt number (Sc) was estimated following Wanninkhof (2014) whereas CO_2 solubility ($\text{CO}_{2\text{sol}}$) was estimated using Weiss (1974). The global mean atmospheric CO_2 ($p\text{CO}_{2\text{air}}$) value of 400 μatm is used as no atmospheric CO_2 measurements were carried out. The measured winds from the automated weather station (AWS) installed on the bank of the river at the height of 15 m were converted to winds at the height of 10 m (u_{10} ; m d^{-1}). The flux of CO_2 (FCO_2 ; $\text{mmolC m}^{-2} \text{d}^{-1}$) is defined as

$$\text{FCO}_2 = k \times (Sc/600)^{-0.5} \times \text{CO}_{2\text{sol}} \times (p\text{CO}_{2\text{water}} - p\text{CO}_{2\text{air}}) \quad \text{-- (4)}$$

The monthly mean CO_2 fluxes were upscaled to the entire TRZ using the annual mean surface area of $36.9 \times 10^6 \text{ m}^2$ (Sridevi et al., 2015) for each discharge period and then summed for annual fluxes.

2.5. Classification of discharge periods

The monthly mean river discharge data was computed from daily measured discharge data from Dowleswaram dam authorities. The peak discharge is defined as the months when river discharge is $>1000 \text{ m}^3 \text{ s}^{-1}$ whereas moderate discharge is >100 and $<1000 \text{ m}^3 \text{ s}^{-1}$ and no discharge is defined as either nil or $<100 \text{ m}^3 \text{ s}^{-1}$.

2.5. Statistical analysis and graphical representation

To determine the increase/decrease in nutrients in different segments of the estuary over time, we plotted the nutrient concentrations with time to determine the line of best fit and tested the null hypothesis that the slope of the best-fit line was not significantly different from zero. Both the r^2 and p-value from those regressions are presented. The correlation analysis of time-series data was carried out after removing the seasonal cycle from each time series to remove the impact of temporal autocorrelation on the trend analysis. The statistical analysis of the data, including estimation of the regression coefficient, p-values, and t-test, was carried out using STATISTICA software. The graphical representation of the data was done using GRAPHER software.

3. Results

3.1. Seasonal and long-term variations in rainfall and river discharge

The mean rainfall from June to September in south and central India, where the Godavari River flows, displayed strong inter-annual variability with high rainfall during 2013 and 2019 and low during 2009, and 2015 (Fig. 2a). The rainfall data between 1990 and 2019 displayed weaker decreasing trends during June ($r^2=0.2$; $p<0.1$), and July ($r^2=0.18$; $p<0.1$) months and increasing trends during August ($r^2=0.22$; $p<0.1$), and September ($r^2=0.32$; $p<0.05$) in the south and central India (Supplementary Fig. S1). The river discharge (Q) data between 2008 and 2019 suggests higher discharge during the past 7 years (2013-2019) compared to before (2008-2012) (Fig. 2b). The monthly mean river discharge data (2008-2019) indicates the occurrence of peak discharge during August and September ($>1000 \text{ m}^3 \text{ s}^{-1}$), moderate discharge between October and December (>100 and $<1000 \text{ m}^3 \text{ s}^{-1}$), and no/low discharge during January to May (nil to $<100 \text{ m}^3 \text{ s}^{-1}$; Fig. 3a). The discharge during peak to moderate and low discharge are statistically significant ($t_{\text{stat}} = -7.5$; $p<0.001$). The mean discharge and rainfall from June to September displayed linear positive relation ($r^2=0.33$; $p<0.001$; $n=13$) between 2008 and 2019.

3.2. Seasonal and long-term variability in salinity and inorganic carbon components

The monthly mean salinity data between 2009 and 2019 of the TRZ of Godavari was above 22 in the middle and lower TRZ from January to May but it was close to 10 in the case of the upper TRZ. The

drop in salinity was noticed during June with close to zero salinity (freshwater) from August to October and increased back to ~20 by December (Fig. 3c). The annual amplitude of variability in salinity was small in the upper TRZ (0-15) whereas it was high in the middle and lower TRZ (0-30) (Fig. 3b). The monthly mean dissolved oxygen concentration were low during peak discharge period and high during moderate discharge period (Fig. 3c). The monthly mean pH and TA followed salinity with high during the dry period (January to May), and low during the wet period (July to December) (Fig. 3d, e). The mean discharge, pH, and $p\text{CO}_2$ during different discharge periods for each studied year are given in Table 1. The pH during the dry period was uniformly high in the entire TRZ whereas relatively low pH was observed in the upper followed by middle and lower TRZ. In contrast, lower TA was observed during all seasons in the upper than middle, and lower TRZ. The climatological monthly mean $p\text{CO}_2$ levels were ~500 μatm from January to May and increased to ~15000 μatm from August to September, and decreased to ~800 μatm by December. The peak in $p\text{CO}_2$ was found during August in the upper and middle TRZ whereas in September in the lower TRZ (Fig. 3f).

The time-series salinity data suggest lower salinity (almost freshwater) during the wet period in the entire estuary and increased to mesohaline conditions (salinity of 5 to 33) during the dry period (Table 1). The amplitude of seasonal variation in salinity was lower (0-20) in the upper than middle and lower TRZ (0-33) (Fig. 4). When the entire salinity data were regressed with river discharge, a significant negative relationship was observed ($r^2=-0.62$; $p<0.001$; $n=108$). High pH and TA were observed associating with low discharge and high salinity and vice versa with high discharge and low salinity (Fig. 4). The seasonal variability in the amplitude of pH was higher in the upper (6.7 to 8.4; $t_{\text{stat}}=-10.6$; $p<0.001$) than in the middle (6.8 to 8.3; $t_{\text{stat}}=-6.4$; $p<0.001$) and lower TRZ (6.9-8.2; $t_{\text{stat}}=-5.0$; $p<0.001$). The decrease in pH to 6.5 was observed during the peak discharge period in the entire TRZ in 2019 associated with the highest river discharge (Fig. 2b). In contrast, the amplitude of TA was lower in the upper TRZ (990-2200 μM) than in the middle (1000-2500 μM) and lower TRZ (1000-2600 μM). The monthly mean $p\text{CO}_2$ varied between 300 and 13000 μatm with an exceptionally high $p\text{CO}_2$ of 20,000 μatm being noticed during September 2019. The seasonal amplitude of $p\text{CO}_2$ decreased from the upper to the lower TRZ (Fig. 4).

The pH in the entire estuary displayed a non-linear relation with salinity (Fig. 5a). The pH was lower in the freshwater region, and it increased sharply to a value of 8 as the shift of salinity took place from 0 and 15. The pH again decreased slowly towards the lower estuary (Fig. 5a; $r^2=0.80$; $p<0.001$). TA displayed significant a linear positive relation with salinity in all three regions of the TRZ (Fig. 5b; $r^2=0.75$; $p<0.001$). $p\text{CO}_2$ was high in the low salinity region and decreased to <1000 μatm after a salinity of 10 (Fig. 5c; $r^2=0.50$; $p<0.001$). The pH and $p\text{CO}_2$ displayed significant positive and negative

linear relations respectively with river discharge in the upper and middle estuaries during the peak and moderate discharge (October to December) periods (Fig. 6). The slope of the relationship between discharge and pH was increased whereas decreased in the case of discharge and $p\text{CO}_2$ from upper to lower TRZ (Fig. 6). The pH and $p\text{CO}_2$ displayed a significant linear positive and negative relation with salinity during the dry period (Fig. 6). AOU in the surface waters displayed a significant linear positive relation with excess CO_2 in the upper, middle and lower TRZ ($p < 0.001$ at all three regions) with a higher slope in the upper and middle (5.4-5.5) than lower TRZ (2.35) (Fig. 7a-c). The high excess CO_2 was observed in the low salinity region and decreased towards high salinity (Fig. 7d-f). The riverine respiratory quotient (Rq) varied between 0.3 and 13 with higher values in the upper than lower TRZ (Fig. 7g-i).

3.3. CO_2 fluxes in the Godavari TRZ

The CO_2 fluxes from the Godavari TRZ were estimated using different parameterizations of transfer velocity (k) (Table 2). The CO_2 fluxes varied between -13 and 1714 $\text{mmolC m}^{-2} \text{d}^{-1}$, based on Raymond and Cole (2001), with higher fluxes during the peak discharge (39-1714 $\text{mmolCm}^{-2} \text{d}^{-1}$) followed by the moderate (63-480 $\text{mmolC m}^{-2} \text{d}^{-1}$) and the dry periods (-14 to 298 $\text{mmolC m}^{-2} \text{d}^{-1}$). The CO_2 flux during the peak discharge period is the highest and contributed to >70 % of annual flux (Fig. 8). The annual mean CO_2 flux from the Godavari TRZ was $246 \pm 309 \text{ mmolC m}^{-2} \text{d}^{-1}$, based on Raymond and Cole (2001) parameterization of k (Table 2).

4. Discussion

4.1. *Potential reasons for the variability in river discharge*

The salinity of the Godavari TRZ is mainly controlled by the river discharge with the dominance of freshwater (near 0 salinity) during the discharge period and saline water during the dry period (Fig. 4). Sridevi et al. (2015) found the development of strong stratification of the water column before (June) and after peak discharge periods (i.e., October to December) due to a decrease in the magnitude of discharge. The entire TRZ was filled with fresh water between June and September when 80 % of the annual rainfall is received at the basin (Soman and Kumar, 1990). Hence, Godavari is called a monsoonal river as the river is fed by monsoonal precipitation (Acharyya et al., 2012; Sridevi et al., 2015). The monthly mean river discharge during the study period (2008-2019) displayed significant inter-annual variability (Fig. 2) with high discharge during 2013 and 2019 associated with a strong monsoon. Chattopadhyay et al. (2015) found that the strong extratropical SST anomalies in the North Pacific and North Atlantic in conjunction with weak tropical SST anomalies (weak La Niña) resulted in above-normal rainfall during 2013 whereas extreme positive Indian Ocean Dipole (IOD)

represented by anomalously high rainfall during 2019 (Ratna et al., 2021). The occurrence of El Niño in 2009 weakened the monsoon resulting in below-normal rainfall and discharge by 23 and 75 % respectively (Acharyya et al., 2012; Sarma et al., 2015). Therefore, extreme atmospheric events modify the strength of the monsoon that alters the river discharge to the TRZ of Godavari. In addition to this, anthropogenic activities also modified the river discharge pattern. For instance, a significant increase in the magnitude of discharge was noticed after 2012 (Fig. 2a) associated with the expansion of the hydropower plant at Sileru in 2013-2014 after the bifurcation of Andhra Pradesh State in India that enhanced electricity demand. As a result, more water is released to the Dowleiswaram dam reservoir beyond its capacity leading to the release of water to the Godavari TRZ even during the dry period. The lack of dredging activities in the Dowleiswaram Dam reservoir for more than 10 years decreased the depth of the reservoir and its capacity in holding water (Dowleiswaram Dam authorities, personal communications, 2022). This enhanced discharge of water to TRZ in recent years. The strong impact of hydraulic modification on CO₂ and CH₄ emissions was reported elsewhere (Borges et al., 2018; Castro-Morales et al., 2022; Crawford et al., 2017). Nevertheless, the enhanced river discharge, either due to natural (monsoon) or anthropogenic (hydropower project or shallowing of dam reservoir) may have a significant impact on the pH, pCO₂ levels, and CO₂ flux to the atmosphere in the Godavari TRZ.

4.2. Role of discharge in controlling pH and pCO₂ of the Godavari TRZ

River water has acidic pH, as the river is fed by monsoon rainfall, which has a pH between 5 and 6 (Prasad et al., 2013; Sarma et al., 2011). Hence, low pH is associated with low salinity, high discharge, and high rainfall. In addition to this, modification of organic matter through microbial and photochemical degradation in the river and dam reservoir would decrease pH (Prasad et al., 2013). Therefore, low pH during the discharge period is contributed by the acidic nature of the source water and the decomposition of organic matter in the dam reservoirs. In contrast, freshwater discharge is minimal and saline water dominates during the dry period resulting in high pH (>7.8) (Fig. 4). The relationship between salinity and pH of the entire data suggests that large variability in pH (6.3 to 7.6) at freshwater region (<0.5 salinity) than high salinity (15-33) region (7.5-8.2) due to large variability in pH of river water that enters to the TRZ (Fig. 5a). A laboratory experiment was conducted by mixing different proportions of seawater (from the mouth of the estuary) with the freshwater (upper estuary) and measuring pH at different proportions. An increase in pH was observed up to 15-20 salinity and it was increased slowly up to a salinity of 30 (Fig. 5a). The overall relationship between pH and salinity was followed by the simple mixing of freshwater and saline water in all three locations. However, the scatter in pH from that of the mixing line suggests some modification caused by the microbial and

photochemical decomposition of organic matter and groundwater discharge. In contrast, Sarma et al. (2001) found a positive relationship between salinity and pH in the Mandovi-Zuari estuaries on the central west coast of India and attributed it to the decrease in pH caused by sediment-water interactions. Nevertheless, the relationship between salinity and pH in the Godavari TRZ suggests dominant mixing process controls pH more than *in situ* modifications, such as microbial and photochemical decomposition of organic matter.

TA displayed a conservative behaviour with an increase from freshwater to seawater endmember in the mixing experiment. Similarly, the entire data collected between 2008 and 2019 displayed a linear positive relationship following the simple mixing line (Fig. 5b). The computed $p\text{CO}_2$ from pH and TA in the mixing experiment decreased sharply from freshwater to 2.5 salinity and slowly to the salinity of 30 (Fig. 5c). The measured data at upper, middle and lower TRZ between 2008 and 2019 followed the typical mixing trend suggesting the spatial and temporal variability in TA and $p\text{CO}_2$ were mainly controlled by the mixing of seawater and freshwater. These data suggest that modifications in the river discharge may significantly modify the inorganic carbon system and fluxes to the atmosphere in the Godavari TRZ.

The increase in river discharge was observed during all seasons associated with a significant negative relationship between river discharge and pH whereas linear positive relation with $p\text{CO}_2$ suggests that enhanced river discharge decreased pH and increased $p\text{CO}_2$ levels in the Godavari TRZ. The high $p\text{CO}_2$, ranging between 12000 and 20000 μatm , was observed during the peak discharge period. The peak in $p\text{CO}_2$ is mainly caused by the removal of upper sediment due to the high flow of discharge, leading to the input of pore water CO_2 into the water column. In addition, a higher rate of bacterial respiration was reported in the TRZ leading to the decomposition of a high amount of organic matter and the release of CO_2 into the atmosphere (Sarma et al., 2011; Gawade et al., 2017). High $p\text{CO}_2$ levels were reported in Rhine (~25000 μatm ; Kempe, 1982), Scheldt (~15200 μatm ; Borges and Frankignoulle, 2002) and Xijiang estuaries (11000 μatm ; Yao et al., 2007) and attributed to the pollutants received to these estuaries. The rate of discharge displayed a significant linear positive relationship with $p\text{CO}_2$ levels during peak ($r^2=0.42$; $p<0.001$) and moderate discharge ($r^2=0.61$; $p<0.001$) periods. Therefore, the magnitude of discharge is important on $p\text{CO}_2$ levels in the TRZ of Godavari. An increase in the number of days with a magnitude of discharge of >5000 , >1000 , and $>500 \text{ m}^3 \text{ s}^{-1}$ was observed from 2008 to 2019 (Supplementary Figure S2a) associated with a decrease in the mean pH and an increase in the mean $p\text{CO}_2$ during the peak discharge period in the upper, middle and lower TRZ (Supplementary Figure S2b, c). This suggests that the magnitude of discharge determines the pH and $p\text{CO}_2$ level of waters in the Godavari TRZ.

4.3. Internal cycling and external sources

In addition to the modifications in the river discharge, modifications in the pH and $p\text{CO}_2$ were also contributed by the internal cycling of organic matter and terrestrial sources as it is evidenced by the scatter in the data from that of a simple mixing line. The perennial existence of heterotrophy was reported in the Godavari TRZ (Sarma et al., 2009), and this would result in a decrease in pH and the formation of CO_2 (Borges and Abril, 2011; Smith and Hollibaugh, 1993). To determine the role of metabolism on $p\text{CO}_2$, ecosystem metabolism was constrained by assessing the trends of regression between AOU and excess CO_2 . Overall, a significant positive relationship was observed between AOU and excess CO_2 during the entire study period (Fig. 7a-c). The positive AOU (0-92 μM) for the entire study period suggests that undersaturation of oxygen in the TRZ may be caused by dominant heterotrophy. The higher excess CO_2 was observed in the upper and it was decreased by half to the lower TRZ of Godavari with a higher slope of AOU to CO_2 excess relationship in the upper (5.3) than in lower TRZ (2.3; 7a-c). The relationship was stronger during peak ($r^2=0.39$; $p<0.001$) and moderate discharge ($r^2=0.49$; $p<0.001$) periods compared to the dry period ($r^2=0.26$; $p<0.01$). This may be due to the input of labile organic matter from the STP (sewage treatment plant)/sewage spread to the entire TRZ during the peak and moderate discharge periods. The isotopic composition of the particulate organic matter suggests possible terrestrial sources including sewage associated with high bacterial respiration rates (Sarma et al., 2014; Gawade et al., 2017) during the peak and moderate discharge than the dry periods. This might have enhanced both AOU and excess CO_2 during the moderate and peak discharge periods. The low oxygen concentrations were observed during the peak discharge period and increased during the moderate discharge period (Fig. 3c) associated with high phytoplankton biomass (Acharyya et al., 2012). Due to the lack of STP discharge data into the TRZ of Godavari, the impact of STP could not be confirmed. The higher excess CO_2 in the low salinity region in the upper estuary, where tidal influence is limited hence residence time is higher, and its exponential decrease to the high salinity (lower TRZ) (Fig. 7d-f) suggests that higher $p\text{CO}_2$ levels in the former regions may be contributed through microbial decomposition of organic matter.

The riverine respiratory quotient (R_q) varied between 0.3 and 13 in the Godavari TRZ with higher values in the upper than lower TRZ (Fig. 7g-i). Any positive deviation of R_q from 1.35 indicates anaerobic respiration (Berggren et al., 2012) or allochthonous inputs, such as groundwater discharge, sewage, terrestrial organic carbon respiration etc. The mean R_q in the upper TRZ was higher (5.3) followed by the middle (4.1) and lower TRZ (2.5) during the peak discharge period when salinity was <0.5 . In contrast, R_q was <1.0 during the dry period when high salinity (>10) was observed suggesting that high water residence time (>10 days; Sridevi et al., 2015) and low suspended load (Sarma et al.,

2009) supported suitable conditions for photosynthetic oxygen production. The R_q during the peak discharge period (>1.35) was higher than aerobic respiration indicating that other drivers such as terrestrial inputs (sewage, effluents) and groundwater may be contributed. This is consistent with Gawade et al. (2017) who reported dominant sources of terrestrial organic matter in the Godavari TRZ during the peak discharge period. Rengarajan and Sarma (2015) measured submarine groundwater discharge (SGD) in the Godavari TRZ during the moderate discharge period and estimated that ~30 % of the nutrients and dissolved inorganic carbon (DIC) in the TRZ were contributed by SGD. The significant contribution of CO_2 , N_2O , and CH_4 from the groundwater to the estuary was reported (Rao and Sarma, 2013; 2016; Sarma et al., 2011) suggesting that a significant source of inorganic carbon components from groundwater modifies pH and $p\text{CO}_2$ levels of TRZ. However, its impact during the peak discharge and dry periods is unknown.

4.4. Fluxes of CO_2 from the Godavari TRZ

The transfer velocity (k) of gas is important in the estimation of the flux of CO_2 to the atmosphere. Numerous methods have been used to parameterize k within different ecosystem types (Borges et al., 2004; Ho et al., 2016; Raymond and Cole, 2001; Wanninkhof, 1992; 2014). Gas exchange is derived as a function of wind speed (Wanninkhof, 1992), a combination of wind speed, depth, and current velocity (Borges et al., 2004), the morphology of the river channels and water velocity (Raymond and Cole, 2001), and wind speed, depth, current velocity, and turbidity (Abril et al., 2009). I compared 6 different transfer velocity models (Table 2) for flux estimations in the Godavari TRZ. The higher k values were estimated using Borges et al. (2004) parameterization and the least using Wanninkhof (2014). The Borges et al. (2004) parameterization is based on the *in-situ* measurement using the floating chamber technique, which includes current velocity, and gives short-term mean k whereas Wanninkhof (2014) method is based on ^{14}C of DIC that gives long-term mean k . The highest annual mean fluxes were estimated based on k parameterizations of Borges et al (2004) ($351 \pm 41 \text{ mmolC m}^{-2} \text{ d}^{-1}$) whereas the least fluxes ($116 \text{ mmolC m}^{-2} \text{ d}^{-1}$) by Wanninkhof (2014). The variability in the magnitude of CO_2 fluxes is caused by the complexity of the k parameterization. Raymond and Cole's (2001) parameterization of k is based on the morphology of the river channels and water velocity, therefore, reflects the better k for the study region. Hence the CO_2 flux estimated by Raymond and Cole (2001) parameterization of k is used for further discussion. The flux of CO_2 during the peak discharge period (June to September) was higher by about 3 times than the moderate discharge period, which is 4 times higher than the dry period (Table 2). The CO_2 fluxes during the entire study period ranged between -13 and $1714 \text{ mmolC m}^{-2} \text{ d}^{-1}$, based on Raymond and Cole's (2001) parameterization, with an annual mean flux of $246 \pm 309 \text{ mmolC m}^{-2} \text{ d}^{-1}$. The higher flux was found during the peak

discharge period (39-1713 (mean 504 ± 378) $\text{mmolC m}^{-2} \text{d}^{-1}$) followed by the moderate discharge (63 to 480 (mean 225 ± 107) $\text{mmolC m}^{-2} \text{d}^{-1}$) and the dry periods (-14 to 298 (mean 29 ± 66) $\text{mmolC m}^{-2} \text{d}^{-1}$). The contribution of flux during the peak discharge period amounts to 48 to 88 % of the annual flux from the Godavari TRZ whereas it was 12 to 52 % and <4 % during the moderate and dry periods respectively (Fig. 8). The mean CO_2 flux and discharge rate displayed a significant linear positive relationship during the peak ($r^2=0.52$; $p<0.001$) and moderate ($r^2=0.41$; $p<0.001$) discharge periods suggesting that enhanced river discharge increased flux of CO_2 to the atmosphere. Interestingly the contribution of CO_2 emission during the moderate discharge period to annual emission was more during 2009 (42 %), 2011 (33 %) and 2017 (38 %) associated with low discharge compared to other years (Fig. 2b). The lower rate of river discharge enhanced stratification of the water column and increased the residence time of water in the TRZ (Sridevi et al., 2015) resulting in more amount of organic matter being decomposed leading to the formation of CO_2 . The concentration of dissolved oxygen was lower during the moderate discharge period of 2009, 2011, and 2017 than in other years by 10-20 μM suggesting that *in situ* decomposition of organic matter (microbial and photochemical) may be a possible contributor to high CO_2 levels and fluxes to the atmosphere.

The annual mean CO_2 flux observed in the Godavari TRZ (-13 to 1714 mean of 246 ± 309 $\text{mmolC m}^{-2} \text{d}^{-1}$) is much higher than that found in the Cochin estuary in India (65-267 $\text{mmolC m}^{-2} \text{d}^{-1}$; Gupta et al., 2009), tropical mangrove systems in Vietnam, Bahamas and Papua New Guinea (32-128 $\text{mmolC m}^{-2} \text{d}^{-1}$; Koné and Borges, 2008; Borges et al., 2003), Australian mangrove system (107 $\text{mmolC m}^{-2} \text{d}^{-1}$; Call et al., 2015) in the tropical region. The CO_2 fluxes from global estuaries are given in Supplementary Table 1. This suggests that CO_2 flux from the Godavari TRZ is the highest per unit area compared to other estuaries in the globe. The mean CO_2 flux ($89.8 \text{ molC m}^{-2} \text{y}^{-1}$) is close to that of Tamar estuary (UK; $74.8 \text{ molC m}^{-2} \text{y}^{-1}$), Thames estuary (UK; $73.6 \text{ molC m}^{-2} \text{y}^{-1}$) and Douro estuary (Portugal; $76 \text{ molC m}^{-2} \text{y}^{-1}$) (Supplementary Table 1). Sarma et al. (2012) estimated seasonal (wet and dry period) CO_2 fluxes in the Indian estuaries and found them to be $60.7 \text{ mmolC m}^{-2} \text{d}^{-1}$ during the wet and $5.5 \text{ mmolC m}^{-2} \text{d}^{-1}$ during the dry periods from the Godavari TRZ. Based on the daily measurements of inorganic carbon components at one location in the Godavari estuary in 2009, Sarma et al. (2011) estimated that $144 \text{ mmolC m}^{-2} \text{d}^{-1}$ of CO_2 is effluxed into the atmosphere. The variability in flux estimation is caused by the spatial and temporal coverage of the measurements in the TRZ. The present study covers high temporal and spatial coverage of $p\text{CO}_2$ measurements than previous estimations (Sarma et al., 2011; 2012). Since the temporal variability in CO_2 flux is very large, as noticed in the present study, the earlier estimations carry large errors. In addition to this, the increase in CO_2 emissions in the present study also contributed to the increase in river discharge in recent years.

These results are consistent with the earlier reports (Borges et al., 2018; Castro-Morales et al., 2022; Crawford et al., 2017) which reported that hydraulic modifications have a significant impact on CO₂ and CH₄ fluxes from the estuaries.

To obtain the annual mean CO₂ emissions from the TRZ of Godavari, monthly mean CO₂ emissions were computed first followed by annual emissions by summing them. The annual mean CO₂ emission between 2008 and 2019 (near decade) to the entire study region (36.9 x 10⁶ m²) amounted to 0.04±0.05 Tg (1 Tg= 10¹² gC) from the Godavari TRZ to the atmosphere. The enhanced mean water-to-air fluxes of CO₂ during the peak discharge period in the entire Godavari TRZ were low during 2009, 2011, and 2017 (0.011 to 0.017 TgC) compared to other years (0.02 to 0.04 TgC) due to low river discharge during the former period (Fig. 8a). The annual mean flux of CO₂ from the entire Godavari TRZ (0.04±0.05 Tg) contributes to ~0.2 % of the CO₂ flux from the tropical estuaries (~18±2 TgC y⁻¹; Laruelle et al., 2010; Roobaert et al., 2019). The annual mean CO₂ flux increased between 2008 and 2019 at the rate of ~0.005 TgC y⁻¹ due to the increase in discharge caused by increased precipitation and expansion of hydropower projects.

Godavari estuary export ~0.45 TgC of dissolved organic carbon (DOC; Krishna et al., 2015), 0.75 TgC of particulate organic carbon (POC; Balakrishna and Probst, 2005) and 1.5 TgC of dissolved inorganic carbon (DIC; Krishna et al. 2019) annually through lateral transport to the Bay of Bengal. The total (inorganic and organic) carbon flux (lateral transport and flux to atmosphere) from the Godavari estuary amounts to 2.7 TgC y⁻¹. The annual mean air-sea flux contributes to ~1.5 % of the total carbon export from the Godavari estuary and it is much less than the global contribution of estuarine flux to the atmosphere (170 TgC y⁻¹) to the total carbon flux (1060 TgC y⁻¹) of 16 % suggesting that less CO₂ effluxed to the atmosphere than the lateral flux of carbon to the coastal ocean from Godavari TRZ.

5. Summary and Conclusion

Freshwater discharge to the TRZ of Indian rivers is strongly controlled by monsoonal rainfall. The long-term trends in the rainfall suggest significant increasing trends during August and September, when maximum discharge occurs, between 1990 and 2019 over the Indian subcontinent leading to an increase in river discharge. Based on near decade-long (2008 to 2019) observations in the Godavari TRZ, it is noted that the magnitude of discharge displayed a negative relationship with pH and positive relation with *p*CO₂ suggesting that discharge played a significant role in variability in the inorganic carbon system. The relation of salinity with pH, TA, and *p*CO₂ suggested that it follows the simple mixing of freshwater with saline water indicating that the fraction of freshwater released to the TRZ determines pH and *p*CO₂ levels. The linear positive relationship between AOU and excess CO₂

suggests a significant role of heterotrophic activity in the release of CO₂. The respiration quotient was above the aerobic respiration value of 1.35 indicating that terrestrial sources, such as sewage, STP, groundwater seepage, etc. are possible. The annual mean CO₂ flux at the water-air interface amounted to 0.04±0.05 Tg (1 Tg=10¹² gC), to which >50 % is contributed during the peak discharge period. The fluxes of CO₂ to the atmosphere increased at the rate of 0.005 TgC y⁻¹ between 2008 and 2019 due to an increase in river discharge.

This study suggests that the modification of river discharge significantly impacts CO₂ fluxes to the atmosphere from the Godavari TRZ. The expansion of hydropower plants increased freshwater discharge to the TRZ, in addition to an increase in monsoonal rainfall resulting in enhanced CO₂ fluxes to the atmosphere in recent years. In contrast, the interlinking of rivers is underway in India to conserve freshwater to meet demand during the dry period. This may decrease fluxes of CO₂ to the atmosphere during the peak discharge period but may increase the fluxes during the moderate discharge period. Nevertheless, the overall decrease in CO₂ fluxes to the atmosphere is anticipated due to interlinking rivers. The contrasting impact of river discharge due to an increase in monsoon rainfall, expansion of thermal power plants, and interlinking rivers may modify the magnitude of discharge and seasonality which has a significant impact on CO₂ fluxes. Close monitoring of these parameters is essential to evaluate future changes in CO₂ fluxes to the atmosphere from the Indian estuaries. Such modification may also influence the ecosystem structure in the TRZ which needs to be evaluated in the future. Therefore, future comprehensive biogeochemical studies are warranted in highly dynamic systems to evaluate the influence of natural and human-made modifications in river discharge on carbon cycling and ecosystem dynamics.

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Table. 1: The mean (\pm standard deviation) magnitude of discharge, pH and pCO₂ levels during different discharge periods between 2008 and 2019 in the Godavari estuary.

Year	Discharge (m ³ s ⁻¹)			pH			pCO ₂ (µatm)		
	Peak discharge	Moderate discharge	Dry period	Peak discharge	Moderate discharge	Dry period	Peak discharge	Moderate discharge	Dry period
2008	2019±2784	1331±1381	7±16	7.300±0.3	7.563±0.5		2430±3861	1772±3386	
2009	665±768	531±381	0±0	7.365±0.3	7.472±0.4	8.017±0.2	1271±2225	1841±4163	502±412
2010	2600±3009	818±958	0±0	7.388±0.4	7.403±0.3	7.987±0.2	2003±3548	1994±3906	583±660
2011	1315±2268	206±295	11±24	7.364±0.4	7.503±0.3	7.890±0.2	2855±4292	1294±2181	601±998
2012	2374±2869	841±1354	0±0	7.361±0.4	7.279±0.4	8.007±0.1	1949±3022	1461±2653	521±303
2013	7319±5192	3478±2485	210±39						
2014	4041±4792	1003±826	252±95						
2015	3364±3844	1111±1365	236±49		7.415±0.5			2050±3593	
2016	4426±3085	5518±8613	173±71	7.181±0.4	7.274±0.4	7.987±0.1	2895±4944	2666±1878	503±160
2017	3122±3875	1104±1205	142±44	7.205±0.4	7.424±0.3	7.983±0.2	1908±3257	1727±2656	578±330
2018	3148±4199	2505±660	179±73	7.236±0.3	7.451±0.4	7.963±0.2	2392±3969	1814±2871	612±344
2019	10208±14000	4870±4360	237±103	7.022±0.5	7.180±0.2	7.679±0.2	3543±7093	2764±4308	979±775

Table 2: Mean water-to-air CO₂ fluxes during different discharge periods in the Godavari estuary using different transfer velocity parameterizations

Transfer velocity Parameterization Method	Transfer velocity (<i>k</i> ; m/d)			Flux (mmolC m ⁻² d ⁻¹)			Annual mean
	Peak discharge	Moderate discharge	Dry period	Peak discharge	Moderate discharge	Dry period	
Raymond and Cole 2001	1.8±0.5	1.2±0.5	1.3±0.2	504±378	225±107	29±66	246±309
Wanninkhof, 1992	2.1±0.5	1.4±0.7	1.5±0.5	319±270	99±84	16±41	143±213
Borges et al., 2004	2.6±0.5	1.8±0.7	1.9±0.5	708±488	328±167	44±97	351±417
Ho et al., 2006	1.0±0.5	0.5±0.2	0.5±0.2	274±232	85±72	13±35	123±183
Wanninkhof, 2014	0.9±0.5	0.5±0.2	0.5±0.2	258±219	80±68	13±33	116±172
Jiang et al., 2008	1.7±0.5	1.3±0.2	1.3±0.2	431±316	215±94	26±56	217±261
Mean of all parameterizations	1.7±0.7	1.1±0.7	1.2±0.6	415±362	171±138	23±60	199±284

Legend to figures:

Figure 1: Map showing the study area with stations in the upper, middle and lower TRZ. The location of Dowleiswaram Dam is shown.

Figure 2: a) Annual mean rainfall over the Godavari River region and b) monthly mean river discharge from 2008 to 2019 to the Godavari estuary. The river discharge data were obtained from Dowleiswaram dam authorities whereas rainfall data was obtained from the Ministry of Earth Sciences (<https://data.gov.in/>).

Figure 3: Climatological mean (2008-2019) a) rainfall (mm; black line), and river discharge ($\text{m}^3 \text{s}^{-1}$; Redline), b) salinity, c) dissolved oxygen (μM), d) pH, e) TA (μM), and f) pCO_2 (μatm) in the upper (blue), middle (red) and lower TRZ (green) in the Godavari estuary.

Figure 4: Monthly time-series variations in river discharge, salinity, TA (μM), and pCO_2 (μatm) in the upper (left panel), middle (centre panel), and lower TRZ (right panel) in the Godavari estuary.

Figure 5: The relationship of salinity with a) pH, b) TA (μM), and pCO_2 (μatm) based on data collected from 2008 to 2019 in the upper (blue), middle (red), and lower TRZ (green). The solid black line represents the mixing line obtained from the laboratory experiment of mixing water from the upper and lower TRZ.

Figure 6: The relationship between discharge with pH and pCO_2 in the summer (left panel), moderate discharge period (centre panel), and relationship of salinity with pH and pCO_2 during the dry period (right panel) in the upper, middle, and lower TRZ.

Figure 7: The relationship of AOU (μM) with excess CO_2 (μM) (upper panel), salinity and excess CO_2 (middle panel), and salinity with respiratory quotient (Rq) in the bottom panel in the upper, middle, and lower TRZ.

Figure 8: Time-series variations in the flux of CO_2 to the atmosphere from the entire Godavari estuary during summer (red) moderate discharge (blue) and dry period (green) and b) the contribution of CO_2 flux during different discharge periods to annual flux from the Godavari estuary to the atmosphere.

Figure 1:

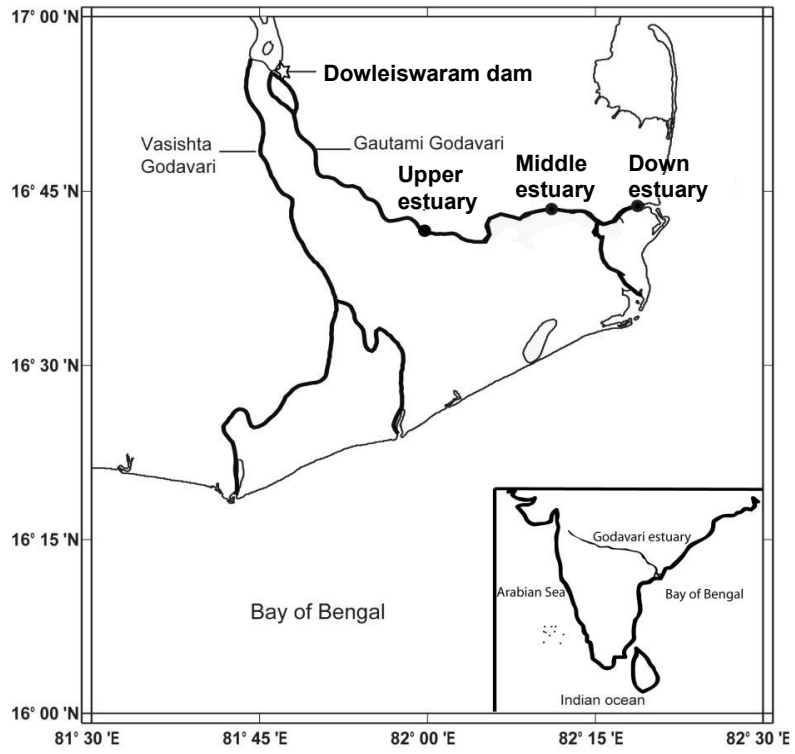


Figure 2:

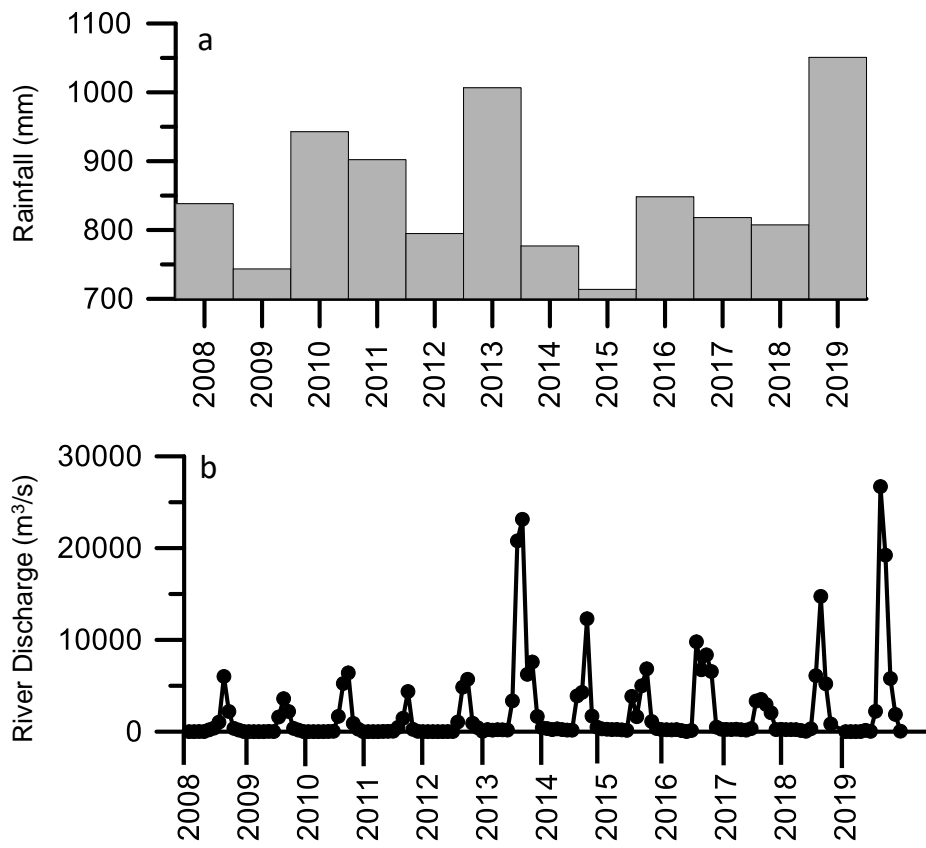


Figure 3:

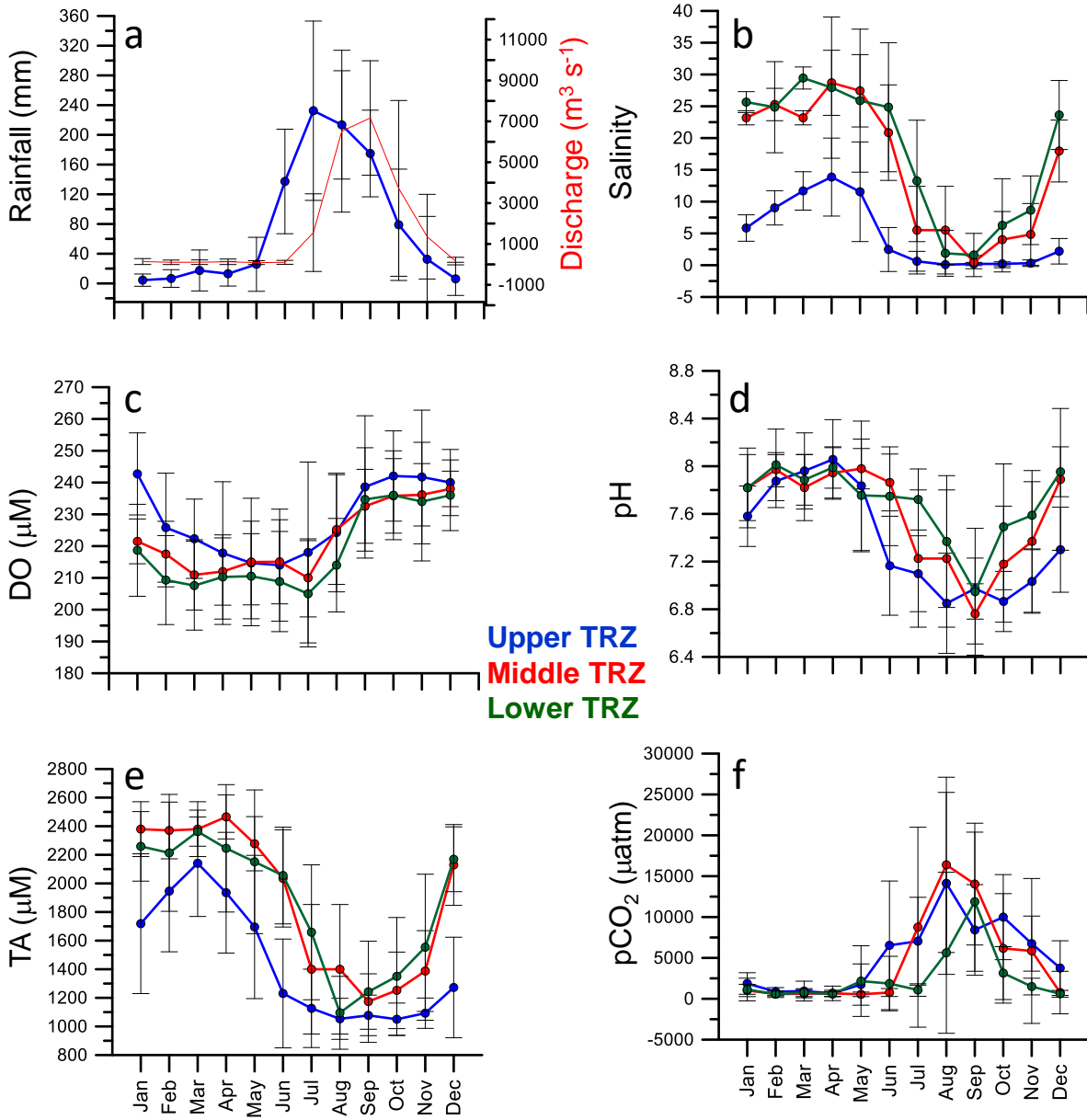


Figure 4:

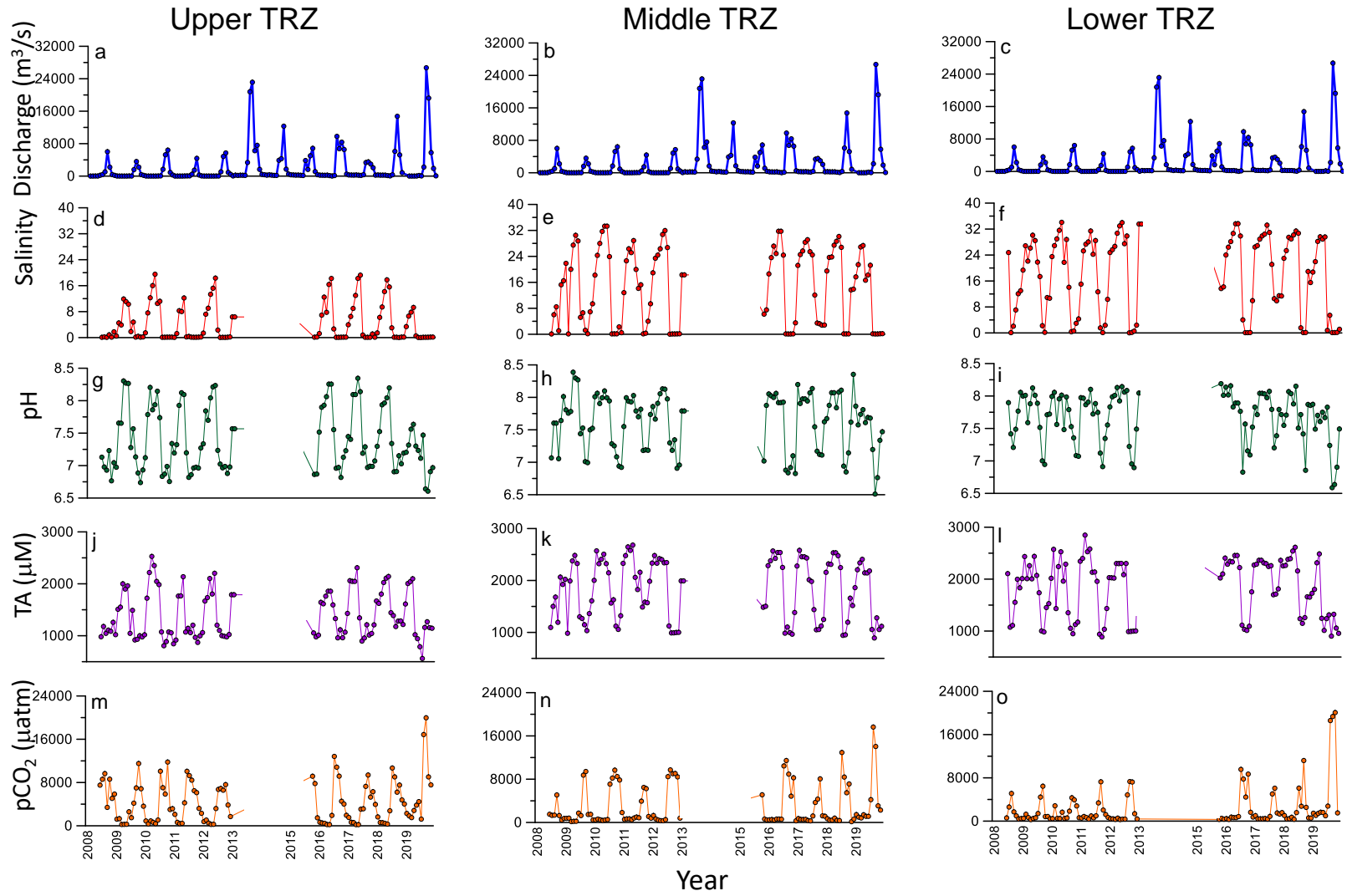


Figure 5:

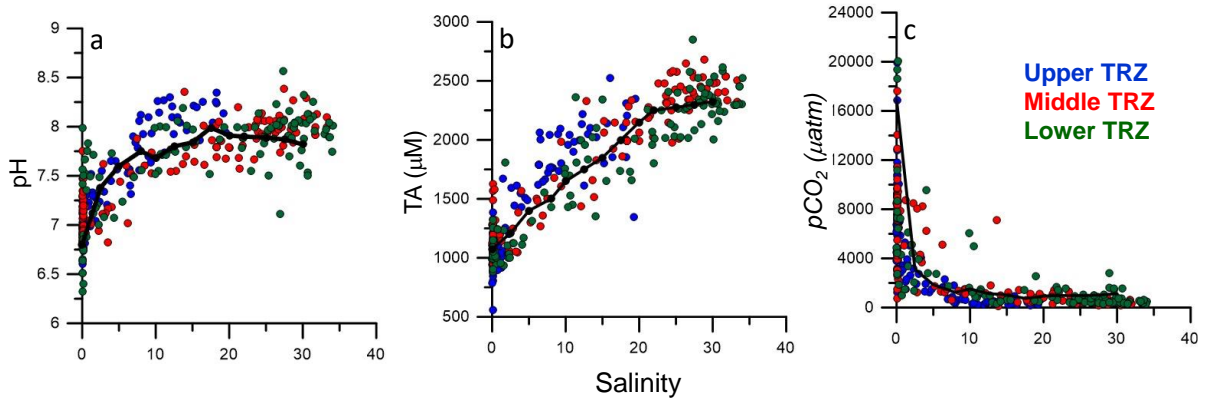


Figure 6:

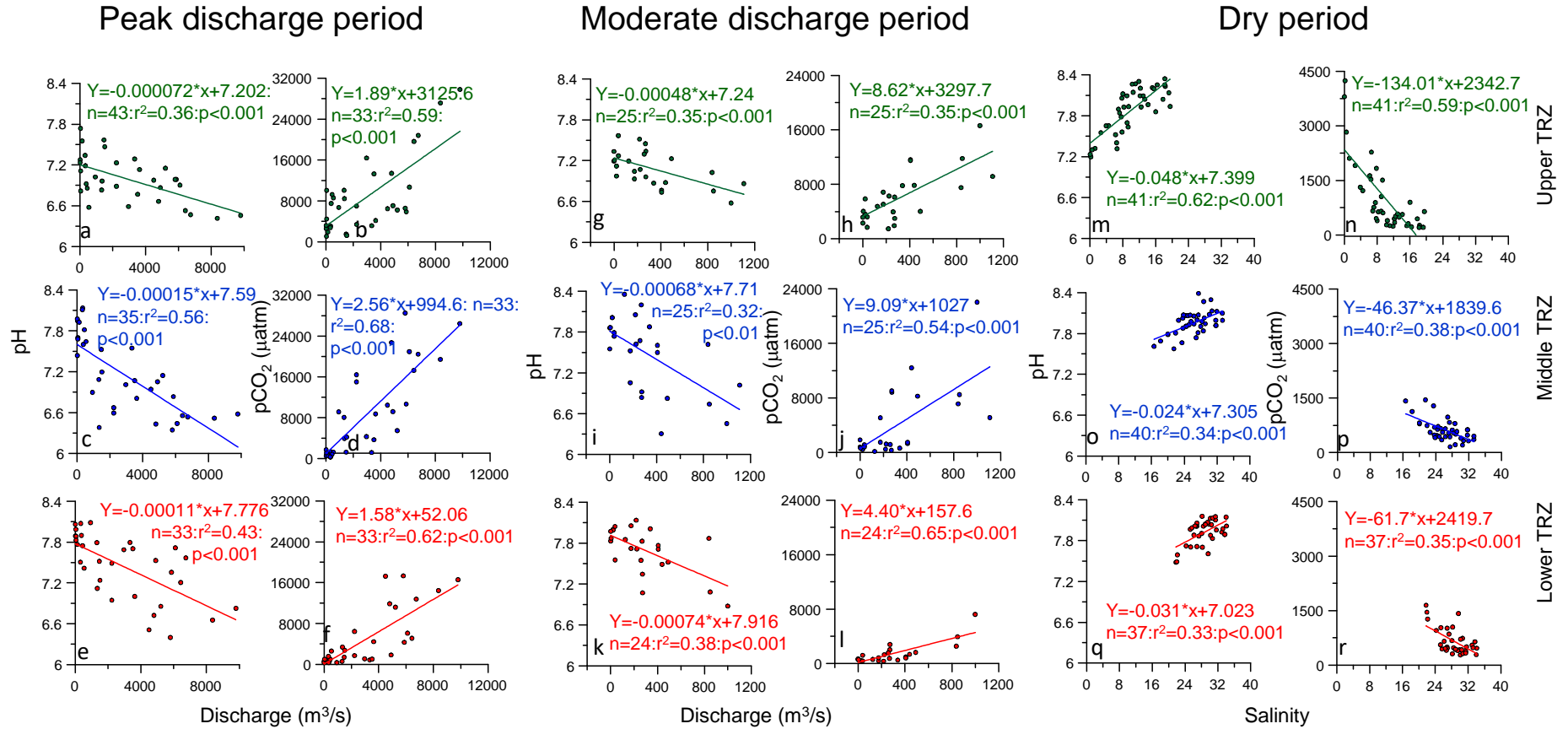


Figure 7:

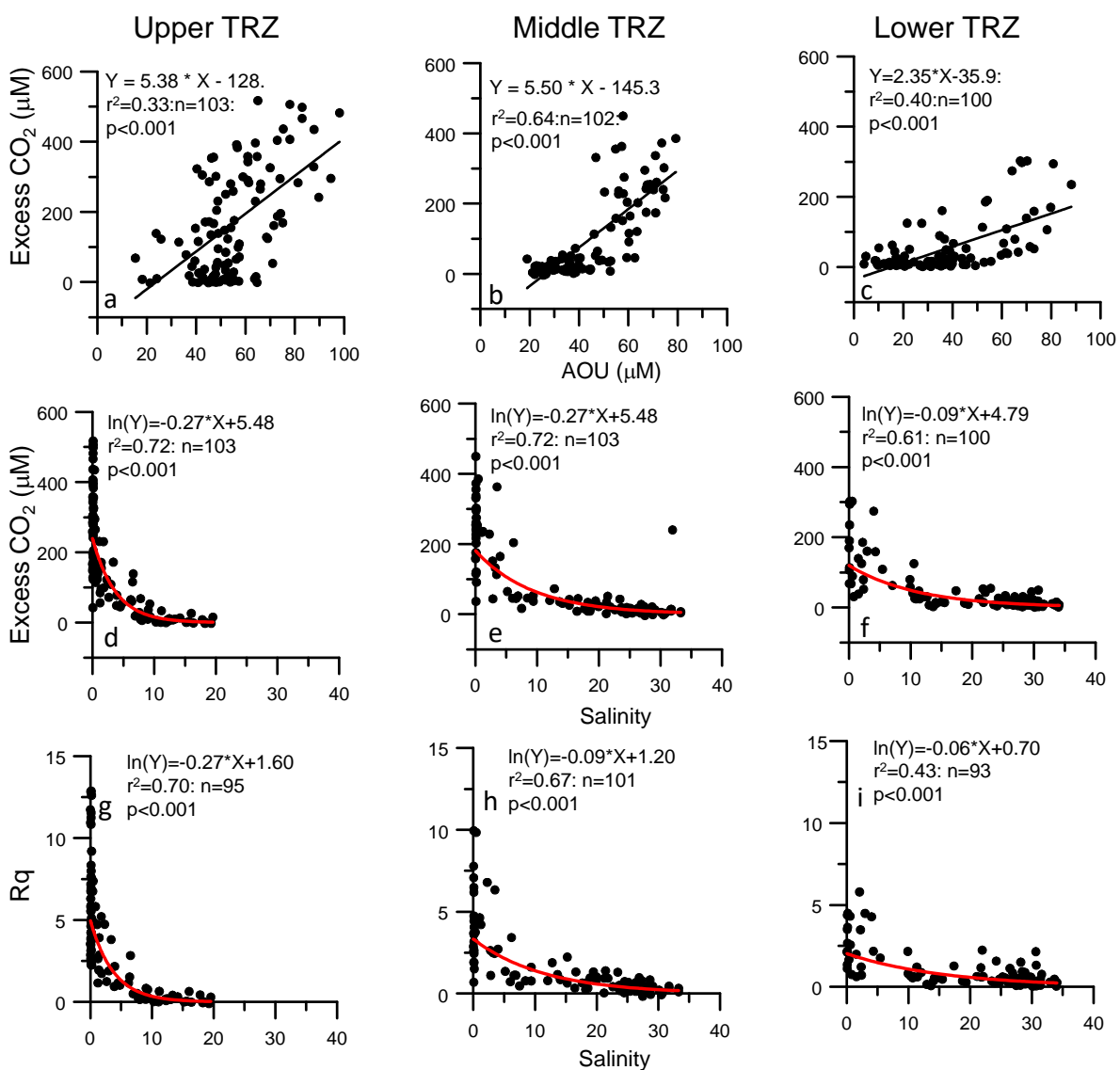
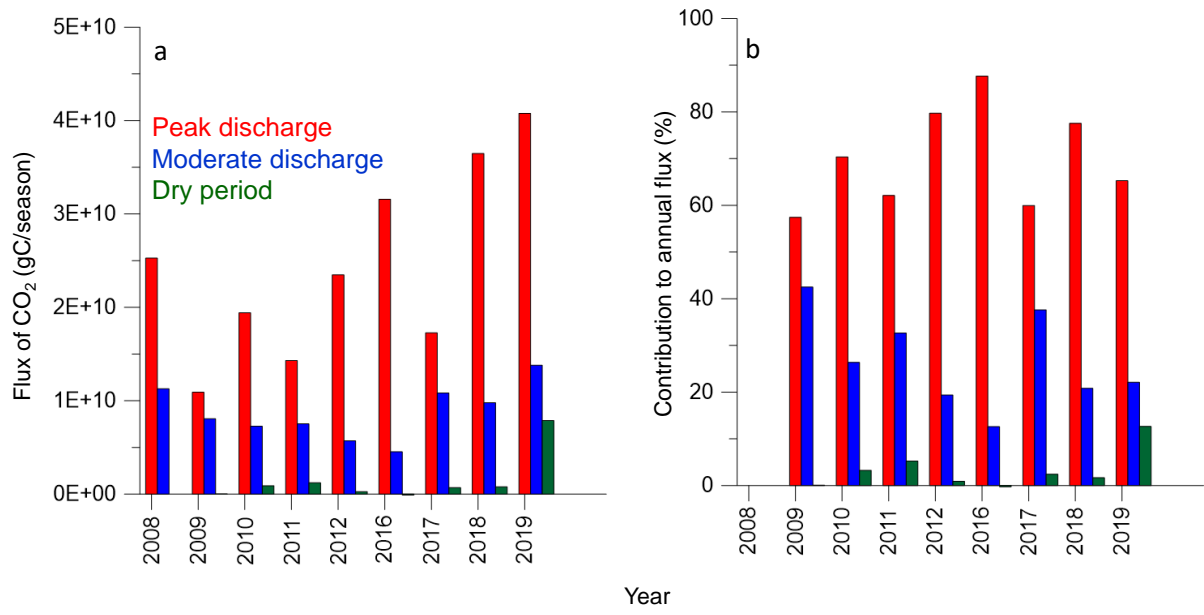


Figure 8:



Supplementary Figure S1: The trend in rainfall between 1990 and 2019 in the Godavari river basin region during summer monsoon (June to September) period.

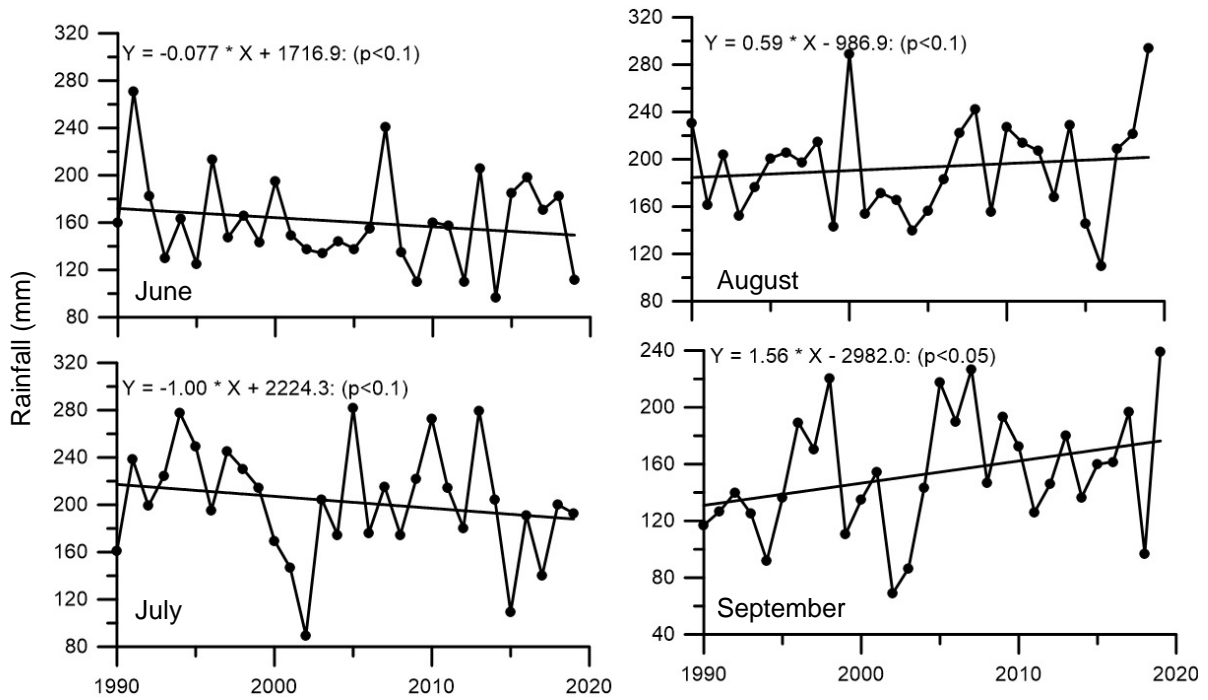
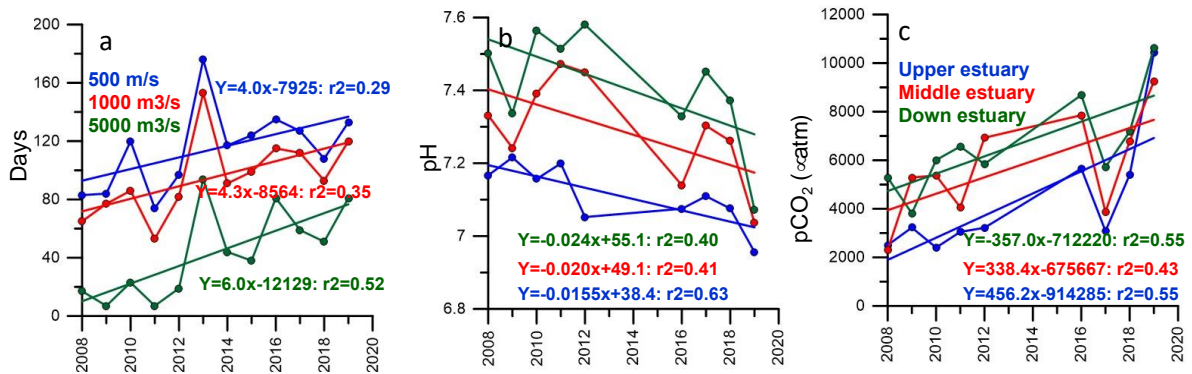


Figure S2: a) time-series variations in a number of days of discharge of >500, >10000 and >5000 m³/s between 2008 and 2019, b) Mean pH, c) pCO₂ (µatm) during summer in the upper (blue), middle (red) and down estuary (green).



Supplementary Table 1: Water-to-air fluxes of CO₂ from the global estuaries.

Estuary (country)	CO ₂ flux molC/m ² /y	Reference
Altamaha Sound (USA)	32.4	Jiang et al., 2008
Bellamy (USA)	3.6	Hunt et al., 2010
Cocheco (USA)	2.4	Hunt et al., 2010
Oyster (USA)	4.0	Hunt et al., 2010
Parker River estuary (USA)	1.1	Raymond and Hopkinson, 2003
Sepelo Sound (USA)	13.5	Jiang et al., 2008
Satilla River (USA)	42.5	Cao and Wang, 1998
York River (USA)	6.2	Raymond et al., 2000
Piaui River estuary (Brazil)	13.0	Souza et al., 2009
Scheldt (Belgium/Netherland)	63.0	Frankignoulle et al., 1998
Elbe (Denmark)	53.0	Frankignoulle et al., 1998
Ems (Denmark)	67.3	Frankignoulle et al., 1998
Gironde (France)	30.8	Frankignoulle et al., 1998
Loire (France)	64.4	Abril et al., 2003
Douro (Portugal)	76.0	Frankignoulle et al., 1998
Sado (Portugal)	31.3	Frankignoulle et al., 1998
Ason Estuary (Spain)	2.2	Ortega et al., 2005
Guadalquivir (Spain)	31.1	De La Paz et al., 2008
Saja-Besaya (Spain)	52.2	Ortega et al., 2004
Urdaibai estuary (Spain)	21.9	Ortega et al., 2005
Rhine (Netherlands)	39.7	Frankignoulle et al., 1998
Tamar (UK)	74.8	Frankignoulle et al., 1998
Thames (UK)	73.6	Frankignoulle et al., 1998
Changjiang (Yantze) (China)	24.9	Zhai et al., 2007
Pearl River (China)	6.9	Guo et al., 2009
Betsiboka (Madagascar)	3.3	Ralison et al., 2008
Tana (Kenya)	47.9	Bouillon et al., 2007
Chilika (India)	25.0	Gupta et al., 2008
Cochin (India)	55.1	Gupta et al., 2009
Godavari (India)	52.6	Sarma et al., 2011
Hooghly (India)	5.1	Mukhopadhyay et al., 2002
Indian estuaries	9.8	Sarma et al., 2012
Godavari estuary (India)	89.8	This study

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