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High CO_2 emissions from the tropical Godavari estuary (India) associated with monsoon river discharges

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Abstract

Estuaries have been under sampled to establish them as sources or sinks of the atmospheric carbon dioxide. Such poor coverage is well known for tropical, particularly monsoon driven, estuaries. In an attempt to study the variability in CO_2 in a tropical monsoon estuary we made systematic time-series observations in the Gautami Godavari estuarine system in the east coast of India. Our 18 month-long extensive monitoring in the tropical Godavari estuarine system revealed pH >7.8 during dry period that decreased by 1.5±0.01 during peak discharge period. The decrease in pH was associated with high nutrients and bacterial activities suggesting significant organic carbon decomposition. High bacterial respiration (20.6±7.2 μMC l^{-1} d^{-1}) in the estuary resulted in very high pCO_2 of ~30,000 μatm during peak discharge period, which otherwise were <500 μatm during dry period. Such high pCO_2 levels were unknown to occur in any aquatic region. Several major and minor estuaries flow into the northern Indian Ocean from the Indian subcontinent and the monsoon associated processes make these systems chimney for emitting CO_2 to atmosphere unrealized hitherto.

1. Introduction

The oceans are known to be a sink for atmospheric CO_2 (*Takahashi et al.,* 2009) but the role of coastal bodies remains unclear (*Borges et al.,* 2005; *Cai et al.,* 2006; *Chen and Borges,* 2009). The evaluated CO_2 uptake by continental shelves (*Borges et al.,* 2005; *Laruelle et al.,* 2010) range between -0.22 and -1.0 PgC y^{-1} while *Laruelle et al.* (2010) estimated emission of CO_2 from estuaries to be +0.27 PgC y^{-1}. All these estimates, however, suffer from large uncertainties, more so in the case of estuaries. Fluxes evaluated for some Asian estuaries (eg. *Zhai et al.*, 2005; *Sarma et al.,* 2001;*Mukhopadhyay et al.*, 2003) are based on limited data in time and space and hence are either under or overestimated. *Mukhopadhyay et al.* (2003), based on monthly variations in the Hooghly estuary, found pCO_2 to range from 220 to 1200 μatm that result in a flux of -3 to 84 mmol m^{-2} d^{-1}. A seasonal study of pCO_2 in the Mandovi estuary in Goa revealed its level to range between 110 and 2300 μatm and a flux variation from -2 to 67 mmol m^{-2} d^{-1}. The pCO_2 measurements in the Godavari estuary, on the other hand, have been made just once during dry period and its levels some times are found to exceed the atmospheric values (*Bouillon et al.,* 2003). Therefore, uncertainties associated with Indian estuarine emissions could be even larger as the biogeochemical processes in the most of these systems are driven by monsoon discharges. Monsoonal estuaries have characteristic runoff periods and exhibit non-steady state behaviour (*Vijith et al.,* 2009). Seasonal runoff into these monsoonal estuaries far exceeds the total volume of the estuary during the times of peak discharges. Hence, the biogeochemical processes in monsoonal estuaries during discharge period could be completely different from that in dry period.

The Godavari, fed by southwest monsoon rainfall in summer (June-September) and the associated water and sediment discharges, is the second largest river in India. We have initiated time-series experiments in the Godavari estuarine system to understand the influence of monsoon discharges on biogeochemical processes. Experiments (*Sarma et al.*, 2010) revealed significant nutrients and suspended discharges along with the river runoff, and perennial dominance of heterotrophy in the Godavari estuary when the annual mean production to respiration ratio (P:R) is found to be 0.14±0.02 (*Sarma et al.,* 2009). The heterotrophic organic carbon demand of ~40-99% of total heterotrophic respiration could be supported by terrigeneous organic matter. This dominant heterotrophy is expected to have significant influence on dissolved CO_2 level and its emissions from the Godavari estuary. We present here results of 18 month-long detailed investigations, comprising daily and monthly observations, to understand the CO_2 system during monsoon discharge period, with particular reference to its saturation in the Godavari estuarine system.

2. Sampling and methods

The Godavari river system ranks 34th and 32nd in the world in terms of catchment area and water discharges, respectively. It is located between 16 and 18° N, and 78 and 82° E and covers an area of ~330,000 km^2. A dam was built on the Godavari river in 1842 at Dowleiswaram, approximately 60 km upstream from the mouth. The monsoon derived fresh water is stored in this dam reservoir for conserved utilization during the dry seasons by the Irrigation Department. With the onset of summer monsoon runoff, the dam reservoir is first filled and the surplus water is released downstream. Downstream of the dam, the Godavari is naturally divided into Gautami and Vashishta distributaries that form respective estuarine systems (Fig. 1) and observations were conducted in the former branch of the estuary.

We collected discharge data from the dam authorities at Dowleiswaram. Observations were carried out in the Gautami Godavari estuary at two time-series scales; daily and monthly. A fixed station, Yanam located in the middle estuary, was sampled daily whereas 10 stations, positioned along the estuarine channel to cover the salinity gradient up to mouth region, were sampled once every month (Fig. 1). Temperature, salinity and depth were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA). Nutrients were measured using autoanalyzer following *Grashoff et al.* (1992). The pH and total alkalinity were measured by potentiometric (Metrohm, Switzerland) Gran titration methods following Standard Operating Procedures (SOP) suggested by *DOE* (1998). Dissolved inorganic carbon (DIC) was measured using a Coulometer (UIC Inc., USA). The precision for pH, TA, and DIC were 0.002, 2.0 and 1.8 $\mu mol\ l^{-1}$ respectively. The pCO_2 was computed using measured salinity, temperature, nutrients (phosphate and silicate), pH and DIC using dissociation constants given by *Millero et al.* (2006) for 0 to 40 salinity ranges using CO_2 sys program (*Lewis and Wallace*, 1998). Total bacteria were counted by epifluoroscence microscope using DAPI technique. Bacterial production and respiration was measured following *Toolan et al.* (2001) and *Griffith et al.* (1990) respectively using 0.7 μm GF/F filters and converted to carbon units following *Lee and Fuhrman* (1987). Air-water flux of CO_2 was estimated following *Wanninkhof* (1992) using measured wind speed.

3. Results and discussion

The dam controlled freshwater discharge into the Godavari estuary was maximal in August (Fig. 2a). There was virtually no discharge between January and May. The inter-annual variability in the discharge was due to differences in precipitation over the catchment area which was more in 2008 than in 2009 (*Dr. S. Venkateswarulu*, Indian Meteorological Department, personal communication). While the estuary was completely filled with freshwater during peak discharge periods whereas waters of >20 salinity were common in the dry period (Fig. 2a).

The pH at Yanam changed from 6.459 to 8.486 with lower values between mid-June and September (Fig. 2b). The decrease in pH coincides with high discharge, when the entire estuary was filled with the fresh water (*Sarma et al.*, 2009; 2010). In contrast, the pH increases (~7.801 to 8.434) during less or no discharge period as the seawater intrudes. The low pH values of June-September period in the middle estuary were associated with high nutrients and bacteria. High dissolved nitrate (average of 41.6±25 μmol l^{-1} with a peak of 80 μmol l^{-1}; Fig. 2c), and high bacterial numbers (average of ~4.0 x 10^8 nos l^{-1} with a high value of ~8 x 10^8 nos l^{-1}; Fig. 2d) during this intense discharge period suggest significant organic matter decomposition leads to the decreased pH.

Sarma et al. (2009) found that dissolved oxygen in the surface is under-saturated by 2-30%, at Yanam, during the peak discharge period while it is relatively supersaturated during dry period (1 to 6%), indicating the utilization of oxygen during the intensified heterotrophic activity during former period. High nutrient concentrations in peak discharge period in the Godavari estuary (Fig. 2b; *Sarma et al.*, 2010) were due to both *in situ* decomposition of organic matter and washed out fertilizer remnants from upstream or across the banks of the river/estuary. As a result high ammonium concentrations are observed during peak discharge period (36.1±22 μmol l^{-1}) than dry period (5.3±μmol l^{-1}; Sarma et al., 2010). The fertilizers use along the east coast of India is high (49.3 kg hectare^{-1}) that amounts almost double to the country's average (Department of Agriculture, http://www.indiastat.com/africulture/2/stats. aspx). Availability of nutrients promotes photosynthesis, although subject to the availability of light, enhancing the organic material loading into water. In addition to this, Godavari river transports 2.81 x 10^6 tons per year of particulate organic carbon (POC) to the estuary (*Gupta et al.*, 1997) from the upstream and about 22% of the riverine POC is estimated to be lost in the main channel of Godavari through oxidation of its labile fraction (*Balakrishna and Probst*, 2005). *Cole et al.* (1988) observed that oxidation of organic carbon to CO_2 by heterotrophy is faster in freshwater than in seawater. Hence, higher organic carbon availability appears to have supported high bacterial respiration (BR 20.6±7.2 μMC l^{-1} d^{-1}) during peak discharge period. In contrast, low BR (10.0±4 μMC l^{-1} d^{-1}) were found during the dry period. *Sarma et al.* (2009) attributed higher rates of BR was supported by external supplies of organic carbon in the estuary. *Shaiah et al.* (2006) observed that increase in BR with increased river discharge in the Changjiang estuary due to availability of more organic carbon. In addition to this, high bacterial activity in the upstream region during storage period, before its discharge to estuary, further decreases pH. Hence low pH during peak discharge period in Fig. 2b was due to intense bacterial decomposition of organic carbon in the estuary and upstream. This led to increase in pCO_2 (up to 33,000 μatm) during peak discharge period whereas it was <500 μatm during dry period (Fig. 2d).

Both pH and pCO_2 exhibited large variability along the main channel in the estuary (Table 1). For convenience of the discussion, the estuary is divided into three regions: the upper estuary which is mostly influenced by freshwater, the middle one with largely brackish water conditions and the lower estuary dominated by marine conditions. The pH variations in the upstream, middle and lower regions of the estuary showed different patterns and were associated with salinity (Table 1). Lower pH (<7.5) and higher pCO_2 (>1000 μatm) occurred in waters of <5 salinity (Fig. 3; supplementary information), and associated with turbidity maxima. These trends were in excellent agreement with those observed elsewhere with respect to particle maxima of Hudson (*Raymond et al.,* 1997), European (*Frankingnoulle et al.,* 1998), and Mandovi estuaries (*Sarma et al.,* 2001). The pCO_2 decreased seaward, in general, in concurrence with the results elsewhere (*Frankignoulle et al.,* 1998; *Sarma et al.,* 2001; *Mukhopadhyay et al.,* 2003).

The averaged pCO_2 values ranged from 221 to 32763, 367 to 34026 and 286 to 14631 μatm in the upstream, middle and lower regions of the estuary, respectively (Table 1). Except in May, the upper estuary was supersaturated with pCO_2 with respect to atmosphere. The measured pCO_2 supersaturation in the upper estuary coincided with the peak discharge. The extent of supersaturation decreased downstream in the estuary, except in August 2008. The pCO_2 levels in the upper estuary during discharge period were 38-86 times higher than the atmospheric concentration of 380 μatm. The values reported for the polluted estuaries such as the Rhine (~25000 μatm; Kempe, 1982) and the Scheldt estuaries (~15200 μatm; *Borges and Frankignoulle,* 2002) are far below the levels found in the Godavari estuary. In most other estuaries, pCO_2 was <10,000 μatm (Table 2; supplementary material). High pCO_2 levels found in the Scheldt estuary have been attributed to discharge of pollutants (*Borges and Frankignoulle,* 2002). The Godavari estuary can not be classified as a polluted estuary based on the average nutrient ratios of N:P 20±7 (*Sarma et al.,* 2010) nor it receives any significant domestic or industrial effluents. *Balakrishna and Probst* (2005) suggested large-scale erosion and deforestation in the catchment area led to export of high amounts of organic carbon into the Godavari estuary compared to other major world rivers. Bacterial respiration of this land derived organic material, besides that produced in situ supported by high nutrients, is leading to yearround supersaturation of CO_2 in the upstream and middle regions and in the entire estuary during monsoon discharge period.

Mean CO_2 emissions across air-water interface decreased in the order 0.24, 0.15 and 0.08 mol C m^{-2} d^{-1} from upper, middle and lower estuarine regions, respectively. *Borges et al.* (2005) estimated the emission of CO_2 from the subtropical and tropical estuaries (-30 to +30^{o} latitudinal belt) to be 16.83 mol C m^{-2} y^{-1}. In their estimates they used flux from the Godavari as 5.5 mol C m^{-2} y^{-1}, which actually represents only dry pre-monsoon period (April-May) (*Bouillon et al.,* 2003). Our presently calculated flux from the Godavari estuary for the year 2009 was 52.6 mol C m^{-2} y^{-1}. Our estimated flux from the Godavari alone far exceeds (over 2 times) that estimated (25.72 mol C m^{-2} y^{-1} or 0.173 TgC y^{-1}) for entire tropical and subtropical band by *Borges et al.* (2005). Several estuaries, major and minor, open into the northern Indian Ocean and creation of conditions observed in this study would make these coastal bodies a very significant CO_2 source to atmosphere unrealized hitherto.

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Legend to Figures

Figure 1. Sampling locations in the Godavari estuary. Daily time-series sampling was conducted at Yanam, in the middle of the estuary, while monthly sampling was done at all stations. River discharge data were collected from the Dowaleswaram reservoir.

Figure 2. Time-series variations in a) salinity, b) pH, c) nitrate and total bacterial counts and d) pCO_2 at Yanam (middle estuary) are shown. The daily mean discharge was drawn as a continuous line.

Table 1: Time-series variations in salinity, pH and pCO$_2$ (μatm) at locations shown in Figure 1. Results from respective stations have been averaged for each box to enable comparison among upstream, middle and downstream regions of the estuary.

	Salinity			pH			pCO$_2$		
month	Upstream	Middle	downstream	Upstream	Middle	downstream	Upstream	Middle	downstream
Jun-08	0.088	4.647	17.151	6.595	7.244	7.786	22768	5298	1055
Jul-08	0.088	6.912	7.856	6.685	7.499	7.617	26514	3446	2376
Aug-08	0.075	0.082	0.092	6.576	6.437	6.855	32763	34026	14631
Sep-08	0.108	0.165	0.594	6.699	6.841	7.151	26032	21997	11898
Oct-08	0.142	5.029	8.553	7.026	7.496	8.053	19363	5372	1132
Nov-08	1.841	1.829	10.305	7.014	7.551	8.016	14696	4941	1282
Dec-08	2.975	13.544	18.499	7.567	7.807	7.847	4844	1528	1277
Jan-09	8.178	17.968	22.149	8.608	8.539	8.370	467	253	344
Feb-09	13.349	24.815	26.900	7.917	7.973	7.976	1175	652	617
Mar-09	15.171	21.664	28.765	8.403	8.410	8.353	519	376	350
Apr-09	13.188	18.635	14.888	8.417	8.368	8.332	558	507	557
May-09	8.017	12.211	25.071	8.601	8.290	7.861	221	409	1202
Jun-09	7.994	26.732	30.788	8.044	8.238	8.268	740	367	332
Jul-09	18.204	29.776	33.521	8.113	8.242	8.321	629	371	286
Aug-09	0.103	1.321	2.003	6.121	7.023	7.235	26165	6172	4789
Sep-09	0.082	1.109	3.111	6.189	7.043	7.258	22366	5893	4539
Oct-09	7.159	15.321	17.243	7.053	7.213	7.721	14876	4899	1021
Nov-09	8.112	16.321	18.235	7.612	7.811	7.863	5780	2500	550
Dec-09	13.982	18.125	19.842	8.167	8.122	8.157	1250	480	400

Figure 1

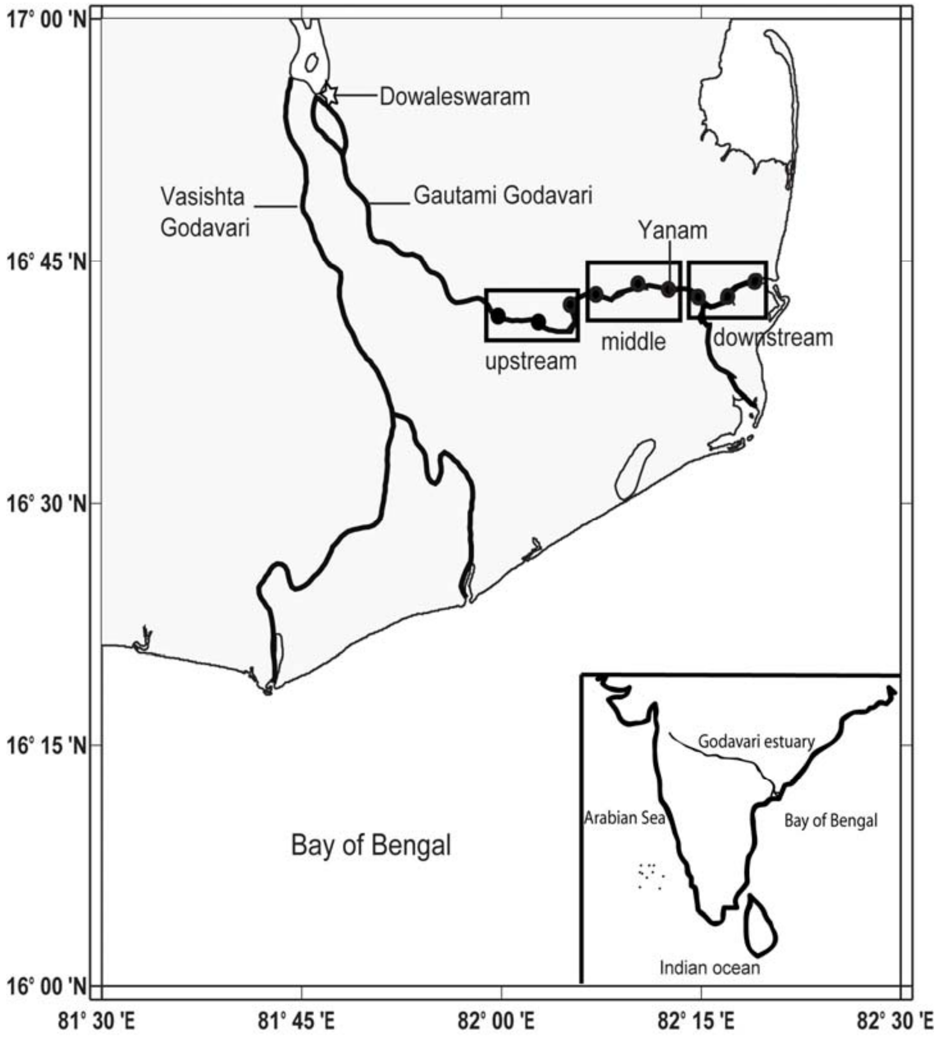
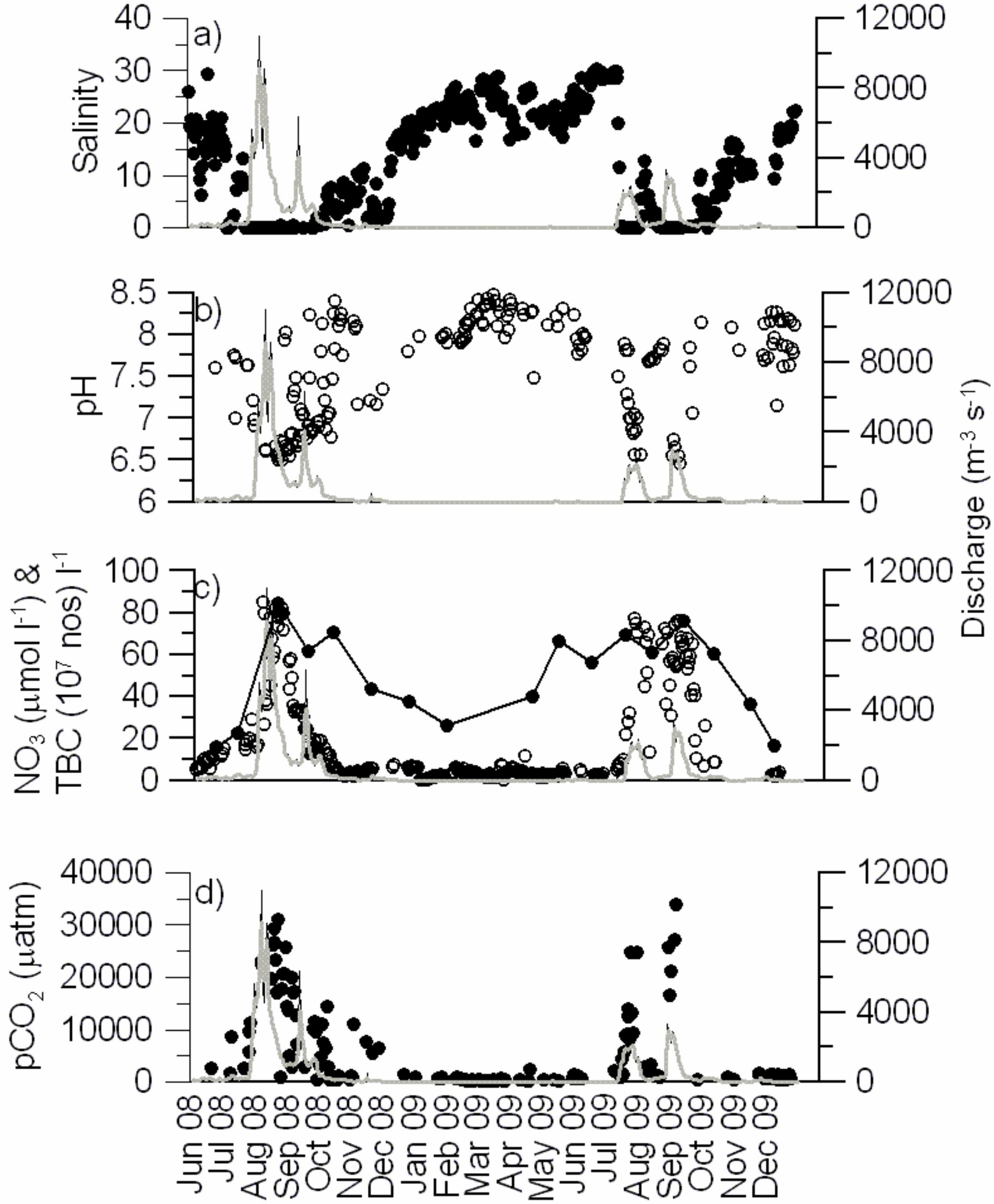

17° 00 'N
Dowaleswaram
Vasishta Godavari
Gautami Godavari
Yanam
16° 45 'N
upstream
middle
downstream
16° 30 'N
16° 15 'N
Bay of Bengal
Godavari estuary
Arabian Sea
Bay of Bengal
Indian ocean
16° 00 'N
81° 30 'E
81° 45 'E
82° 00 'E
82° 15 'E
82° 30 'E

Figure 2


a)
Salinity
0
10
20
30
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0
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8000
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b)
pH
6
6.5
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7.5
8
8.5
0
4000
8000
12000
Discharge (m^{-3} s^{-1})
c)
NO_3 (μmol l^{-1}) &
TBC (10^7 nos) l^{-1}
0
20
40
60
80
100
0
4000
8000
12000
d)
pCO_2 (μatm)
0
10000
20000
30000
40000
0
4000
8000
12000
Jun 08
Jul 08
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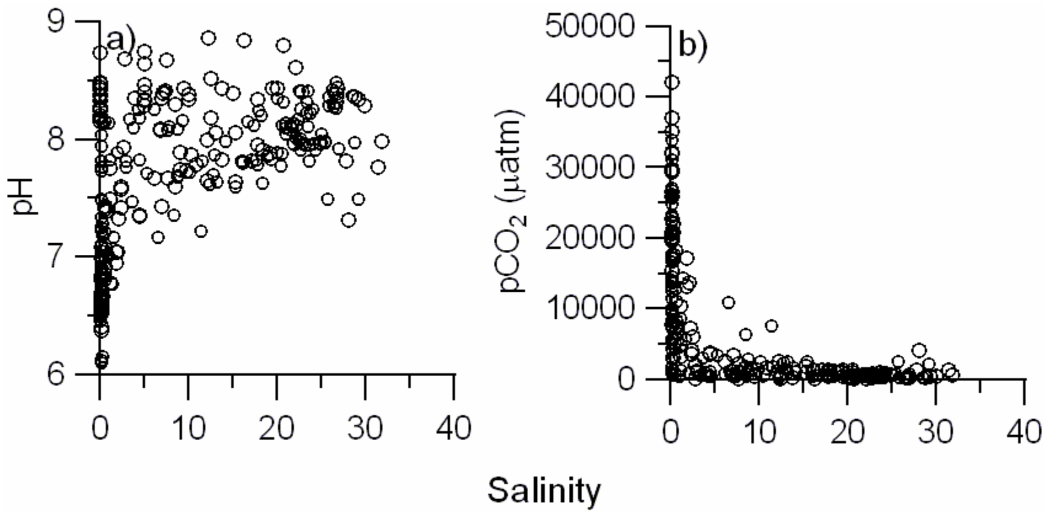
Supplementary Figure S1



Supplementary Table 2

Table 2: The ranges of pCO_2 (μatm) measured in different estuaries in the world.

Estuary (location)	pCO_2	Reference
Scheldt (Belgium/Netherlands)	100-15,200	Borges and Frankignoulle (2002)
Saja-Besaya (Spain)	264-9728	Ortega et al (2005)
Urdaibai (Spain)	256-1569	Ortega et al (2005)
Ason (Spain)	246-436	Ortega et al (2005)
Sado (Portugal)	450-5700	Frankignoulle et al (1998)
Douro (Portugal)	385-2200	Franakignoulle et al (1998)
Elbe (Germany)	340-1100	Frankignoulle et al (1998)
Ems (Germany/Netherlands)	525-3755	Frankiguoulle et al (1998)
Rhine (Netherlands)	340-25000	Kempe et al (1982)
Randers Fjords (Denmark)	320-3400	Gazeau et al (2005)
Loire (France)	600-2900	Abril et al (2003)
Gironde (France)	440-2860	Frankignoulle et al (1998)
Thames (UK)	468-5200	Frankignoulle et al (1998)
Tamar (UK)	380-2200	Frankignoulle et al (1998)
Satilla (US-Georgia)	420-8200	Cai and Wang (1998)
Altamaha (US-Georgia)	380-7800	Cai and Wang (1998)
Hudson (US-New York)	503-2270	Raymond et al (1997)
York (US-Virginia)	352-1896	Raymond et al (2000)
Rappanhannock (US-Virginia)	474-1613	Raymond et al (2000)
James (US-Virginia)	284-1361	Raymond et al (2000)
Columbia (US-Oregon)	560-950	Park et al (1969)
Potomac (US-Maryland)	646-878	Raymond et al (2000)
Changjiang (China-Shanghai/Jiangsu)	168-2264	Gao et al (2008)
Changjiang/Yangtze River (China)	700-1950	Chen et al (2008)
Pearl River (China-Guangdong)	360-4785	Zhai et al (2005)
Xijiang River (China)	600-11000	Yao et al (2007)
Mandovi-Zuari (India)	400-2250	Sarma et al (2001)
Cochin Estuary (India)	1228-2843	Gupta et al (2009)
Chilka (India)	76-7878	Gupta et al (2008)
Hoogly (India)	320-1200	Mukhopadyay et al (2003)
Godavari estuary (India) (premonsoon)	293-500	Bouillon et al (2003)
Godavari estuary (India)	100-33391	This study

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