

Carbon dioxide emissions from Indian monsoonal estuaries

V.V.S.S. Sarma, R. Viswanadham, G.D. Rao, V.R. Prasad, B.S.K. Kumar, S.A. Naidu, N.A. Kumar, D.B. Rao, T. Sridevi, M.S.R. Krishna, N.P.C. Reddy, Y. Sadhuram, and T.V.R. Murty

National Institute of Oceanography, Council of Scientific and Industrial Research, 176 Lawsons Bay Colony, Visakhapatnam – 530 017, India

Email: sarmav@nio.org

Estuaries are known to be strong source for atmospheric CO₂, however, little information is available from Indian estuaries. In order to quantify CO₂ emissions from the Indian estuaries, samples were collected at 27 estuaries all along the Indian coast during discharge (wet) period. The emissions of CO₂ to the atmosphere from Indian estuaries were 4-5 times higher during wet than dry period. The pCO₂ ranged between ~300 and 18492 μ atm which are within the range of world estuaries. The mean pCO₂ and particulate organic carbon (POC) showed positive relation with rate of discharge suggesting availability of high quantities of organic matter that led to enhanced microbial decomposition. The annual CO₂ fluxes from the Indian estuaries, together with dry period data available in the literature, amounts to 1.92 TgC which is >10 times less than that from the European estuaries. The low CO₂ fluxes from the Indian estuaries are attributed to low flushing rates and less human settlements along the banks of the Indian estuaries.

1. Introduction

The oceans act as a net sink for atmospheric CO₂ (Gruber *et al.*, 2009; Takahashi *et al.*, 2009); however, the role of coastal bodies on global CO₂ fluxes remains unclear due to lack of data (Borges *et al.*, 2005; Cai *et al.*, 2006; Chen and Borges, 2009; Laurelle *et al.*, 2010). The estimated absorption of CO₂ from the continental shelves, with limited data, is 0.22 to 1.0 PgC y⁻¹ (1 Pg=10¹⁵ g; Borges, 2005; Borges *et al.*, 2005; Cai *et al.*, 2006; Chen and Borges, 2009), and of CO₂ emission by estuaries to the atmosphere is 0.27 PgC y⁻¹ (Laruelle *et al.*, 2010). An estimation of CO₂ emissions from European Estuaries, based on data of 9 estuaries, which were relatively polluted with organic matter, was between 30 and 60 TgC (1 Tg=10¹² g) which represents 5 to 10% of present anthropogenic CO₂ emission for Western Europe (Frankignoulle *et al.*, 1998). The estimates from the estuaries suffer from large uncertainties due to large variability and lack of systematic data collection. It is especially true for Southeast Asian estuaries as the biogeochemical cycling of material are different due to high atmospheric temperature, seasonality driven by monsoons, seasonal discharge etc (Sarma *et al.*, 2011). These regions are also highly under-sampled with reference to time and space.

Estuaries in India are influenced by monsoonal rainfall and therefore called Monsoonal estuaries and 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 and entire estuary assumes riverine condition (Sarma *et al.*, 2009; 2010, 2011). Discharges of variable magnitudes occur for a period of 4-6 months and the upstream rivers almost dries up during the other periods allowing for the dominance of seawater in the estuary. Hence, the biogeochemical processes in monsoonal estuaries during discharge period could be completely different from those in dry period. Recently Sarma *et al.* (2011) reported record levels of partial CO₂ pressures (pCO₂) of >30,000 µatm in the Godavari estuary during discharge period of 2008 whereas close to atmospheric saturation was noticed during dry period. Similarly, enhanced pCO₂ levels during discharge period was also noticed in other Indian estuaries, such as Mandovi-Zuari (Sarma *et al.*, 2001), Cochin estuary (Gupta *et al.*, 2009), Chilka estuary (Gupta *et al.*, 2008) whereas several fold lower pCO₂ levels (<1000 µatm) were found during dry periods in these estuaries. The objective of this study is to estimate contribution of CO₂ emissions from the Indian estuaries to the atmosphere.

2. Sampling and measurements

Earlier observations in the Indian estuaries suggested that the emission from the Indian estuaries during discharge period (wet period) was higher by 4 to 5 times than that of dry period (*Sarma et al.*, 2001; *Gupta et al.*, 2008, 2009; *Sarma et al.*, 2011), hence sampling was carried out in all major estuaries along the Indian coast during discharge period. We have simultaneously estimated surface pCO₂ and related atmospheric fluxes during discharge period in 27 Indian estuaries all along the Indian coast (Figure 1). River discharge data were collected from the dam authorities and no data were available from minor river where no dams were constructed. From each estuary, samples were collected at 3 to 5 locations spanning from mouth to upstream of the estuary. All samples were collected within 3 weeks (28th July to 18th August 2011). Temperature, salinity and depth were measured using a CTD system (Sea Bird Electronics, SBE 19 plus, USA). Nutrients were measured using spectrophotometric method following *Grashoff et al.* (1992). Dissolved Oxygen (DO) was measured using Winkler's titration method of *Carritt and Carpenter* (1966). The analytical precision, expressed as standard deviation, was 0.07% for DO. About 1 litre of water samples was filtered through pre-combusted GF/F filter, at 300° C for 6 h, at low vacuum and dried at 60° C for at least 24 h. Filters were acid fumigated for 12 h in the desiccators to remove inorganic carbon and POC on the filter was measured using Elemental analyzer (Thermo Fisher, Germany). 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 µmol l⁻¹ respectively. The accuracy of the DIC measurement were tested using Certified Reference Material supplied by Dr. A.G. Dickson, Scripps Institute of Oceanography, USA and internal standards and found to be within 1.5%. The pCO₂ 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 *CO₂ sys* program (*Lewis and Wallace*, 1998). Daily wind speed data were obtained from the Indian Meteorological Department (IMD) from the stations close to the respective estuaries. The CO₂ fluxes were estimated using seasonal mean wind speed, pCO₂ difference between water and atmosphere and transfer velocity coefficient given by *Wanninkhof* (1992). The flux estimates based on *Wanninkhof's* coefficients may provide under-estimates due to the tidal enhancement of turbulence (*Zappa et al.*, 2003; *Borges et al.*, 2004). Atmospheric pCO₂ data obtained from a nearest station in India (Cape Rama, 15.08° N, 73.83° E)

corresponding to the period of study (Global view, 2011). Excess CO₂ was computed based on Abril et al (2000) and Apparent oxygen utilization (AOU) was computed using Garcia and Gordon (1992).

3. Results and discussions

The data collected in the Indian estuaries display a range of different hydrological conditions, from low freshwater flow and longer residence time in the estuary to high freshwater flow and short residence time in other estuaries. The rate of mean annual discharge from the Indian estuaries varied from ~28 to 3500 m³ s⁻¹ and relatively higher discharge was found in the estuaries located in the northern than southern part of India. Discharge has significant impact on magnitude of organic matter brought to the estuary and its residence time in the estuary. These two processes are key for modification of organic matter in the estuary and formation of CO₂.

The pCO₂ showed wide variations in the Indian estuaries (Table 1). It varied between ~300 and 15210 µatm in the estuaries located along the east coast of India and between 1840 and 18492 µatm in the west coast of India. The pCO₂ levels observed in the Indian estuaries are in the range of world estuaries (Table S1; supplementary information). Low pCO₂ values were observed in estuaries which receive less discharge and due to mixing with the seawater (Rushikulya, Nagavali, Ambalyaar and Vaigi). Close to or >10,000 µatm of pCO₂ were noticed in 6 estuaries (Table 1), out of which four of them (Haldia, Mahanadi, Godavari, Ponniyaar estuaries) were located along the east coast of India (Fig. 1). Though the mean pCO₂ values of the estuary showed strong positive relation with the rate of discharge ($r^2=0.71$; $p<0.001$; Fig. 2a), except in Tapti which is highly polluted estuary, suggesting that the magnitude of discharge has significant impact on the CO₂ fluxes. Higher POC concentrations were found (339±60 µM) in estuaries receiving >1000 m³ s⁻¹ of discharge than lower discharge (<300 m³ s⁻¹) estuaries (152±40 µM) and positive relation with pCO₂ (Supplementary figure S1a) suggesting that increased inputs of substratum (POC) led to enhanced bacterial degradation of organic matter. *Sarma et al.* (2011) observed that high bacterial respiration (20.6±7.2 µMC l⁻¹d⁻¹) in the Godavari estuary resulted in very high pCO₂ levels of ~30,000 µatm during wet season. Similarly high pCO₂ levels were observed in other Indian estuaries such as Cochin estuary (*Gupta et al.*, 2009), Chilka estuary (*Gupta et al.*, 2008) and Mandovi-Zuari estuarine systems (*Sarma et al.*, 2001) associated with dominant heterotrophic respiration than autotrophic production (*Ram et al.*, 2003; *Gupta et al.*, 2009; *Sarma et al.*, 2009). The dissolved oxygen in the Indian estuaries was mostly below the saturation levels during wet period and

ranged between 62 and 99% and slight super-saturation was noticed only at Penna, Vellar, Cauvery and Vaigai estuaries, where the rate of discharge was small ($<100 \text{ m}^3 \text{ s}^{-1}$) and pCO_2 levels were close to the atmospheric values (Table 1). In addition to this, high concentrations of nitrate, by an order of magnitude, were noticed in the estuaries along the west coast of India (12-70 μM) than east coast of India (2-6.5 μM) and this pattern was consistent with the dissolved oxygen saturation. The oxygen saturation showed strong negative correlation with pCO_2 ($r^2=0.56$; $p<0.001$; Fig. 2b) suggesting that intense organic matter decomposition in the estuaries resulting in a decrease in pH and enhanced pCO_2 levels. In addition to this, apparent oxygen utilization (AOU) was positively correlated with excess CO_2 (Supplementary Figure S1b). This clearly indicates that the magnitude of discharge has significant impact on microbial processes and associated carbon and nitrogen cycling. This observation is consistent with the recent observations in the Godavari estuary where perennial dominance in heterotrophy was observed and ~40-80% of the heterotrophic carbon demand was supported by terrestrial organic matter brought by river discharge resulting in high nutrients levels (Sarma *et al.*, 2009, 2010). On the other hand, it has been observed that most of the labile carbon, which is respired by heterotrophs, is anthropogenic in polluted European estuaries (Kempe, 1982; Wollast, 1988; Frankignoulle *et al.*, 1998). Other pollution-related processes, such as nitrification may also acidify estuarine water and favor the CO_2 flux to the atmosphere (Billen, 1975; Frankignoulle *et al.*, 1996). The ammonium concentrations in the Indian estuaries are high– they are relatively higher in the estuaries located along the west coast (1.4-16.6 μM) than east coast of India (0.2-7.0 μM) suggesting that occurrence of nitrification is also possible mechanism, besides organic matter decomposition, to enhance pCO_2 levels in the Indian estuaries.

The CO_2 efflux from the Indian estuaries ranged between -0.0.2 and 362 $\text{mMC m}^{-2} \text{ d}^{-1}$ during wet period. Higher fluxes were noticed in the Baitarini, Godavari, Penniyaar, Tapti, Netravathi estuaries while low fluxes were ($<20 \text{ mMC m}^{-2} \text{ d}^{-1}$) found in other estuaries (Table 1). Such high fluxes in these estuaries were driven by not only high pCO_2 levels but also winds. The mean flux from the Indian estuaries amounts to 27 $\text{mMC m}^{-2} \text{ d}^{-1}$. India houses 14 major, 44 medium and 162 minor estuaries and the total surface area of Indian estuaries comes to 27000 km^2 calculated from the mouth of the estuary to the region where tidal oscillations are almost negligible. The mean flux of CO_2 from the Indian estuaries (27 $\text{mM C m}^{-2} \text{ d}^{-1}$) is an order of magnitude less than that found in the European estuaries (mean flux of 170

mMC m⁻² d⁻¹; *Frankignoulle et al.*, 1998). The emission of CO₂ from the Indian estuaries amounts to 1.60 TgC during wet period of 6 months.

The contribution of CO₂ fluxes to the atmosphere from Indian estuaries differs significantly from wet to dry period. Earlier observations in the Indian estuaries suggested that pCO₂ levels during dry period were less than 1000 µatm in Godavari (*Bouillon et al.*, 2003; *Sarma et al.*, 2011), Mandovi-Zuari (*Sarma et al.*, 2001), Cochin estuary (*Gupta et al.*, 2009), Chilika estuary (*Gupta et al.*, 2008), Mahanadi and Krishna rivers (our unpublished data). Such low pCO₂ levels were attributed to occurrence of phytoplankton blooms supported by increased flushing time (residence time of water column), and decreased suspended matter (increase in light penetration depth). Our daily observations in the Godavari estuary over 3 years show (*Sarma et al.*, 2011; and our unpublished data) that sometimes the pCO₂ is below equilibrium during peak bloom period, and similar observations were made elsewhere (*Borges and Frankignoulle*, 1999). Nevertheless, the contribution of CO₂ fluxes to the atmosphere during dry period of 6 months were <20% to that of wet period.

The above considerations have been used to estimate annual CO₂ emission from Indian estuaries that amounts to 1.92 TgC y⁻¹. In the case of European estuaries, *Frankignoulle et al.* (1998) estimated CO₂ fluxes as 30-60 TgC, representing 5 to 10% of the European anthropogenic emission of 1995. The anthropogenic carbon emission from the Indian subcontinent is 508 TgC y⁻¹ for 2009 (*Boden et al.*, 2011). Recently *Patra et al.* (2011) estimated CO₂ absorption by Indian landmass to be 300 TgC y⁻¹. Our results suggest that Indian estuaries contribute negligible percentage to the anthropogenic CO₂ emission and land mass absorption by the Indian subcontinent.

4. Concluding remarks

Our study suggests that Indian estuaries do act as source for atmospheric CO₂, stronger during wet season. The ranges of pCO₂ observed in some of the Indian estuaries were less than those found in the world estuaries except in the case of a few estuaries where record levels of pCO₂ were found. The magnitude of discharge is proportional to the pCO₂ levels and organic matter concentrations indicating that aerobic microbial respiration due to the large amounts of organic matter brought to the estuaries is a major mechanism leading to CO₂ efflux to the atmosphere. Since the river discharge is concentrated for only a period of a couple of months in the Indian estuaries and the mean flushing time for the Indian estuaries is <10 days whereas it is >40 days for the estuaries from Europe and USA (calculated from

mean discharge and volume of the estuary from Vijith *et al.*, 2009), there is less time available for the microbes to decompose organic matter before it is removed from the estuary, leading to incomplete decomposition. The mean CO₂ flux from the Indian estuaries (27 mM C m⁻² d⁻¹) is significantly lower than European estuaries (170 mM C m⁻² d⁻¹). Such low fluxes in the Indian estuaries are attributed to significantly low flushing time of water in the estuary during wet period and less human settlement along the riverine banks compared to developed regions in the world. Exceptions are a few estuaries such as Mahanadi where the population density and port activities are high and Narmada and Tapi where pollution related to industry and domestic pollution is high. As a result, Indian estuaries emit relatively less CO₂ to the atmosphere than elsewhere in the world.

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Legend to figures

Figure 1: Station locations map where major rivers are shown with larger font letters. The main course of the river is shown as dark line while tributaries were shown in grey color.

Figure 2. The relationship of $p\text{CO}_2$ with a) river discharge and b) dissolved oxygen saturation in the Indian estuaries. Encircled point from Tapti estuary in the figure 2a has been removed when correlation coefficient was calculated.

Table 1: Variations in annual mean discharge, temperature, salinity, oxygen saturation, DIC, pH and pCO₂ in the Indian estuaries. Values in the parenthesis in the flux column represents dry period. Values in the square brackets in pCO₂ column represents during dry period.

Estuary	Area (km ²)	Annual mean discharge (m ³ s ⁻¹)	Tidal [#] amplitude (m)	Tempe rature (°C)	Salinity	DIC (µM)	pH	pCO ₂ (µatm) mean (range)	Flux (mMC m ⁻² d ⁻¹)
Rivers reaching Bay of Bengal									
Haldia	18.15	1600	7.01	30.44	0.71	1816	7.10	9752 (2926-21906)	12.32
Subarnalekha	23.15	392 [#]	*	32.09	3.97	1340	7.96	866 (773-1012)	0.03
Baitarani	22.69	903 [#]	*	32.47	0.09	862	6.95	7247 (5920-8130)	20.72
Rushikulya	12.57	*	*	33.35	20.70	1809	8.34	293 (263-323)	-0.02
Mahanadi	13.56	2121 [#]	2.82	29.63	0.07	1252	6.87	11632 (11708-11726) [328-901]	3.07 (0.6)
Vamsadhara	15.05	*	*	30.29	13.26	2262	8.14	669 (597-774)	0.39
Nagavali	13.94	*	2.17	31.07	28.78	2023	8.12	515 (471-561)	0.17
Godavari	241.1	3505 [#]	2.10	30.15	0.16	1216	6.66	15210 (10231-26521) [253-1202]	60.67 (5.5)
Krishna	36.49	2213 [#]	1.98	29.34	5.27	2915	7.29	7473 (5217-8614) [302-1008]	6.81 (1.2)
Penna	27.97	200 [#]	*	29.82	9.27	3068	7.90	1767 (868-2182)	5.22
Vellar	20.63	*	1.51	31.27	11.57	4166	7.89	2351 (1891-3049)	17.01
Ponnayyar	9.89	*	*	29.24	0.29	3447	7.38	11153 (10310-11759)	96.32
Cauvery	20.63	677 [#]	*	30.17	12.04	3420	7.69	2989 (1556-5826)	2.23
Ambalayaar	4.57	28	*	31.85	4.20	2686	8.61	359 (276-381)	-0.02
Vaigai	0.22	36	*	31.73	27.89	2033	8.23	400 (362-450)	0.21
Rivers reaching Arabian Sea									
Kochi back waters	231.1	391	1.34	27.27	3.50	455	7.11	1804 (1514-1867)	8.06
Chalakkudi	9.69	*	*	27.98	0.05	400	6.29	7617 (6397-8131)	12.86
Bharatakulza	19.12	*	*	29.70	0.10	280	5.98	6944 (4957-7111)	11.71
Netravathi	18.54	*	*	25.51	0.06	582	6.26	10779 (7193-12971)	70.65
Sharavathi	16.44	*	*	25.74	0.14	700	6.51	9816 (7693-10112)	10.23
Kali	17.59	152	*	27.91	5.86	682	7.25	1840 (1652-2010)	3.24
Zuari	14.62	103	2.70	27.87	7.32	837	7.27	2076 (1360-2511) [354-728]	6.43 (1.3)
Mandovi	27.68	105	2.70	26.29	0.42	361	6.50	4993 (4090-5312) [351-558]	18.06 (2.5)
Narmada	115.5	1447 [#]	10.9	30.16	0.14	2240	7.51	5875 (3862-6069)	8.77
Tapti	41.04	472 [#]	*	26.99	0.10	3484	7.15	18492 (13531-20421)	362.45
Sabarmathi	66.29	120 [#]	*	26.53	0.04	1760	7.17	9109 (5549-10311)	13.84
Mahisagar	14.28	*	7.63	25.93	0.11	1899	7.33	6786 (4788-6978)	10.16

*Data not available and # represents data taken from *Kumar et al.*, 2005 and others taken from Dam authorities of respective river.

[#] Dr. S.R. Shetye Personal communication.

Figure 1:

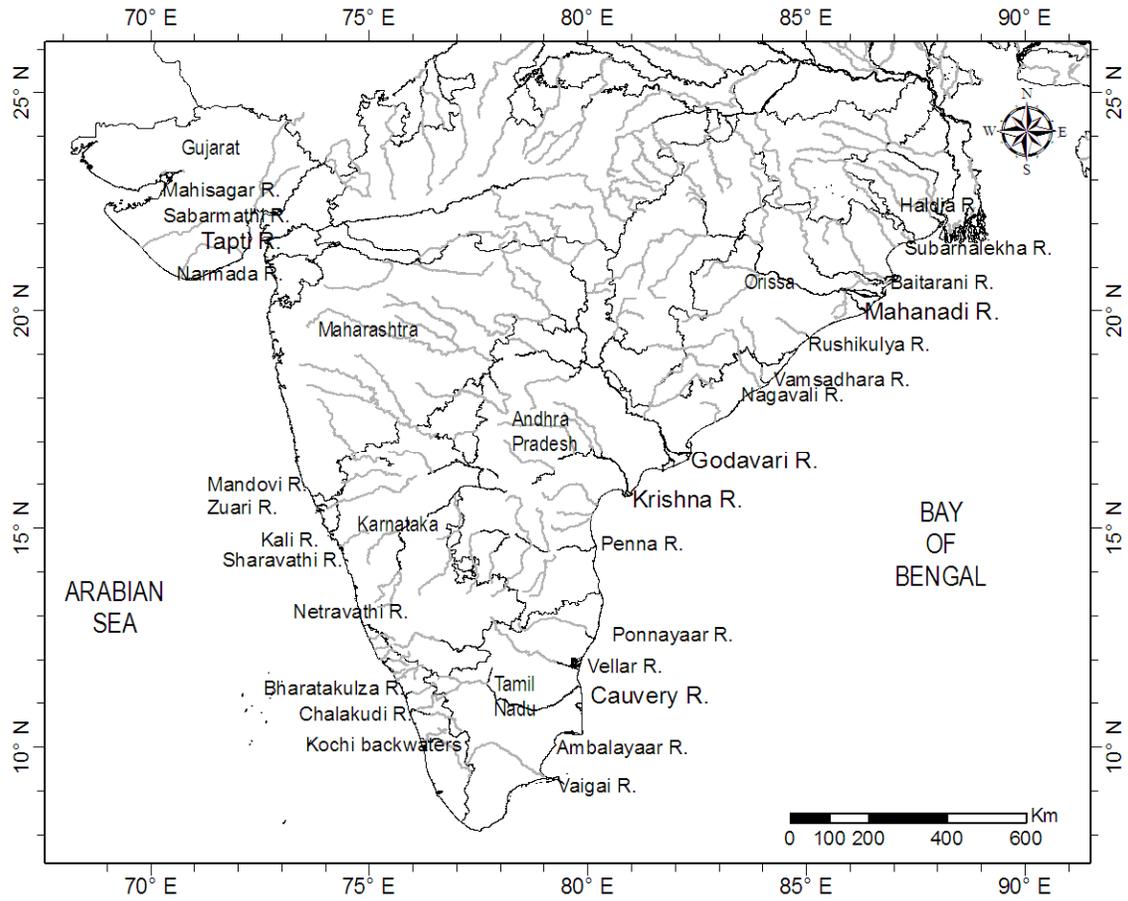
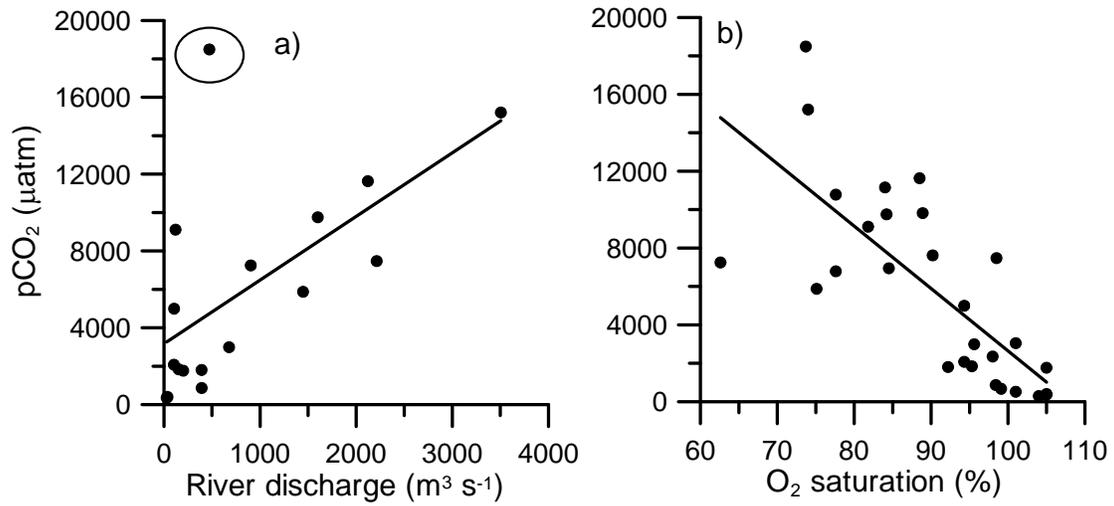


Figure 2:



SUPPLEMENTARY INFORMATION

Table S1: Water-air CO₂ fluxes in the different estuaries in the world

Estuary/Country	CO ₂ Flux (mol C m ⁻² y ⁻¹)	Reference
Altamaha Sound (US)	32.4	Jiang et al., 2008
Bellamy (US)	3.6	Hunt et al., 2010
Cocheco (US)	3.1	Hunt et al., 2010
Great Bay (US)	3.6	Hunt et al., 2010
Little Bay (US)	2.4	Hunt et al., 2010
Oyster (US)	4.0	Hunt et al., 2010
Parker River estuary (US)	1.1	Raymond and Hopkinson, 2003
Sepelo Sound (US)	13.5	Jiang et al., 2008
Satilla River (US)	42.5	Cai and Wang, 1998
York River (US)	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	<i>Ortega et al., 2005</i>
Guadalquivir (Spain)	31.1	De La Paz et al., 2008
Saja-Besaya (Spain)	52.2	Ortega et al., 2004
Urdaibai Estuary (Spain)	21.9	<i>Ortega et al., 2005</i>
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
Chilka (India)	25.0	Gupta et al., 2008
Cochin (India)	55.1	Gupta et al., 2009
Godavari (India)	5.5	Bouillon et al., 2003
Godavari (India)	52.6	Sarma et al., 2011
Hooghly (India)	5.1	Mukhopadhyay et al., 2002
Mandovi-Zuari (India)	14.2	Sarma et al., 2001
Indian estuaries	9.8	This study

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Figure S1: a) Relation between POC and pCO₂ and b) AOU and excess CO₂ in the Indian monsoonal estuaries.

