AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER

10.1002/2016GL070716

Key Points:
- River-dominated Hugli Estuary emits 14 times more CO_2 than the marine-dominated Matla Estuary
- In the last 14 years the CO_2 efflux rate from the Hugli Estuary has increased more than twofold
- The fCO_2 (water) value of the Matla, a mangrove estuary, is at the lower end of the reported data from other mangrove ecosystems of the world

Supporting Information:
- Supporting Information S1
- Figure S1
- Data Set S1

Correspondence to:
A. Akhand,
anirban.akhand@gmail.com

Citation:
Akhand, A., et al. (2016), A comparison of CO_2 dynamics and air-water fluxes in a river-dominated estuary and a mangrove-dominated marine estuary, *Geophys. Res. Lett.*, *43*, 11,726–11,735, doi:10.1002/2016GL070716.

Received 4 AUG 2016
Accepted 24 OCT 2016
Accepted article online 26 OCT 2016
Published online 17 NOV 2016

A comparison of CO_2 dynamics and air-water fluxes in a river-dominated estuary and a mangrove-dominated marine estuary

Anirban Akhand[1,2], Abhra Chanda[1], Sudip Manna[1], Sourav Das[1], Sugata Hazra[1], Rajdeep Roy[3], S. B. Choudhury[3], K. H. Rao[3], V. K. Dadhwal[3], Kunal Chakraborty[4], K. M. G. Mostofa[5], T. Tokoro[2], Tomohiro Kuwae[2], and Rik Wanninkhof[6]

[1]School of Oceanographic Studies, Jadavpur University, Kolkata, India, [2]Coastal and Estuarine Environment Research Group, Port and Airport Research Institute, Yokosuka, Japan, [3]National Remote Sensing Centre, Department of Space, Government of India, Hyderabad, India, [4]Indian National Centre for Ocean Information Services, Hyderabad, India, [5]Institute of Surface-Earth System Science, Tianjin University, Tianjin, China, [6]Atlantic Oceanographic and Meteorological Laboratory, NOAA, Miami, Florida, USA

Abstract The fugacity of CO_2 (fCO_2 (water)) and air-water CO_2 flux were compared between a river-dominated anthropogenically disturbed open estuary, the Hugli, and a comparatively pristine mangrove-dominated semiclosed marine estuary, the Matla, on the east coast of India. Annual mean salinity of the Hugli Estuary (≈7.1) was much less compared to the Matla Estuary (≈20.0). All the stations of the Hugli Estuary were highly supersaturated with CO_2 (annual mean ~ 2200 μatm), whereas the Matla was marginally oversaturated (annual mean ~ 530 μatm). During the postmonsoon season, the outer station of the Matla Estuary was under saturated with respect to CO_2 and acted as a sink. The annual mean CO_2 emission from the Hugli Estuary (32.4 mol C m^{-2} yr^{-1}) was 14 times higher than the Matla Estuary (2.3 mol C m^{-2} yr^{-1}). CO_2 efflux rate from the Hugli Estuary has increased drastically in the last decade, which is attributed to increased runoff from the river-dominated estuary.

1. Introduction

Estuaries are large sources of carbon dioxide (CO_2) to the atmosphere [*Jiang et al.*, 2008; *Borges and Abril*, 2011], but the global estimates of estuarine CO_2 emissions that range between 0.27 and 0.50 Pg C yr^{-1} are based on limited spatial and temporal data [*Chen and Borges*, 2009; *Laruelle et al.*, 2010]. In particular, few data-based flux estimates from the abundant Asian estuaries are available [*Sarma et al.*, 2011; *Sarma et al.*, 2001; *Mukhopadhyay et al.*, 2002; *Zhai et al.*, 2005; *Akhand et al.*, 2013]. Most of the estuaries studied were strongly heterotrophic. However, some recent estimates showed less heterotrophy or even autotrophy in the estuaries and lower air-water CO_2 fluxes [*Crosswell et al.*, 2012; *Maher and Eyre*, 2012; *Kuwae et al.*, 2016], which were expected to show high effluxes based on the spatially explicit global typology approach of *Laruelle et al.* [2010]. The large variability between and within estuarine systems make it essential to improve knowledge of estuarine air-water CO_2 fluxes in order to produce better estimates of global estuarine CO_2 exchange [*Evans et al.*, 2013]. Carbon cycling in the abundant estuaries and mangrove systems in Asia is relatively understudied and plays an important role in Blue Carbon [*Donato et al.*, 2011]. The sequestration capacity and, in particular, changes thereof can play a major role in coastal carbon cycling.

Most of the river-dominated estuaries are supersaturated with respect to CO_2 leading to high emissions [*Guo et al.*, 2009]. The CO_2 input into these systems mainly occurs via the main stem river and groundwater discharge [*Cai*, 2011]. The freshwater flow maintains a steady input of labile organic matter that stimulates the bacterial respiration. The high suspended sediment load limits the availability of light and hence phytoplankton growth, which in turn makes the net ecosystem metabolism negative [*Borges and Abril*, 2011; *Maher and Eyre*, 2012]. Both these factors lead to net heterotrophy in river-dominated estuaries and the air-water CO_2 flux toward the atmosphere [*Jiang et al.*, 2008].

In tropical regions mangroves often surround estuaries and are known as one of the most productive coastal intertidal ecosystems of the world capable of fixing 218 ± 72 Tg C yr^{-1} globally [*Bouillon et al.*, 2008]. The mangrove ecosystem as a whole is net autotrophic, but the water column in most cases is found to be net heterotrophic [*Borges et al.*, 2003]. A substantial part of the carbon cycled in the mangrove ecosystems are either remineralized to dissolved inorganic carbon or enter the estuaries in the form of particulate and dissolved organic carbon. This carbon is partially remineralized and exported to coastal ocean or to the atmosphere via gas exchange [*Bouillon et al.*, 2008]. The net heterotrophy exhibited by the mangrove-dominated estuaries is attributed to the factors like porewater and groundwater exchange through tidal pumping [*Borges et al.*, 2003; *Bouillon et al.*, 2008; *Maher et al.*, 2013; *Call et al.*, 2015] and to some extent by high turbidity, canopy shadow, and large fluctuations in salinity leading to limited aquatic primary production. Input of labile organic carbon by means of leaf and wood litter from the overlying canopy can also contribute [*Jennerjahn and Ittekkot*, 2002; *Borges et al.*, 2003].

In this study, the fugacity of CO_2 in water (i.e., fCO_2 (water)), which is the partial pressure of CO_2 corrected for nonideality, and air-water CO_2 fluxes was compared between the Hugli, a river-dominated estuary, and the Matla, a mangrove-dominated semiclosed marine estuary situated close to each other within the same bio-climatic zone. We hypothesize that the air-water CO_2 fluxes differ between an anthropogenically disturbed river-dominated estuary and a comparatively less human affected mangrove estuary. Additionally, the present CO_2 flux rates from Hugli Estuary were compared with respect to previous observations. No previous data on CO_2 fluxes are available along the tract of the Matla Estuary. The results show the large differences in fluxes between adjacent estuaries and the need for quantification along with elucidation of the causes.

1.1. Study Site and Sampling Strategy

The studies were conducted in the lower stretches of Hugli River (see Figure S1 in "supporting information"), a 260 km long tributary of the River Ganges flowing through several major cities and industrial belts, and in the Matla River, both in the state of West Bengal, India. The Hugli receives a perennial freshwater discharge from the Ganges, and its lower stretches act as an open estuary throughout the year. The Matla River forms a wide estuary surrounded by the Sundarban mangrove forest. It lost its connection from the mainstream Ganges long ago, and it is at present a semiclosed estuary where the seawater encroaches and recedes by means of tidal cycle. Both these estuaries are known to be "well-mixed" mesotidal-macrotidal estuaries characterized by a large semidiurnal tide (2.5–7 m) having mean current velocities varying between 117 and 108 cm s^{-1} during ebb and flood tide, respectively [*De et al.*, 2011]. The depth of the Hugli Estuary varies along the channel from ~21 m at Diamond Harbour to ~8 m at the mouth of the estuary [*Central Inland Fisheries Research Institute*, 2012]. The Matla River, on the other hand, no longer receives freshwater influx either from the River Hugli or Bidyadhari and thus becomes an enclosed tidal inlet of the sea with limited wave action and water movements. The region generally becomes filled with seawater during high tide, and most of the water gets drained away toward the sea at low tide leaving a narrow stream of 0.9–1.2 m water in some places [*Sarkar et al.*, 2004]. The seasonality can be described as premonsoon (February–May), monsoon (June–September), and postmonsoon (October–January), respectively.

Four equidistant stations in the Hugli Estuary and three along the tract of the Matla Estuary were sampled during the course of this study. Approximately 740 and 330 km^2 water surface area has been explored under the present study in Hugli and Matla Estuaries, respectively. The data were collected from anchored boats hired for research purpose at the selected stations. Sampling was carried out at all the stations twice each month throughout a complete annual cycle. Sampling was done at 1 h interval at a stretch for 24 h in each system of different seasons to examine diel and tidal variability. The entire study was carried out between August 2013 and July 2014.

2. Methodology

2.1. Field and Laboratory Measurements

Water surface salinity, temperature, dissolved oxygen (DO), apparent oxygen utilization (AOU), euphotic depth, turbidity, underwater photosynthetically active radiation (PAR), and chlorophyll *a* (Chl *a*) were measured by using standard protocols. pH and total alkalinity (TAlk) were directly measured. Fugacity of CO_2 in water (fCO_2 (water)) and dissolved inorganic carbon (DIC) were computed from TAlk and pH by using the software CO_2SYS.EXE [*Lewis and Wallace*, 1998]. Air temperature, atmospheric pressure, wind velocity, solar radiation, and CO_2 concentration in the ambient air were also measured by using standard instrumentation (see Text S1 in supporting information for details).

2.2. Computation of the Air-Water CO_2 and O_2 Fluxes

The air-water CO_2 and O_2 fluxes have been measured by standard bulk formula method. Gas transfer velocity was calculated according to the wind speed based formulae of *Ho et al.* [2011] (see Text S2 in supporting information for details).

2.3. Uncertainty in the Computation

The uncertainty in fluxes is dominated by the empirical relationships of gas transfer with environmental forcing and to lesser extent by the uncertainty in calculated fCO_2 (water). The uncertainty of CO_2 mol fraction in air was estimated at ± 1 ppm based on calibration against standards of 0 ppm, 300 ppm, and 600 ppm CO_2. The calibration of TAlk against certified reference standards had an uncertainty of ± 45 μmol kg^{-1}. The calibration of the pH meter with standard buffers showed an uncertainty of 0.011 pH. Combining the two uncertainties of pH and TAlk yields an error of ± 40 μatm in computed fCO_2 (water), which is an order of magnitude greater than that obtained from direct measurement of fCO_2 (water). The combined estimate of error of fCO_2 (air) and fCO_2 (water) in the computation of ΔfCO_2 varies between 3 and 5%. The uncertainty in the air-water CO_2 flux is dominated by the uncertainty in gas transfer velocity. Considering the depth and width of the River Hugli and Matla, and their comparability with Hudson River Estuary, we have used the model of *Ho et al.* [2011] for gas transfer velocity parameterization. Following *Ho et al.* [2011], we assume that wind, rather than currents, has the primary control of gas transfer in these large estuaries. For three studies *Ho et al.* [2011] obtained an average root-mean-square error of ≈25% for the fit against the observations. However, from *Ho et al.* [2011, Table 3] the difference between the relationships used by *Raymond and Cole* [2001], *Borges et al.* [2004], and *Jiang et al.* [2008] and the field observations in the *Ho et al.* [2011], the uncertainty in gas transfer is ≈50%. For our uncertainty estimates of flux (Figure 1) we use the Hudson specific lower value.

3. Results and Discussion

3.1. Atmospheric and Hydrological Parameters

Air temperature, pressure, and solar intensity in the two estuaries did not exhibit any statistically significant difference ($p > 0.05$) between the estuaries as they are situated within 1° longitudinal distance (see Table S1 in supporting information). fCO_2 (air) and surface water temperature also showed similar magnitudes in both the estuaries throughout the year. However, the wind velocity and hence the computed gas transfer velocity according to *Ho et al.* [2011] were much higher in the river-dominated Hugli Estuary compared to the mangrove encompassed Matla Estuary. The comparatively greater width of the Hugli Estuary facilitated the free flow of wind. On the contrary, in the Matla Estuary the presence of mangroves which act as wind shelter can reduce the wind velocity [*Elnwishy et al.*, 2009].

Surface salinities were markedly different in the two estuaries. Due to the freshwater input, the mean salinity in the Hugli Estuary was ~3 times less than the Matla Estuary in all seasons. During the monsoonal discharge, the surface salinity in the inner stations of the Hugli Estuary was as low as 0.1. In the Matla Estuary the salinity was quite high (≈20) since the incoming seawater gets diluted only by the runoff through the mangroves. Spatially, surface salinity increased toward the ocean in both the estuaries. DO was slightly lower and chl *a* concentrations were marginally higher in the Hugli Estuary (annual mean of 175 ± 19 μmol kg^{-1} and 3.23 ± 0.96 mg m^{-3}, respectively) compared to the Matla (annual mean of 185 ± 25 μmol kg^{-1} and 2.97 ± 0.97 mg m^{-3}, respectively). DO was found to increase from the inner stations toward the river mouth in both the Hugli and the Matla Estuaries; however, no such spatial trend was observed in case of chl *a*. The euphotic depth and PAR was slightly higher in the Matla Estuary compared to Hugli, whereas turbidity showed an opposite trend. The perennial discharge in Hugli Estuary from the mainstream of Ganges brings in a high suspended matter load throughout the year, whereas in Matla Estuary, the sedimentary input originates mainly from the mangrove soils from tidal flushing and runoff and is much smaller compared to the Hugli.

3.2. Carbonate System

pH displayed a systematic increase from the inner to the outer estuarine stations of the Hugli (Figure 1a). During the monsoon season, pH as low as 7.4 was observed at the innermost station (H1) of the Hugli Estuary, whereas in the lower reaches it was more than 8.0. This type of increasing trend through the estuary was observed in Matla only during the monsoon, and no such trend existed in the other two seasons (Figure 1b).

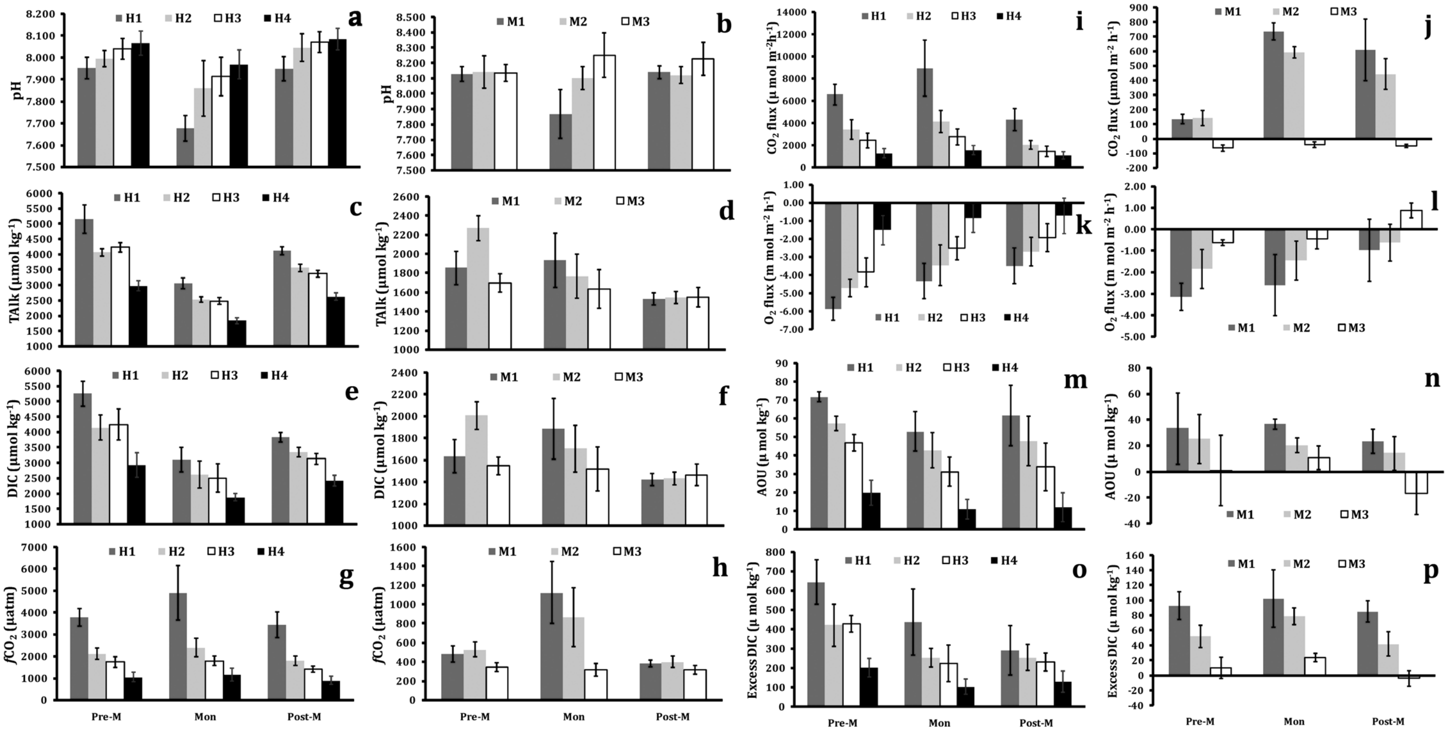

Figure 1. The seasonal and spatial variabilities of pH in (a) the Hugli and (b) the Matla; TAlk in (c) the Hugli and (d) the Matla; calculatedDIC in (e) the Hugli and (f) the Matla; calculated fCO_2 (water) in (g) the Hugli and (h) the Matla; air water CO_2 flux in (i) the Hugli and (j) the Matla and air-water O_2 flux in (k) the Hugli and (l) the Matla; AOU in (m) the Hugli and (n) the Matla, and excess DIC in (o) the Hugli and (p) the Matla Estuaries for the premonsoon (Pre-M), Monsoon (Mon), and post-monsoon (Post-M) seasons. Note the differences in scale for the results of the Hugli and the Matla.

The magnitude of pH in the two estuaries was substantially different for all the seasons. In the Hugli the annual mean pH at H1 was 7.850, whereas at M1 it was 8.044. The lower reaches of the Hugli (H4) had a mean annual pH of 8.040, while at M3 (lower reach of Matla) the mean pH was 8.205.

Similarly, the fCO_2 (water) varied greatly between the two estuaries (Figures 1g and 1h). The annual mean fCO_2 (water) in the Hugli was 4 times higher (~2200 µatm) than that found in Matla (~550 µatm). High fCO_2 (water) values (4000–6000 µatm) at the inner stations of the Hugli were associated with low pH (~7.6) and low salinity (0.1–3.0). Similar trend of high fCO_2 (water) values in low-salinity waters was also found in the Mandovi Estuary [*Sarma et al.*, 2001], the Hudson River [*Raymond et al.*, 1997], and other European estuaries [*Frankignoulle et al.*, 1998]. The magnitude of fCO_2 (water) gradually decreased from the inner stations toward the lower reaches in case of the Hugli Estuary for all seasons. *Sarma et al.* [2001] and *Mukhopadhyay et al.* [2002] observed similar decreasing trend from inner stations toward the ocean in other Indian estuaries. However, throughout the annual cycle the surface waters of Hugli Estuary remained supersaturated. Even in the lower reaches of the Hugli, fCO_2 (water) rarely went below ~600 µatm. However, the magnitudes documented in polluted estuaries like the Rhine (~25,000 µatm [*Kempe*, 1982]) and the Scheldt (~15,200 µatm [*Borges and Frankignoulle*, 2002]) was much higher than observed in the present study. The monthly discharge in the Hugli Estuary, with discharge data taken from *Rudra* [2014], exhibited a statistically significant correlation ($R^2 = 0.71$, $p < 0.05$) with the monthly mean fCO_2 (water) values observed for all four stations of the Hugli Estuary. This suggests that large allochthonous input of land-derived organic material along with high nutrient supply that facilitates high phytoplankton biomass (chl *a*: up to 4.98) leads to high bacterial respiration, which in turn leads to supersaturation of CO_2, which was also observed by *Sarma et al.* [2011] in the Godavari Estuary. In contrast, the surface waters of the station of the Matla closest to the ocean (M3) was mostly undersaturated with CO_2 with a seasonal mean fCO_2 (water) between 289 and 347 µatm. The inner two estuarine stations exhibited higher values of fCO_2 (water) with the maximum during the monsoon (~2850 µatm). Measured TAlk and computed DIC followed a similar trend to fCO_2 (water) in the respective estuaries (Figures 1c–1f). However, the fCO_2 (water) values of mangrove dominated water bodies of Matla

Estuary are at the low end of the reported range of mangrove waters [e.g., *Bouillon et al.*, 2003; *Call et al.*, 2015]. There have been few works reporting such a low fCO_2 (water) but was also observed by *Biswas et al.* [2004] while working in the river mouth (Muriganga, Saptamukhi, and Thakuran Rivers) of the mangrove waters of Sundarban. They found the mangrove water undersaturated with respect to atmosphere during all the postmonsoon months and two months during monsoon. *Borges et al.* [2003] also reported lesser pCO_2 (water) of 380 to 750 μatm from the mangrove water of Bahamas. We assume that this lesser magnitude of fCO_2 (water) in comparison with other mangrove waters of the world is attributed to lack of river-derived freshwater input in this estuary [*Sarkar et al.*, 2004] and sole dependence on the carbon export from the mangrove, majorly in the form of DIC [*Bouillon et al.*, 2008], and possible high ratio of surface water area to mangrove-populated shoreline compared to other systems studied to date. However, this issue should be a focus of future work on nearshore and benthos. Supersaturation of CO_2 with several folds higher fCO_2 (water) values in the Hugli than in the Matla is the key factor for low pH value observed in the river mouth of the Hugli Estuary.

3.3. Diurnal and Diel Variability of fCO_2 (Water)

The semidiurnal tidal cycle is found to play a crucial role in regulating the diurnal as well as diel variability of fCO_2 (water). Salinity varied over a range of 2–3 within one semidiurnal tidal cycle (~6 h) at all the stations. In both the estuaries, highest fCO_2 (water) values coincided with the lowest low tide (Figure 2). Even when the low-tide conditions coincided with the photosynthetic maxima during the day, the effect of low tide overruled the photosynthetic CO_2 uptake leading to increases in fCO_2 (water). In the Hugli Estuary, during low tide the organic material-rich freshwater attains its peak. Similarly, in Matla, during low tide, such increases in fCO_2 (water) could be due to pore water/groundwater mixing with the estuarine waters and subsequent change in the chemical properties of it during ebb and low tide until inundation of sediment surface during flood tide [*Ovalle et al.*, 1990; *Middelburg et al.*, 1996; *Alongi et al.*, 1998; *Kristensen et al.*, 2000; *Maher et al.*, 2013; *Akhand et al.*, 2013].

The scatterplot between the monthly mean fCO_2 (water) and salinity (Figures 2g and 2h) exhibited a negative relationship. In Hugli Estuary, the negative relationship was observed throughout all the seasons; however, in Matla, it was clearly observed only in case of postmonsoon season. The goodness of fit of the linear trend between these two parameters was better for the Hugli ($R^2 = 0.48$, $p < 0.05$) than for the Matla ($R^2 = 0.37$, $p < 0.05$). This observation signifies that apart from the role of tidal cycling a biological control of fCO_2 (water) also existed. This biological control was more apparent in the Matla compared to the Hugli. For both the estuaries, extremely highly fCO_2 (water) was observed corresponding with the lower values of salinity, which implies that the higher the freshwater content, the higher the fCO_2 (water).

3.4. Air-Water CO_2 and O_2 Flux

The estimated mean air-water CO_2 fluxes ranged from 1626 to 16944, 942 to 10016, 395 to 9743, and 121 to 4349 $\mu mol\ m^{-2}\ h^{-1}$ for the H1, H2, H3, and H4 stations, respectively (Figures 1i and 1j). In the Hugli Estuary, the supersaturation of fCO_2 (water) was so high with respect to atmospheric CO_2 concentration that the fluxes closely followed the variability of fCO_2 (water) throughout the annual cycle. Higher effluxes were observed in the inner estuarine stations, which gradually decreased toward the oceanic end. The positive air-water CO_2 fluxes were accompanied by negative O_2 fluxes (into the water) during all the seasons with varying magnitudes (Figures 1k and 1l). High negative O_2 fluxes were observed in the inner stations of the Hugli, which indicates the utilization of oxygen and thus high AOU values due to intense heterotrophic activity in the water column in turn leading to the high CO_2 effluxes. Results of mixing calculations in conjunction with the estimated undersaturated levels of dissolved O_2 suggest that biological respiration and organic carbon degradation dominate over biological production in the Hugli Estuary [*Samanta et al.*, 2015]. The corresponding high fCO_2 (water) could be aided from the simultaneous photo-induced respiration and/or degradation of dissolved organic matter and primary producers [*Mostofa et al.*, 2016]. *Mukhopadhyay et al.* [2006] also observed that due to excessive turbidity in the water column of the Hugli Estuary, the euphotic depth was always very shallow. Despite having high nutrient levels, the autotrophic productivity in the euphotic zone did not exceed the community respiration of the entire water column.

In the Matla Estuary, the CO_2 fluxes were much lower than that observed in the Hugli. They ranged from −303 to 3033, −249 to 1764, and −358 to −328 $\mu mol\ m^{-2}\ h^{-1}$ in M1, M2, and M3 stations, respectively. This shows

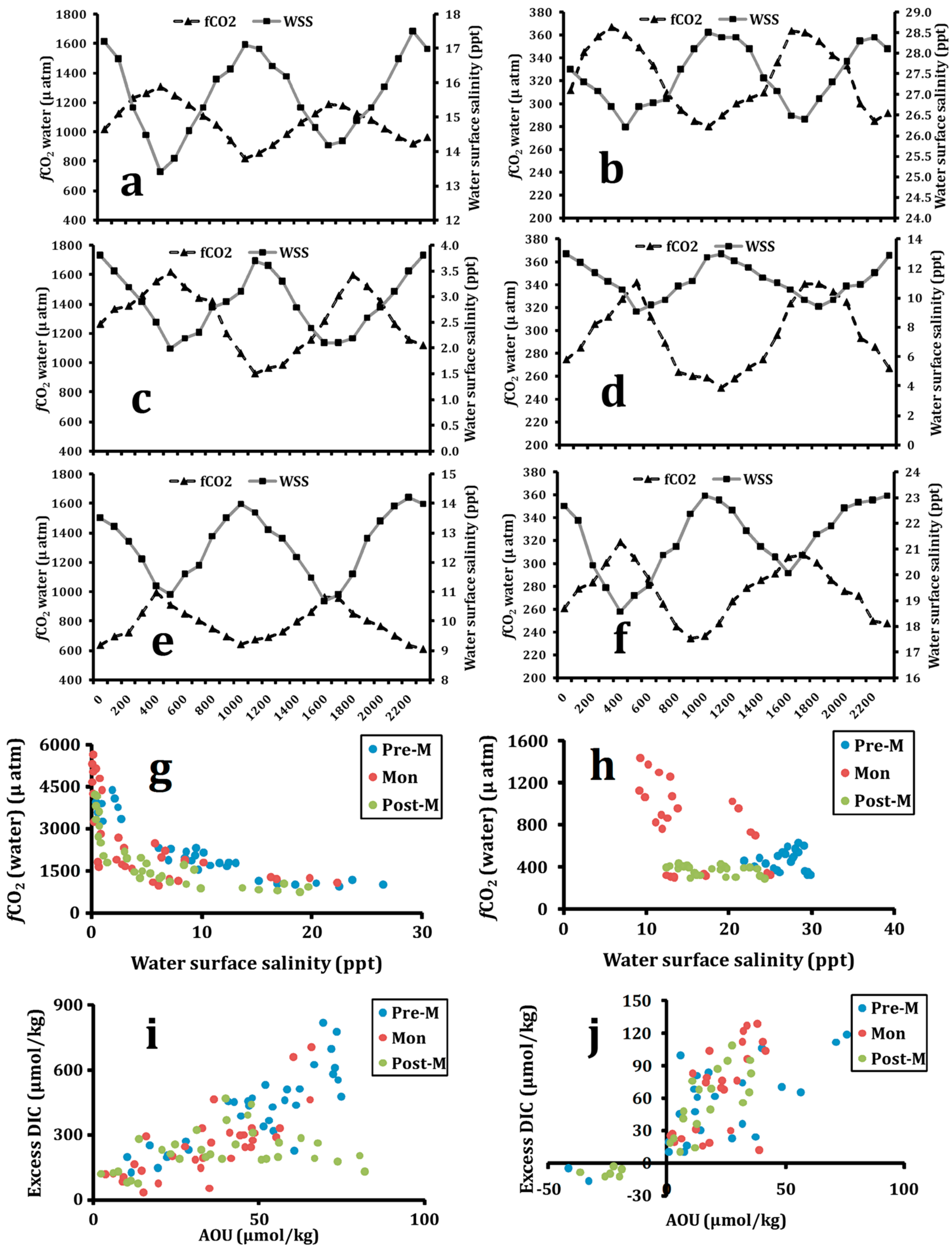

Figure 2. The hourly variability of surface water salinity (WSS) and fCO_2 (water) over a complete tidal cycle on 16 April 2014 (pre-monsoon season) in (a) Hugli station H4 and (b) Matla station M3, on 13 August 2014 in (c) Hugli H4 and (d) Matla M3, and on 6 January 2015 in (e) Hugli H4 and (f) Matla M3. The scatterplot of monthly mean surface water salinity (WSS) and fCO_2 (water) in the (g) Hugli and (h) Matla Estuaries and excess DIC and AOU in the (i) Hugli and (j) Matla Estuaries.

that the inner and middle estuarine stations of Matla Estuary exhibited net heterotrophic character throughout the year; while the outer estuarine station (M3) acted as a small CO_2 sink. This implies that while in the mouth of Hugli Estuary the water column still retains a substantial organic load, which is enough to make it act as a source; the lower estuary of the Matla has a much lower load. In the Matla Estuary the main source of organic load is derived from the pore waters and runoff through the mangroves, as it is stated in *Sarkar et al.* [2004], that due to excessive siltation, the Matla in its upper reaches has lost its connection with freshwater. The magnitude of this load is quite low compared to the freshwater-derived organic load of Hugli.

Hence, it is apparent that at the site M3 the water column of Matla Estuary is getting diluted to a large extent by the seawater, which causes the fCO_2 (water) values in the water surface to go below the atmospheric CO_2 levels. Thus, this station is a sink for CO_2. *Borges and Frankignoulle* [2002] also observed that many of the outer estuarine regions are characterized by less intense carbon and nutrient remineralization and higher net productivity, which leads to a reversal of trends of air-water CO_2 fluxes compared to the corresponding inner estuarine stations. The O_2 fluxes were negative in the Hugli Estuary and in the Matla. Even in the river mouth of Matla which was slightly undersaturated with CO_2, the O_2 fluxes were negative (into the water) in premonsoon and monsoon season; however, in the postmonsoon season the O_2 flux was found positive (toward atmosphere). This is attributed to the differences in O_2 versus CO_2 dynamics, where O_2 is more sensitive to local productivity/respiration change than CO_2 that is chemically buffered.

Excess DIC (the difference between the in situ DIC and a theoretical DIC at atmospheric equilibrium) in Hugli Estuary ranged from 458 $\mu mol\ kg^{-1}$ at H1 to lowest 33 $\mu mol\ kg^{-1}$ at H4; while in the Matla Estuary the range was from 129 $\mu mol\ kg^{-1}$ at M1 to -17 $\mu mol\ kg^{-1}$ at M3. AOU in the Hugli Estuary showed values from 102 $\mu mol\ kg^{-1}$ at H1 to -5 $\mu mol\ kg^{-1}$ in H4, while in the Matla Estuary AOU ranged from 53 $\mu mol\ kg^{-1}$ at M1 to -48 $\mu mol\ kg^{-1}$ at M3. Excess DIC and AOU were mildly correlated with $R^2 = 0.43$ for the Hugli and $R^2 = 0.51$ for the Matla (Figures 2i and 2j). The excess DIC was always found higher than the AOU in both Hugli and Matla Estuaries. The ratio of excess DIC/AOU was 9 in Hugli, whereas in Matla it was 4. According to *Hamilton et al.* [1995] the excess CO_2 that cannot be accounted for by the oxygen depletion might either originate from root respiration of superior plants in suspended solids or anaerobic bacterial metabolism in water and sediments. A second factor that contributes to higher excess DIC compared to O_2 is the tenfold slower response of excess DIC compared to O_2 to gas exchange causing a greater accumulation of excess DIC in the estuaries.

3.5. Comparison of Air-Water CO_2 Flux With Other Estuaries

On an annual basis, the Hugli Estuary emitted 32.4 $mol\ C\ m^{-2}\ yr^{-1}$, whereas the Matla Estuary acted as a source of CO_2 of magnitude 2.3 $mol\ C\ m^{-2}\ yr^{-1}$. Hence, the river-dominated Hugli Estuary emits 14 times more CO_2 than the marine-dominated semiclosed Matla Estuary. Similar findings have been previously found in other locations [e.g., *Jiang et al.*, 2008; *Maher and Eyre*, 2012]. According to the estimates derived from *Ganguly et al.* [2011], the Mahandi Estuary lying close to the Hugli and the Matla in the eastern coast of India exhibited a mean emission of 2.6 $mol\ C\ m^{-2}\ yr^{-1}$. In contrast, *Sarma et al.* [2011] observed a high mean annual efflux of 56.2 $mol\ C\ m^{-2}\ yr^{-1}$ from the Godavari Estuary located in the east coast of India. Two other significant estuaries terminating in the Bay of Bengal (i.e., lying in the east coast of India), namely, Krishna and Cauvery, emitted CO_2 at the rate of 2.4 and 0.8 $mol\ C\ m^{-2}\ yr^{-1}$ [*Sarma et al.*, 2012]. *Borges et al.* [2005] estimated a mean efflux of 25.72 $mol\ C\ m^{-2}\ yr^{-1}$ for estuaries in the tropics and subtropics. The present assessment of the Hugli Estuary is close to this magnitude; however, the mangrove-dominated Matla Estuary falls far below this value.

3.6. Decadal Change of Air-Water CO_2 Flux in the Hugli Estuary

Mukhopadhyay et al. [2002] found the Hugli to be a net source of CO_2 at a mean rate of 8.1 $mol\ C\ m^{-2}\ yr^{-1}$ in 1999 but a CO_2 sink during the monsoon season. Monthly fCO_2 water values in the Hugli Estuary in 1999 ranged from 300 to 1200 ($\pm$200) μatm [*Mukhopadhyay et al.*, 2002], which is appreciably less than that observed during the present course of sampling. While in our study, ΔfCO_2 values were multiplied by monthly mean gas transfer velocity to derive the fluxes. When a constant gas transfer velocity of 9.3 $cm\ h^{-1}$ as used by *Mukhopadhyay et al.* [2002] is applied, the annual mean flux is 42.4 $mol\ C\ m^{-2}\ yr^{-1}$, which is fivefold the annual flux in 1999. The global average XCO_2 of air has been increased approximately by 30 ppm over this period, which would decrease the efflux of the present study compared to the work of 1999 if fCO_2 (water) remained unchanged. Thus, it is clear that the air-water CO_2 efflux has increased substantially in the Hugli Estuary over the last 14 years. *Banerjee* [2013] observed an increase of 0.5°C in water surface temperature accompanied by a decrease in salinity of 2.2 psu in the last decade in Hugli Estuary, suggesting more freshwater discharge. The associated higher organic load could lead to the higher CO_2 fluxes. Increase in surface temperature can enhance the efflux of CO_2 since thermodynamics will increase fCO_2 water by about 2% for the observed 0.5°C temperature rise. But more importantly greater transformation of organic carbon to DIC is expected at higher temperature due to higher bacterial respiration rates. *Mitra et al.* [2015] observed large-scale temporal changes of nutrient concentration in this estuary with nitrate, phosphate, and silicate concentration at site H1 (Diamond Harbour) increasing at the rate of 9.49, 1.96, and 64.57 $\mu g\,L^{-1}$ decade^{-1}. This increase in nutrient could enhance primary productivity, also lead to high bacterial respiration and hence supersaturation of CO_2. *Ray Choudhuri et al.* [2015] observed that pH in site H1 decreased at a rate of ~0.08 in the last decade. Moreover, *Mitra et al.* [2009] throughout a 30-yearlong study observed that the abundance of freshwater steadily increased in the Hugli Estuary accompanied by an equivalent decrease in transparency and pH of the water column in the last decades. These appear to be the main causal factor behind such a change in its CO_2 efflux rates.

3.7. Conclusion

The tropical river-dominated Hugli Estuary emits more CO_2 than the mangrove-dominated marine Matla Estuary. The Hugli being a perennial estuary that flows through several major industries and metropolis of the north and east India carries with it a large organic load leading to very high fCO_2 (water) and hence acts as a substantial source for CO_2. The magnitude of CO_2 efflux has substantially increased in the last decade. The marine estuary of Matla almost disconnected at present with any perennial rivers in the north shows much lower fCO_2 (water) values as well as CO_2 fluxes. This study did not investigate the sources of extremely high fCO_2 (water) values in the Hugli Estuary, which should be the focus for future study including water column and sediment analyses. Due to lack of previous data in the Matla Estuary, no temporal comparison could be carried out in this estuary; however, this type of long-term assessments should also be carried out in these mangrove-dominated estuaries in order to assess their temporal change and anthropogenic impacts in fluxes in light of increased interest and importance of Blue Carbon reservoirs.

Acknowledgments
Authors are grateful to the funding agencies of this work which include National Remote Sensing Centre, Indian Space Research Organization, and Department of Space, Government of India. The work was partly supported by the Strategic R&D Area Project (S-14) of the Environmental Research and Technology Development Fund (Strategic Research on Global Mitigation and Local Adaptation to Climate Change). R.W. was supported by the Office of Oceanic and Atmospheric Research of the National Oceanic and Atmospheric Administration of the USA. The entire data set is annexed in Data Set S1 in the supporting information.

References

Abril, G., H. Etcheber, A. V. Borges, and M. Frankignoulle (2000), Excess atmospheric carbon dioxide transported by rivers into the Scheldt estuary, *Comptes Rendus de l'Academie des Sci. Ser. IIA-Earth Planet. Sci.*, *330*(11), 761–768.

Akhand, A., A. Chanda, S. Dutta, S. Manna, P. Sanyal, S. Hazra, K. H. Rao, and V. K. Dadhwal (2013), Dual character of Sundarban estuary as a source and sink of CO_2 during summer: An investigation of spatial dynamics, *Environ. Monit. Assess.*, *185*(8), 6505–6515.

Alongi, D. M., A. Sasekumar, F. Tirendi, and P. Dixon (1998), The influence of stand age on benthic decomposition and recycling of organic matter in managed mangrove forests of Malaysia, *J. Exp. Mar. Biol. Ecol.*, *225*, 197–218.

Banerjee, K. (2013), Decadal change in the surface water salinity profile of Indian Sundarbans: A potential indicator of climate change, *J. Mar. Sci. Res. Dev.*, *S11*, doi:10.4172/2155-9910.S11-002.

Benson, B. B., and J. R. Krause (1984), The concentration and isotopic fractionation of oxygen dissolved in freshwater and seawater in equilibrium with atmosphere, *Limnol. Oceanogr.*, *29*, 620–632.

Biswas, H., S. K. Mukhopadhyay, T. K. De, S. Sen, and T. K. Jana (2004), Biogenic controls on the air–water carbon dioxide exchange in the Sundarban mangrove environment, northeast coast of Bay of Bengal, India, *Limnol. Oceanogr.*, *49*, 95–101.

Borges, A. V., and G. Abril (2011), Carbon dioxide and methane dynamics in estuaries, in *Treatise on Estuarine and Coastal Science*, edited by E. Wolanski and D. S. Mclusky, pp. 119–161, Elsevier Academic Press, Waltham.

Borges, A. V., and M. Frankignoulle (2002), Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast, *Biogeochemistry*, *59*, 41–67, doi:10.1023/A:1015517428985.

Borges, A. V., S. Djenidi, G. Lacroix, J. Théate, B. Delille, and M. Frankignoulle (2003), Atmospheric CO_2 flux from mangrove surrounding waters, *Geophys. Res. Lett.*, *30*(11), 1558, doi:10.1029/2003GL017143.

Borges, A. V., B. Delille, L. S. Schiettecatte, F. Gazeau, G. Abril, and M. Frankignoulle (2004), Gas transfer velocities of CO_2 in three Europian estuaries (Randers Fjord, Scheldt and Thames), *Limnol. Oceanogr.*, *49*, 1630–1641.

Borges, A. V., B. Delille, and M. Frankignoulle (2005), Budgeting sinks and sources of CO_2 in the coastal ocean: Diversity of ecosystems counts, *Geophys. Res. Lett.*, *32*, L14601, doi:10.1029/2005GL023053.

Bouillon, S., M. Frankignoulle, F. Dehairs, B. Velimirov, A. Eiler, G. Abril, H. Etcheber, and A. V. Borges (2003), Inorganic and organic carbon biogeochemistry in the Gautami Godavari estuary (Andhra Pradesh, India) during pre-monsoon: The local impact of extensive mangrove forests, *Global Biogeochem. Cycles*, *17*(4), 1114, doi:10.1029/2002GB002026.

Bouillon, S., et al. (2008), Mangrove production and carbon sinks: A revision of global budget estimates, *Global Biogeochem. Cycles*, *22*, GB2013, doi:10.1029/2007GB003052.

Cai, W. J., Y. Wang, and R. E. Hodson (1998), Acid-base properties of dissolved organic matter in the estuarine waters of Georgia, USA, *Geochim. Cosmochim. Acta*, *62*(3), 473–483.

Cai, W.-J. (2011), Estuarine and coastal ocean carbon paradox: CO_2 sinks or sites of terrestrial carbon incineration?, *Annu. Rev. Mar. Sci.*, *3*, 123–145.

Call, M., et al. (2015), Spatial and temporal variability of carbon dioxide and methane fluxes over semi-diurnal and spring–neap–spring timescales in a mangrove creek, *Geochim. Cosmochim. Acta*, *150*, 211–225, doi:10.1016/j.gca.2014.11.023.

Chen, C.-T. A., and A. V. Borges (2009), Reconciling opposing views on carbon cycling in the coastal ocean: Continental shelves as sinks and near-shore ecosystems as sources of atmospheric CO_2, *Deep Sea Res., Part II*, *56*, 579–590.

CIFRI (2012), Present status of Hilsa in Hugli-Bhagirathi river, Central Inland Fisheries Research Institute, [Available at www.cifri.ernet.in.179.pdf].

Crosswell, J. R., M. S. Wetz, B. Hales, and H. W. Paerl (2012), Air-water CO_2 fluxes in the microtidal Neuse river estuary, North Carolina, *Geophys. Res. Lett.*, *117*, C08017, doi:10.1029/2012JC007925.

De, T. K., M. De, S. Das, C. Chowdhury, R. Ray, and T. K. Jana (2011), Phytoplankton abundance in relation to cultural eutrophication at the land-ocean boundary of Sunderbans, NE Coast of Bay of Bengal, India, *J. Environ. Stud. Sci.*, *1*(3), 169–180.

Dey, M., C. Chowdhury, A. A. Pattnaik, D. Ganguly, S. K. Mukhopadhyay, T. K. De, and T. K. Jana (2013), Comparison of Monsoonal change of water quality parameters between 1983 and 2008 in a tropical estuary in Northeastern India: Role of phytoplankton and community metabolism, *Mar. Ecol.*, *34*(1), 14–29.

Donato, D., J. Kauffman, D. Murdiyarso, S. Kurnianto, M. Stidham, and M. Kanninen (2011), Mangroves among the most carbon-rich forests in the tropics, *Nat. Geosci.*, *4*, 293–297.

Elnwishy, N., H. Abichou, M. Labiadh, and S. Zalat (2009), A promising vegetation type to sustain development in drylands, *J. Arid Land Stud.*, *19*(1), 113–116.

Evans, W., B. Hales, and P. G. Strutton (2013), pCO_2 distributions and air–water CO_2 fluxes in the Columbia River estuary, *Estuarine Coastal Shelf Sci.*, *117*, 260–272.

Frankignoulle, M., I. Bourge, and R. Wollast (1996), Atmospheric CO_2 fluxes in a highly polluted estuary (the Scheldt), *Limnol. Oceanogr.*, *41*, 365–369.

Frankignoulle, M., G. Abril, A. V. Borges, I. Bourge, C. Canon, B. De Lille, E. Libert, and J. M. Theate (1998), Carbon dioxide emissions from European estuaries, *Science*, *282*, 434–436, doi:10.1126/science.282.5388.434.

Ganguly, D., M. Dey, C. Chowdhury, A. A. Pattnaik, B. K. Sahu, and T. K. Jana (2011), Coupled micrometeorological and biological processes on atmospheric CO_2 concentrations at the land-ocean boundary, NE coast of India, *Atmos. Environ.*, *45*, 3903–3910.

Guo, X., M. Dai, W. Zhai, W.-J. Cai, and B. Chen (2009), CO_2 flux and seasonal variability in a large subtropical estuarine system, the Pearl River Estuary, China, *J. Geophys. Res.*, *114*, G03013, doi:10.1029/2008JG000905.

Hamilton, S. K., S. J. Sippel, and J. M. Melack (1995), Oxygen depletion and carbon dioxide and methane production in waters of the Pantanal wetland of Brazil, *Biogeochemistry*, *30*, 115–141.

Ho, D. T., P. Schlosser, and P. M. Orton (2011), On factors controlling air-water gas exchange in a large tidal river, *Estuaries Coasts*, doi:10.1007/s12237-011-9396-4.

Jennerjahn, T. C., and V. Ittekkot (2002), Relevance of mangroves for the production and deposition of organic matter along tropical continental margins, *Naturwissenschaften*, *89*, 23–30.

Jiang, L.-Q., W.-J. Cai, and Y. Wang (2008), A comparative study of carbon dioxide degassing in river-and marine-dominated estuaries, *Limnol. Oceanogr.*, *53*, 2603–2615.

Kempe, S. (1982), Long-term records of CO_2 pressure fluctuations in freshwaters, in *Transport of Carbon and Minerals in Major World Rivers*, vol. 52, edited by E. T. Degens, pp. 91–332, Mitt. Geol. Palaont. Inst. Univ. Hamburg, Hamburg.

Khoo, K. H., R. W. Ramette, C. H. Culberson, and R. G. Bates (1977), Determination of hydrogen ion concentrations in seawater from 5 to 40 °C: Standard potentials at salinities from 20 to 45‰, *Anal. Chem.*, *49*(1), 29–34.

Kristensen, E., F. O. Andersen, N. Holmbe, M. Holmer, and N. Thongtham (2000), Carbon and nitrogen mineralization in sediments of Bangrong mangrove area, Phuket, Thailand, *Aquat. Microb. Ecol.*, *22*, 199–213.

Kuwae, T., J. Kanda, A. Kubo, F. Nakajima, H. Ogawa, A. Sohma, and M. Suzumura (2016), Blue carbon in human-dominated estuarine and shallow coastal systems, *Ambio*, *45*, 290–301, doi:10.1007/s13280-015-0725-x.

Laruelle, G. G., H. H. Dürr, C. P. Slomp, and A. V. Borges (2010), Evaluation of sinks and sources of CO_2 in the global coastal ocean using a spatially-explicit typology of estuaries and continental shelves, *Geophys. Res. Lett.*, *37*, L15607, doi:10.1029/2010GL043691.

Lewis E., Wallace D. W. R. (1998), Program developed for CO_2 system calculations, ORNL/CDIAC – 105, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, Oak Ridge, Tenn.

Maher, D. T., and B. D. Eyre (2012), Carbon budgets for three autotrophic Australian estuaries: Implications for global estimates of the coastal air-water CO_2 flux, *Global Biogeochem. Cycles*, *26*, GB1032, doi:10.1029/2011GB004075.

Maher, D. T., I. R. Santos, L. Golsby-Smith, J. Gleeson, and B. D. Eyre (2013), Groundwater-derived dissolved inorganic and organic carbon exports from a mangrove tidal creek: The missing mangrove carbon sink?, *Limnol. Oceanogr.*, *58*(2), 475–488, doi:10.4319/lo.2013.58.2.0475.

Middelburg, J. J., J. Nieuwenhuize, F. J. Slim, and B. Ohowa (1996), Sediment biogeochemistry in an East African mangrove forest (Gazi Bay, Kenya), *Biogeochemistry*, *34*, 133–155.

Mitra, A., A. Gangopadhyay, A. Dube, A. C. Schmidt, and K. Banerjee (2009), Observed changes in water mass properties in the Indian Sundarbans (northwestern Bay of Bengal) during 1980–2007, *Curr. Sci.*, *97*(10), 1445–1452.

Mitra, A., S. Trivedi, S. Zaman, P. Pramanick, S. Chakraborty, N. Pal, P. Fazli, and K. Banerjee (2015), Decadal variation of nutrient level in two major estuaries in Indian Sundarbans, *Jordan J. Biol. Sci.*, *8*(3), 231–236.

Mostofa, K. M., et al. (2016), Reviews and syntheses: Ocean acidification and its potential impacts on marine ecosystems, *Biogeosciences*, *13*(6), 1767–1786.

Mukhopadhyay, S. K., H. Biswas, T. K. De, S. Sen, and T. K. Jana (2002), Seasonal effects on the air-water carbon dioxide exchange in the Hooghly estuary, NE coast of Bay of Bengal, India, *J. Environ. Monit.*, *4*, 459–552.

Mukhopadhyay, S. K., H. Biswas, T. K. De, and T. K. Jana (2006), Fluxes of nutrients from the tropical River Hooghly at the land–ocean boundary of Sundarbans, NE Coast of Bay of Bengal, India, *J. Mar. Syst.*, *62*(1), 9–21.

Ovalle, A. R. C., C. E. Rezende, L. D. Lacerda, and C. A. R. Silva (1990), Factors affecting the hydrochemistry of a mangrove creek, Sepetiba Bay, Brazil, *Estuarine Coastal Shelf Sci.*, *31*, 639–650.

Parsons, T. R., Y. Maita, and C. M. Lalli (1992), *A Manual of Chemical and Biological Methods for Sea Water Analysis*, pp. 101–103, Pergamon, New York.

Peng, T.-H., T. Takahashi, W. S. Broecker, and J. Olafsson (1987), Seasonal variability of carbon dioxide, nutrients and oxygen in the northern North Atlantic surface water: Observation and a model, *Tellus*, *39B*(5), 439–458.

Ray Choudhuri, T., K. Banerjee, S. Zaman, S. Chakraborty, T. Rudra, A. Guha, D. Karmakar, P. Pramanick, P. Fazli, and A. Mitra (2015), Diluted proxies of climate change in the inshore estuarine complex of Bay of Bengal: A case of overlapping noise and facts, *J. Environ. Sci. Computer Sci. Eng. Technol.*, *4*(2), 601–614.

Raymond, P. A., and J. J. Cole (2001), Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, *Estuaries*, *24*, 269–274.

Raymond, P. A., N. F. Caraco, and J. J. Cole (1997), Carbon dioxide concentration and atmospheric flux in the Hudson River, *Estuaries*, *20*, 381–390, doi:10.2307/1352351.

Rudra, K. (2014), Changing river courses in the western part of the Ganga-Brahmaputra delta, *Geomorphology*, *227*, 87–100, doi:10.1016/j.geomorph.2014.05.013.

Samanta, S., T. K. Dalai, J. K. Pattanaik, S. K. Rai, and A. Mazumdar (2015), Dissolved inorganic carbon (DIC) and its δ 13 C in the Ganga (Hooghly) River estuary, India: Evidence of DIC generation via organic carbon degradation and carbonate dissolution, *Geochim. Cosmochim. Acta*, *165*, 226–248.

Sarkar, S. K., S. Frančišković-Bilinski, A. Bhattacharya, M. Saha, and H. Bilinski (2004), Levels of elements in the surficial estuarine sediments of the Hugli River, northeast India and their environmental implications, *Environ. Int.*, *30*, 1089–1098.

Sarma, V. V. S. S., M. D. Kumar, and M. Manerikar (2001), Emission of carbon dioxide from a tropical estuarine system, Goa, India, *Geophys. Res. Lett.*, *28*, 1239–1242, doi:10.1029/2000GL006114.

Sarma, V. V. S. S., et al. (2011), High CO_2 emissions from the tropical Godavari estuary (India) associated with monsoon river discharges, *Geophys. Res. Lett.*, *38*, L08601, doi:10.1029/2011GL046928.

Sarma, V. V. S. S., et al. (2012), Carbon dioxide emissions from Indian monsoonal estuaries, *Geophys. Res. Lett.*, *39*, L03602, doi:10.1029/2011GL050709.

Wanninkhof, R. (2014), Relationship between wind speed and gas exchange over the ocean revisited, *Limnol. Oceanogr. Methods*, *12*, 351–362.

Weiss, R. F. (1974), Carbon dioxide in water and seawater: The solubility of non-ideal gas, *Mar. Chem.*, *2*, 203–215.

Yang, B., R. H. Byrne, and M. Lindemuth (2015), Contributions of organic alkalinity to total alkalinity in coastal waters: A spectrophotometric approach, *Mar. Chem.*, *176*, 199–207.

Zhai, W., M. Dai, W. J. Cai, Y. Wang, and Z. Wang (2005), High partial pressure of CO_2 and its maintaining mechanism in a subtropical estuary: The Pearl River estuary, China, *Mar. Chem.*, *93*, 21–32, doi:10.1016/j.marchem.2004.07.003.