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CO_2 Supersaturation and Net Heterotrophy in a Tropical Estuary (Cochin, India): Influence of Anthropogenic Effect

Carbon Dynamics in Tropical Estuary

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Abstract

Carbon biogeochemistry of a tropical ecosystem (The Cochin Estuary, India) undergoing increased human intervention was studied during February (premonsoon), April (early monsoon) and September (monsoon) 2005. The Cochin estuary sustains high levels of pCO_2 (up to 6000 μatm) and CO_2 effluxes (up to 274 mmolC m^{-2} d^{-1}) especially during monsoon. A first-order estimate of the carbon mass balance shows that net production of dissolved inorganic carbon is an order of magnitude higher than the net loss of dissolved and particulate organic carbon from the estuary. This imbalance is attributed to the organic inputs to the estuary through anthropogenic supplies. The bacteria-mediated mineralization of organic matter is mainly responsible for the build-up of pCO_2 and increased CO_2 emission to the atmosphere indicating heterotrophy. The linear correlation between excess CO_2 and apparent oxygen utilization indicates respiration as the chief mechanism for CO_2 supersaturation. An increase in the net negative ecosystem production (–ve NEP) between premonsoon (−136 mmolC m^{-2} d^{-1} or −376 MgC d^{-1}) and monsoon (−541 mmolC m^{-2} d^{-1} or −1500 MgC d^{-1}) is supported by a corresponding increase in O_2 influxes from 17 mmol O_2 m^{-2} d^{-1} (126 MgC d^{-1}) to −128 mmol O_2 m^{-2} d^{-1} (−946 MgC d^{-1}) and CO_2 emissions from 65 mmolC m^{-2} d^{-1} (180 MgC d^{-1}) to 267 mmolC m^{-2} d^{-1} (740 MgC d^{-1}). There is a significant north-south gradient in metabolic rates and CO_2 fluxes attributable to the varying flow patterns and anthropogenic inputs into the estuary. The study reveals that the Cochin estuary, a previously autotrophic (CO_2 sink) system, has been transformed to a heterotrophic (CO_2 source) system following rapid urbanization and industrialization. Moreover, the export fluxes from the Cochin estuary appear to be quite important in sustaining net heterotrophy in the southeastern Arabian Sea.

Key words: Cochin estuary; seasonality; organic carbon; anthropogenic inputs; respiration; heterotrophy; CO_2 supersaturation.

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Introduction

Increased emissions of greenhouse gases, in particular of CO_2, and changes in solar irradiance are the main agents of climate change in the latter half of the 20th century (IPCC 2001). A significant fraction of CO_2 emission is from coastal and marine regions including wetlands and river-estuarine systems (Cole and others 2000, 2007; Cole and Caraco 2001; Bouillon and others 2003, 2007; Borges and others 2008; Gupta and others 2008). Hence, studies on these systems have increased because of the importance based on their potentials to emit greenhouse gases to the atmosphere. An estimate shows that globally the CO_2 emissions from estuaries are 0.43 Pg C y^{-1} (Borges and others 2005) and from lakes are 0.14 Pg C y^{-1} (Cole and others 1994). These coastal systems, when supplemented with excess organic matter, can serve as sources of CO_2 and become net heterotrophic (Smith and Hollibaugh 1993; Gattuso and others 1998; Chen and others 2003). There is a growing evidence that estuaries receiving large anthropogenic wastes are found to sustain high rates of respiration over production and produce excess CO_2 (Frankignoulle and others 1998; Taylor and others 2003; Cai and others 2004; Borges and others 2008). Conversely, estuaries that receive insignificant anthropogenic inputs are also found to exhibit heterotrophy and sustain high levels of biogenic gas production (Raymond and others 2000) due largely to the mineralization of river-driven organic matter (Cole and others 2000; Cole and Caraco 2001). This behavior is potentially seen in some Indian estuaries which mineralize up to 90% of terrestrial organic loads during high-flow conditions (Pradeep Ram and others 2007; Gupta and others 2008). In all these situations, the bacterial community, varying widely in response to the quality and quantity of dissolved organic matter (Kirchman and others 2004), controls the degree of mineralization of organic matter.

Although the importance of estuaries as potential sources of CO_2 is obvious (Raymond and others 2000; Taylor and others 2003; Cai and others 2004; Borges and others 2005; Bouillon and others 2007), there are only a very few studies from Indian estuaries (Sarma and others 2001; Mukhopadhyay and others 2002; Bouillon and others 2003; Biswas and others 2004; Gupta and others 2008) to document this behavior. The Cochin estuary, an eutrophic estuary along the southwest coast of India, was reported to be a site of positive net ecosystem production (Qasim and others 1969), in view of high nutrient loadings and phytoplankton biomass (Qasim 2003; Jyothibabu and others 2006; Madhu and others 2007). However, recent findings on bacterioplankton metabolic capabilities (Thottathil and others 2008a) suggest that microbial activity is very important in this estuary. Hence, the present study in the Cochin estuary was undertaken to examine its (i) trophic status, (ii) degree of CO_2 saturation among seasons, (iii) inter-system variability in CO_2 concentration, and (iv) relative influence of anthropogenic inputs on the CO_2 fluxes.

Materials and Methods

Site Description

The Cochin estuary (CE), a micro tidal estuary ($\leq$ 1.0 m) situated on the southwest coast of India (Figure 1), is connected to the Arabian Sea through two inlets at Cochin and Azhikode, the former is wider (450 m) than the latter (250 m). It is the second largest estuarine system in India, fed by six rivers discharging about 2×10^{10} m^3 y^{-1} of fresh water (Srinivas and others 2003a, b), of which more than 60% occurs in the summer monsoon (June–September), 10–25% in the winter monsoon (November–December) and the balance during the rest of the year. It has a surface area of 231 km^2 (calculated from satellite image) and a volume of 0.55 km^3 (Gopalan and others 1983). The sediment flux from catchments is about 32×10^6 tons y^{-1} (Thomson 2002), and the consequent siltation has caused shrinkage of the estuarine area considerably. The estuary is generally wide (0.8–1.5 km) and deep (4–13 m) towards the south, but narrow (0.05–0.5 km) and shallow (0.5–2.5 m) towards the north. Due to the peculiar topography, the circulation patterns in the northern and southern arms of the CE are distinctly different; the northern arm frequently develops flow-restrictions due to converging tides entering from two adjacent inlets (Balachandran and others 2008), whereas the southern arm experiences tidal amplification. Stratification is restricted to the lower estuary during monsoon, which slowly transforms into partially mixed and fully mixed conditions, and propagates upstream during post- and premonsoon seasons, respectively. From December to March, the two hydraulic barriers situated respectively at Thannermukkam (43 km south of Cochin inlet) and Pathalam (28 km north of Cochin inlet) prevent salinity intrusion further upstream.

Human intervention in the CE has occurred since 1836, but has accelerated during the last five

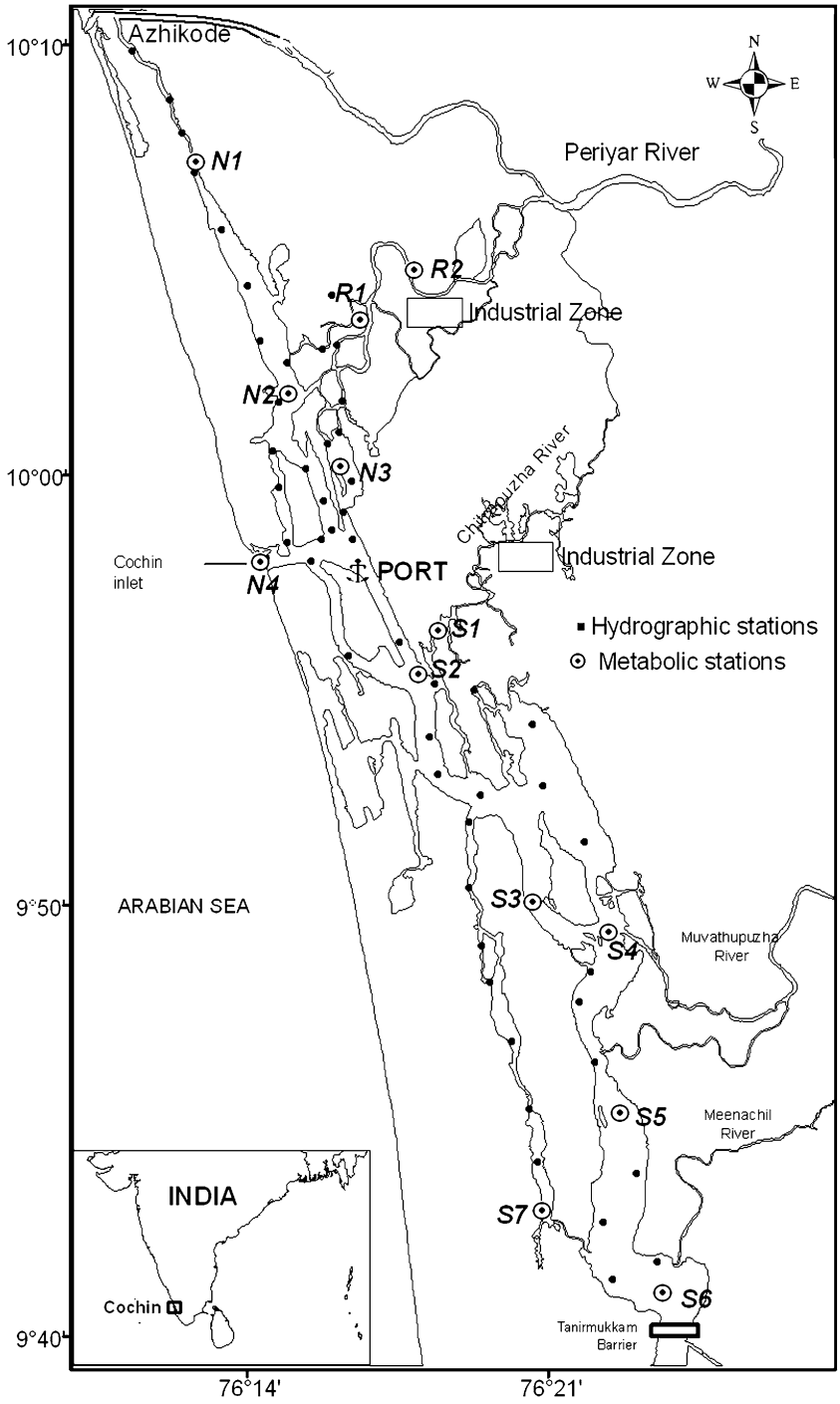

Figure 1. Map of the Cochin estuary with station locations.

decades. There has been significant change in the hydrological cycle following massive deforestation, construction of numerous dams across the rivers, engineering modifications in the estuary and extensive reclamation of wetland (Balachandran and others 2008). Originally a mangrove forest, this wetland has been subjected to changes in its functions and land-use patterns following exacerbated human settlements (10^7, Department of Economics and Statistics 2001). Rapid industrialization and urbanization in the last few decades resulted in discharge of about 1.04×10^5 m^3 d^{-1} of effluents and 260 m^3 d^{-1} of sewage into the CE (Qasim 2003; Balachandran and others 2005). In addition, wastes from aquaculture fields (62 km^2) and agricultural fields (80 km^2) have increased the organic pollution in the estuary (Thomson 2002). Brackish waters of the CE are used as coconut husk

retting yards by coir manufacturing industries. An all-weather natural port is located in the lower estuary (near Cochin inlet), where the navigation and cargo handling (1225 vessels, 13.9×10^6 tons during 2005–06) is facilitated by an annual maintenance dredging of 10×10^6 m^3 (www.cochinport.com).

Sampling and Analysis

Seasonal observations were carried out in the CE during February, April and September 2005 from 56 stations, at 2 km intervals (Figure 1). Eleven stations in the estuary and two stations in the river Periyar were selected for in situ measurement of metabolic rates. The observation periods can be generally classified into three seasons based on climatology: February (low flow period) is considered as premonsoon and September (high flow period) as peak summer monsoon. Although April (moderate flow) is normally late premonsoon, due to unusually heavy rains that occurred continuously for two weeks prior to our sampling, similar to the onset of the monsoon period, we considered it as early monsoon. Water samples collected from 0.5 m depth using 5 L Hydrobios samplers were kept cool in ice-boxes, transported to the laboratory and analyzed within 2–3 h for various parameters. Water temperature was recorded using a thermometer (±0.1°C precision). Salinity was determined using a Salinometer (DIGI AUTO 3G, Tsurumi Seiki, Japan, accuracy ±0.001). Light transparency measured using a Secchi disc was represented as photic depth. Dissolved oxygen (O_2) was measured following Winkler's method (Grasshoff and others 1999) using a Multi-Dosimat (645 Hydrobios, Kiel) and its solubility was computed following Garcia and Gordon (1992). For the estimation of suspended particulate matter (SPM), a known volume of water was filtered through a preweighed 0.45 µm membrane filter, oven dried at 60°C for 12 h and the difference of initial and final weight was taken. The filtrate was used for the estimation of nutrients (Grasshoff and others 1999) using a spectrophotometer (1650 Shimadzu). Acetone extracts of particulate matter retained on a GF/F filter pad were used for spectrophotometric determination of chlorophyll *a* (Chl *a*) (Parsons and others 1984).

Samples for dissolved organic carbon (DOC) and particulate organic carbon (POC) were collected in 100 ml glass bottles (precombusted at 450°C for 4 h) and kept in ice. In the laboratory, known volumes of samples were filtered through 25 mm Whatman GF/F filters (precombusted at 450°C for 4 h), oven dried at 60°C for 12 h and stored at −20°C. The filtrates were acidified to pH 3–4 using 1% phosphoric acid and stored in precombusted 10 ml air-tight glass tubes at about 10°C until analysis. DOC in these samples was estimated following the high-temperature catalytic oxidation method using a TOC analyzer (Shimadzu TOC-V_{CPH}). The accuracy of DOC measurements, when checked with Certified Reference Material supplied by Dr. D. Hansell, University of Miami, USA (Batch 5 FS) and internal standards prepared using potassium hydrogen phthalate (1 and 5 mg l^{-1}), was within ±1%. POC in the filters (decarbonated by HCl fumes) was analyzed using an Elemental Analyzer (Thermo Finningan, Flash EA1112) with L-cystine as standard and the precision of analysis checked against NIST 1941b was found to be within ±0.1%.

Samples for pH and dissolved inorganic carbon (DIC) were collected in 100 ml glass bottles, poisoned with 100 µl of saturated mercuric chloride and sealed air-tight. pH was measured using a ROSS combination glass electrode (ORION 8102U) and pH meter (ORION 555A) after calibrating against NBS buffers (Frankignoulle and Borges 2001). Analytical precision for pH of freshwater samples was ±0.008 and for other samples it was ±0.005. The measured values on the NBS scale were first converted to in situ pH and then to the total scale. DIC was measured using a coulometer (UIC Inc., USA; Model CM 140-02). The accuracy of measurements tested using the certified reference material (Batch No. 67 supplied by Dr. A. G. Dickson of Scripps Institution of Oceanography, USA) and internal standards (100–1000 µmol kg^{-1} sodium carbonate) was found to be within 1.5–2.0%, and accordingly, corrections were made to the data. Total alkalinity (TA) and pCO_2 were computed from pH and DIC couple using the carbonic acid dissociation constants for the entire estuarine salinity range (Cai and Wang 1998) with a precision of 9–13 µatm for pCO_2 using the CO_2-SYS.XLS (version 14) program developed by Pelletier and others (2007). The CO_2 fluxes across the air-water interface were computed according to:

$$F = k * (CO_{2\,water} - CO_{2\,sat}) \quad (1)$$

where F is the air-water CO_2 flux (mmol m^{-2} d^{-1}), k is the gas transfer velocity of CO_2 (m d^{-1}), $CO_{2\,water}$ is the concentration of CO_2 in the water and $CO_{2\,sat}$ is the concentration the water would have were it in equilibrium with the air. For computing the atmospheric concentration of CO_2,

the pCO_2 data for dry air obtained from a nearest station in India (Cape Rama, 15.08°N; 73.83°E) corresponding to the periods of study (GLOBALVIEW-CO_2 2007) were used after correcting for water vapor (Weiss and Price 1980). Accordingly, the atmospheric pCO_2 in wet air was computed to be 377.1, 377.3 and 378.3 µatm, respectively, for February, April and September. k was computed as a function of wind speed, water current and water column depth according to Borges and others (2004):

$$k_{600} = 0.24 + 0.4126\, w^{0.5} h^{-0.5} + 0.619\, u_{10} \quad (2)$$

where k_{600} is the gas transfer velocity of CO_2 normalized to a Schmidt number (Sc) of 600 in m d^{-1}, w is the water current (cm s^{-1}), h is the water column depth (m) and u_{10} is the wind speed (m s^{-1}). The computed k_{600} values were converted to in situ conditions, assuming that the gas transfer velocity is proportional to $Sc^{-0.5}$. Sc was computed for a given salinity (Wanninkhof 1992), assuming that Sc varies linearly with salinity. Wind speed data were collected from a hand-held anemometer (Lutron, AM4201). Water currents were extracted from a 2D hydrodynamic model developed for this estuary (Balachandran and others 2008).

Air-water fluxes of O_2 were computed using the equation:

$$F = k \times \Delta O_2 \quad (3)$$

where k is the gas transfer velocity of O_2 (m d^{-1}) and ΔO_2 is the difference between measured O_2 and its solubility.

Net primary production (NPP) was measured by in situ ^{14}C assimilation method (UNESCO 1994). Surface waters in Nalgene bottles (two light and one dark) were inoculated with labeled $NaH^{14}CO_3$ (activity 5 µCi ml^{-1}; BARC, Mumbai) and incubated at in situ conditions for 12 h (06:00–18:00 h) during the day. On retrieval, samples were immediately passed through Whatman GF/F filter paper under gentle suction. The filters, after exposing to concentrated hydrochloric acid fumes for a minute, were preserved in scintillation vials until analysis. Later, these filters were treated with 5 ml scintillation cocktail in dioxane and the radioactivity was measured using a liquid scintillation counter (Wallac 1409 DSA, Perkin Elmer, USA). NPP rates were calculated based on a 12 h photo-period and expressed as mgC m^{-3} d^{-1}. Parallelly, water samples in dark BOD bottles (in triplicate) were incubated at in situ depth for 24 h. The difference in O_2 concentrations measured before and after incubations was considered as community respiration (autotrophs + heterotrophs) (R). Similarly, bacterial respiration (BR) was estimated by subjecting the samples to sequential size fractionation (3.0 and 0.8 µm) followed by in situ incubation for 24 h (Biddanda and Cotner 2002). This method, however, may lead to some errors due to rupture of cells and removal of bacteria attached to larger particles (>0.8 µm). But prior to adopting this method, we checked the bacterial counts in filtered and unfiltered waters and found that they are not significantly different, thereby ruling out the possibility of bacteria loss during filtration. From all these incubations, the oxygen consumed was converted to carbon respired assuming a respiratory quotient of one.

The trophic status of a system is defined either based on CO_2 fluxes, O_2 fluxes or as the ratio of gross primary production (GPP) to R, where GPP = net ecosystem production (NEP) during day light + R. NEP is an integrated ecosystem rate, whereas NPP determined in this study is close to the net production by phytoplankton only, thereby NEP = NPP − respiration by heterotrophs (BR). Using this approach, GPP is calculated as, GPP = NPP − BR + R.

Results

Based on the differences in hydrology and input characteristics, the study area has been categorized to two regions, that is, north and south estuaries, with respect to the Cochin inlet (Figure 1). Water temperature across the estuary was generally uniform and varied between 26.5 and 35.2°C. The moderately warm estuary during premonsoon (31.2 ± 1.1°C) became warmer during early monsoon (33.1 ± 0.8°C) and cooler during monsoon (29.5 ± 1.3°C). The river discharge (personal communication from Central Water Commission, India) was negligible during premonsoon (142 m^3 s^{-1}), which increased marginally during early monsoon (205 m^3 s^{-1}) and reached a maximum during monsoon (1346 m^3 s^{-1}). The seasonal salinity fluctuation (Table 1) was in accordance to the river discharge. With fairly high saline conditions in premonsoon (17.5 ± 6.3), the rainfall during early monsoon lowered it by 4.4 ± 6.6 in the north estuary and by 1.4 ± 3.2 in the south estuary, indicating the hydrological difference between them. Similar to salinity, pH was also marginally high during premonsoon (7.436 ± 0.505) and early monsoon (7.226 ± 0.543) but decreased substantially during monsoon (6.629 ± 0.400). O_2 concentrations were saturated during premonsoon which decreased to 87 ± 28% during early mon-

Table 1. Average Concentrations and Ratios of Various Parameters in Different Seasons

	Premonsoon			Early monsoon			Monsoon		
	North	South	Total	North	South	Total	North	South	Total
Temperature (°C)	30.9 (1.4)	31.4 (0.8)	31.2 (1.1)	32.7 (0.6)	33.3 (0.8)	33.1 (0.8)	28.7 (1.4)	30.1 (0.7)	29.5 (1.3)
Salinity	19.2 (7.6)	16.2 (4.8)	17.5 (6.3)	14.7 (9.4)	14.7 (5.0)	14.7 (7.2)	1.27 (1.93)	0.69 (1.65)	0.95 (1.79)
pH	7.506 (0.419)	7.380 (0.565)	7.436 (0.505)	7.280 (0.429)	7.184 (0.622)	7.226 (0.543)	6.657 (0.443)	6.606 (0.368)	6.629 (0.400)
SPM (mg l^{-1})	36.5 (8.7)	26.8 (10.9)	31.1 (11.0)	27.0 (18.5)	27.9 (18.0)	27.5 (18.1)	17.7 (8.9)	16.4 (8.6)	17.0 (8.7)
O_2 (%)	97.5 (16.1)	104 (23.0)	101 (20.3)	71.6 (23.4)	99.1 (25.2)	87.1 (27.9)	82.9 (8.5)	87.2 (11.3)	85.3 (10.3)
DIN (μM)	33.9 (38.9)	13.4 (7.2)	22.5 (28.2)	40.6 (27.6)	19.0 (10.9)	28.4 (22.5)	40.9 (12.5)	20.4 (14.1)	29.5 (16.8)
DIP (μM)	1.73 (0.77)	1.25 (1.39)	1.46 (1.17)	2.61 (1.17)	1.40 (1.07)	1.93 (1.26)	2.55 (1.09)	1.79 (1.05)	2.13 (1.12)
DSi (μM)	54.1 (26.1)	75.2 (19.2)	65.8 (24.7)	54.5 (21.3)	27.1 (15.1)	39.1 (22.5)	88.1 (48.6)	84.3 (31.0)	86.0 (39.5)
TA (μmol kg^{-1})	1268 (480)	828 (430)	1024 (500)	1202 (563)	722 (537)	931 (594)	326 (181)	213 (127)	263 (162)
DIC (μmol kg^{-1})	1212 (405)	797 (350)	983 (427)	1192 (461)	713 (481)	931 (526)	413 (144)	281 (112)	340 (142)
DOC (μmol kg^{-1})	342 (91)	338 (128)	340 (108)	242 (71)	300 (83)	275 (83)	158 (113)	222 (84)	193 (102)
POC (μmol kg^{-1})	119 (33)	111 (69)	115 (56)	144 (51)	146 (130)	145 (102)	65 (34)	101 (78)	85 (64)
pCO_2 (μatm)	1228 (880)	1291 (1270)	1263 (1104)	2043 (1165)	1427 (1211)	1696 (1220)	2853 (1460)	2323 (1002)	2560 (1245)
CO_2 flux (mmolC m^{-2} d^{-1})	65 (70)	64 (86)	65 (80)	139 (93)	109 (124)	121 (112)	258 (109)	274 (148)	267 (131)
O_2 flux (mmol O_2 m^{-2} d^{-1})	−9.0 (95)	38 (150)	17 (129)	−163 (146)	13 (179)	−64 (186)	−140 (68)	−118 (99)	−128 (87)
Chl *a* (μg l^{-1})	6.45 (6.92)	6.01 (5.29)	6.20 (6.02)	16.7 (8.7)	15.5 (10.9)	16.1 (9.9)	6.08 (4.03)	4.53 (3.58)	5.20 (3.83)
Net primary production (NPP) (mgC m^{-3} d^{-1})	72 (39)	120 (42)	104 (45)	101 (48)	113 (68)	109 (59)	50 (43)	14 (5)	27 (30)
Gross primary production (GPP) (mgC m^{-3} d^{-1})	101 (34)	170 (76)	145 (72)	115 (68)	174 (74)	153 (66)	128 (81)	68 (31)	90 (58)
Community respiration (R) (mgC m^{-3} d^{-1})	104 (27)	193 (102)	160 (92)	188 (55)	230 (68)	215 (52)	154 (66)	224 (166)	198 (138)
Bacterial respiration (BR) (mgC m^{-3} d^{-1})	70 (36)	134 (96)	110 (83)	173 (43)	169 (40)	171 (39)	76 (49)	167 (154)	134 (131)
GPP/R	1.12 (0.72)	1.09 (0.65)	1.10 (0.66)	0.64 (0.24)	0.76 (0.31)	0.72 (0.28)	0.62 (0.26)	0.39 (0.25)	0.47 (0.23)

Values in parentheses indicate standard deviation.

soon and to 85 ± 10% during monsoon (Table 1), the undersaturation being intense in the north estuary. Seasonality in O_2 fluxes followed very closely to its concentrations, that is, increased from premonsoon (17 $mmolO_2\ m^{-2}\ d^{-1}$) to early monsoon (−64 $mmolO_2\ m^{-2}\ d^{-1}$) and to monsoon (−128 $mmolO_2\ m^{-2}\ d^{-1}$). SPM generally increased with salinity, but the waters gradually became clear between premonsoon (31 ± 11 $mg\ l^{-1}$) and monsoon (17 ± 9 $mg\ l^{-1}$). Despite a drop in SPM between the seasons, the photic depth represented 19–23% of water column depth. Nutrients were, in general, very high (Table 1) and behaved non-conservatively with salinity. Ammonia was the dominant form (50–65%) of dissolved inorganic nitrogen.

DIC, DOC and POC concentrations in the rivers draining into the CE are much lower than those of Indian rivers (Table 2). The DIC levels measured in the lower estuary (1901–2028 $\mu mol\ kg^{-1}$) are comparable with the values reported for the shelf waters of the Arabian Sea (~1950 $\mu mol\ kg^{-1}$, Sarma and others 1998). DOC and POC are high in the mesohaline region (salinity 10–20) compared to other regions of the CE. In general, DIC, DOC and POC concentrations decreased from premonsoon to monsoon. Chl *a* was about 3-fold higher in early monsoon (16.1 ± 9.9 $\mu g\ l^{-1}$) compared to premonsoon (6.2 ± 6.0 $\mu g\ l^{-1}$) and monsoon (5.2 ± 3.8 $\mu g\ l^{-1}$) with maximum values in the mesohaline regions.

CO_2 was highly supersaturated (up to 19 times) with respect to its concentration in the atmosphere during all the seasons. With a 2-fold rise from premonsoon to monsoon (Table 1), the pCO_2 levels generally decrease with increase in salinity in the north during premonsoon and early monsoon. It is consistently low (<1500 µatm) in the south, but showed high values (2000–6000 µatm) in the mesohaline region. During monsoon, it is very high upstream and decreases exponentially along the salinity gradient.

The maximum NPP observed during premonsoon (104 ± 45 $mgC\ m^{-3}\ d^{-1}$) and early monsoon (109 ± 59 $mgC\ m^{-3}\ d^{-1}$) is reduced considerably during monsoon (27 ± 30 $mgC\ m^{-3}\ d^{-1}$). Similarly, GPP also decreased between premonsoon (145 ± 72 $mgC\ m^{-3}\ d^{-1}$) and monsoon (90 ± 58 $mgC\ m^{-3}\ d^{-1}$). Community respiration (R), corrected for nitrification (Miranda and others 2008), is 160 ± 92, 215 ± 52 and 198 ± 138 $mgC\ m^{-3}\ d^{-1}$ during premonsoon, early monsoon and monsoon, respectively. Bacterial respiration (BR) contributed 64 (±23) %, 81 (±17) % and 61 (±22) % of R during premonsoon, early monsoon and monsoon,

Table 2. Comparison of Water Quality with Respect to Inorganic and Organic Carbon Concentrations in Rivers Entering the Cochin Estuary with Other Indian Rivers

System	DIC ($\mu mol\ kg^{-1}$)	DOC ($\mu mol\ kg^{-1}$)	POC ($\mu mol\ kg^{-1}$)	pCO_2 (µatm)	Reference
Rivers entering Cochin estuary	162–332	64–121	35–55	2975–6001	Present study
Mandovi-Zuari rivers	~500	–	–	1500–2250	Sarma and others (2001)
Godavari river	>2000	100–300	80–100	433 ± 77	Sarin and others (2002); Bouillon and others (2003)
Ganges and Brahmaputra rivers	–	260–380	–	–	Spitzy and Leenheer (1991)
Hooghly river	1900–2500	–	–	–	Mukhopadhyay and others (2006)
Rivers entering Chilka Lake	400–2900	650–2800	77–448	3912–14640	Gupta and others (2008)

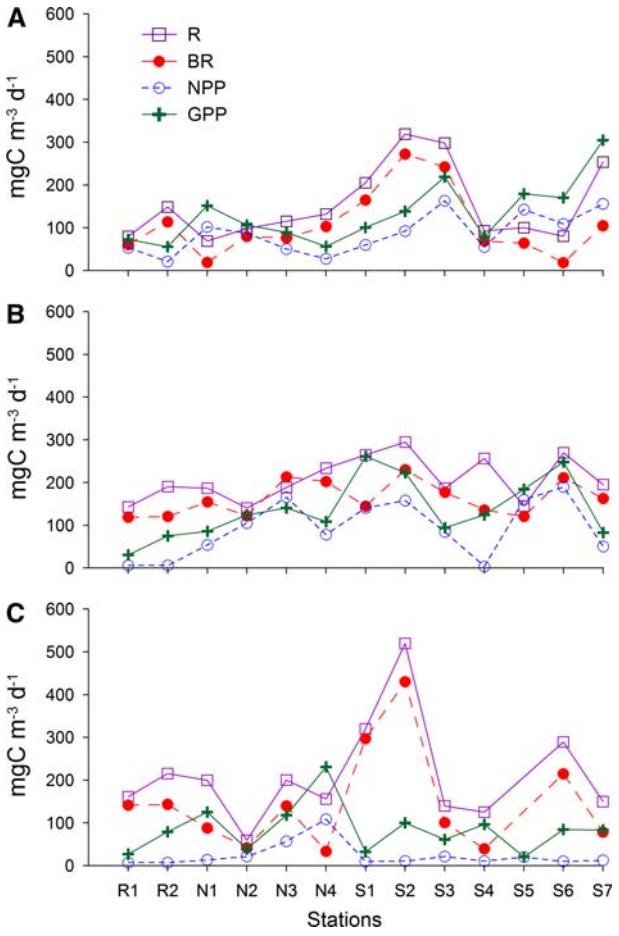

Figure 2. Metabolic rates during (**A**) premonsoon, (**B**) early monsoon, and (**C**) monsoon.

respectively. All metabolic rates were generally high in the south estuary compared to north estuary (Table 2) and increased seaward (Figure 2).

Discussion

The persistently high levels of CO_2 (Table 1) indicate that the CE is net heterotrophic irrespective of seasons. A rise in CO_2 supersaturation between premonsoon and monsoon corresponds to a 2-fold rise in the excess CO_2 (ECO_2) levels ($DIC_{in\ situ} - DIC_{theoretical}$ at atmospheric equilibrium, refer to Gupta and others 2008 for details) from 7.3 ± 6.4% in premonsoon to 10.1 ± 8.3% in early monsoon and further to 22.6 ± 15.0% in monsoon. Similarly, the CO_2 flux also showed a 4-fold increase between premonsoon (65 ± 80 mmolC m^{-2} d^{-1}) and monsoon (267 ± 131 mmolC m^{-2} d^{-1}), with fluxes higher than those observed in other estuaries of India: 11 and 67 mmolC m^{-2} d^{-1} for the Mandovi estuary (Sarma and others 2001), 21.9 and 26.1 mmolC m^{-2} d^{-1} for the Godavari estuary (Bouillon and others 2003), 1.2 and 3.0 mmolC m^{-2} d^{-1} for the Sundarban mangrove estuarine system (Biswas and others 2004) and 9.8 and 141.4 mmolC m^{-2} d^{-1} for the Chilka Lake (Gupta and others 2008). A comparison with temperate estuaries shows that these fluxes are higher than reported for the Tana estuary (58 ± 45 mmolC m^{-2} d^{-1}; Bouillon and others 2007), but are comparable with the Loire estuary (30–280 mmolC m^{-2} d^{-1}; Abril and others 2003) and the Scheldt estuary (200–1200 mmolC m^{-2} d^{-1}; Frankignoulle and others 1998). This clearly shows that the CE is unique among Indian estuaries in terms of CO_2 fluxes as it resembles polluted estuaries elsewhere.

The major processes that regulate the production and consumption of CO_2 in the CE are net ecosystem metabolism and carbonate precipitation. A first-order budget on total carbon has been constructed to explain the net ecosystem metabolism of the CE. For this, the estuary is considered as a single box at steady-state conditions with negligible precipitation/evaporation and an export volume equivalent to the total river discharge. Although the above assumptions have limitations, they do not significantly alter the conclusions drawn from the observations. Net ecosystem production (NEP) is estimated as the difference between total carbon exported (to sea and atmosphere) and imported (from rivers). It is clear from Figure 3 that although the organic carbon inputs from rivers are almost equal to their export fluxes during pre-monsoon and early monsoon, they are fairly high during monsoon. The NEP always remained negative, indicating heterotrophy, which increased from premonsoon (−136 mmolC m^{-2} d^{-2} or −376 MgC d^{-1}) to early monsoon (−250 mmolC m^{-2} d^{-2} or −693 MgC d^{-1}) and monsoon (−541 mmolC m^{-2} d^{-1} or −1500 MgC d^{-1}). This corresponds to a rise in O_2 flux from 17 mmol O_2 m^{-2} d^{-1} (126 Mg O_2 d^{-1}) in premonsoon to −128 mmol O_2 m^{-2} d^{-1} (−946 Mg O_2 d^{-1}) in monsoon and supported a rise in CO_2 emission from 65 mmolC m^{-2} d^{-1} (180 MgC d^{-1}) to 267 mmolC m^{-2} d^{-1} (740 MgC d^{-1}) between the seasons. The estimated NEP for the CE during monsoon is approximately 1.7 times higher than that reported for the Chilka Lake (Gupta and others 2008) and more than 10 times higher than that of the Scheldt estuary (Gazeau and others 2005; Borges and others 2008). ECO_2 fluxes from rivers contributed only 4.7% of total CO_2 emissions during premonsoon and 27.8% during monsoon, suggesting that rivers play a minor role in the estuarine CO_2 effluxes (Borges and others 2006; Gupta and others 2008). The carbon budgets show

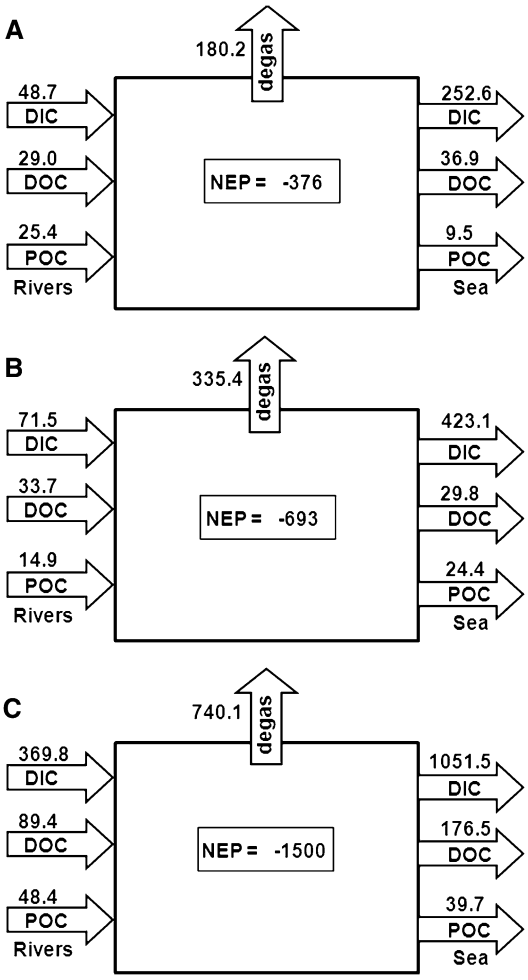

Figure 3. Total carbon budgets (MgC d^{-1}) during (**A**) premonsoon, (**B**) early monsoon, and (**C**) monsoon.

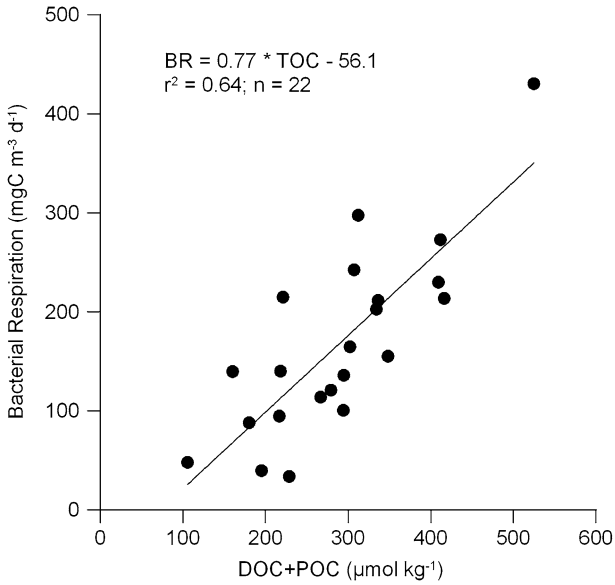

Figure 4. Relationship between total organic carbon and bacterial respiration in the entire study.

that there are major unquantified sources of organic carbon in the CE. For example, during premonsoon (Figure 3A), the net production of DIC (outflow + degas-inflow) is 384 MgC d^{-1}, the net loss of organic carbon is only 8.0 MgC d^{-1}. This suggests that the net production of DIC (–ve NEP) is caused by organic inputs that are not estimated. Further, there is a progressive increase in the net production of DIC during early monsoon (−693 MgC d^{-1}) and monsoon (−1500 MgC d^{-1}). This unquantified organic carbon, which is 7–11 times higher than river inputs, appears to be due to anthropogenic inputs. This is supported by our finding that lateral inputs contributed to high DOC and POC concentrations in the mesohaline regions of the CE (Thottathil and others 2008b). Indiscriminate release of industrial, urban, agricultural and aquaculture wastes is contributing to organic enrichment in the estuary (Vijayan and others 1976; Qasim 2003). The coconut retting yards (Verma and others 2002) are found to release large amounts of DOC (>1000 µmol kg^{-1}) into the southern estuary during premonsoon. The port activities also contribute significantly to organic carbon production. Nitrification rates in the CE are very low (Miranda and others 2008) and hence do not contribute significantly to organic production. Thus, the respiration of these anthropogenic organic carbon sources is mainly responsible for the CO_2 supersaturation leading to heterotrophy in the CE. Exceedingly high pelagic respiration over production (Table 1, Figure 2), especially during early monsoon and monsoon, support this. Further, the high bacterial respiration in the CE (68 ± 23% of community respiration) is sustained by high organic carbon concentrations (Figure 4), leading to O_2 depletion and CO_2 supersaturation. The significant correlation between ECO_2 and apparent oxygen utilization (Figure 5) also supports respiration to be the major cause for CO_2 supersaturation in the CE. But it is expected that a large fraction of CO_2 production is from the bottom compartment relative to the photic compartment (19–23% of water column). Experiments conducted at station N3 in the north estuary (Figure 1) during monsoon showed a benthic respiration of 1378 mgC m^{-2} d^{-1} (M.V.M. Wafar, personal communication). This is equivalent to a benthic flux of 6088 mgC m^{-3} d^{-1}, which is almost 30 times higher than the corresponding pelagic respiration rate (Figure 2C) and suggests the strong influence of benthic processes on CO_2 production. Although benthic respiration rates are known for

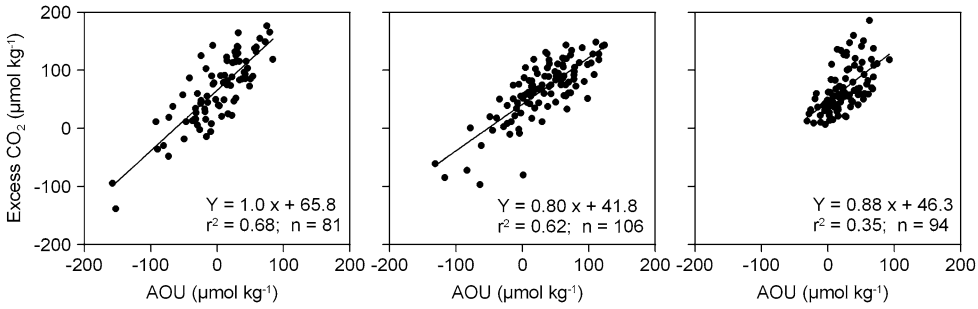

Figure 5. Seasonality in excess CO_2 along apparent oxygen utilization gradient.

their high degree of spatial and seasonal variations, the regions around the port and the northern arm of the CE, where sediments rich in organic carbon (3–5%) and clay (60–90%) resuspend largely, are expected to have a high potential relative to other regions. High respiration rates observed at stations N4, S1, S2 and S3 (Figure 2) also support the strength of this process in the lower estuary where turbidity is at a maximum. Therefore, the integrated effects of in situ processes are chiefly responsible for CO_2 supersaturation, which is supported by the good agreement between seasonality in CO_2 effluxes and O_2 influxes with GPP/R ratios (Figure 6).

The budgets show that about 50% of the carbon mineralized in the estuary is ventilated to the atmosphere as CO_2, whereas the balance is exported to the sea as DIC (Figure 3). This is in contrast to Chilka Lake, where 90% of river-born organic carbon is siphoned out as CO_2 to the atmosphere (Gupta and others 2008). The export fluxes of organic carbon to the Arabian Sea during monsoon (Figure 5C) are significant as this together with upwelling fuels the prevalence of hypoxic conditions in the coastal waters (Sarma and others 1998, 2003; Naqvi and others 2000) and may influence the CO_2 dynamics of this region.

Consistently low levels of pH, DIC and TA along with very high pCO_2 in the south estuary could be due to carbonate precipitation. Previous studies have shown that this region has the potential for shell deposition (Gopalan and others 1983; Arun 2005). The O_2 undersaturation (70–90%) in this region is due to high community respiration (150–290 mgC m^{-3} d^{-1}), which indicates that $CaCO_3$ precipitation is tightly coupled with aerobic respiration. It is, however, difficult to separately quantify CO_2 production or consumption due to $CaCO_3$ precipitation, photosynthesis and respiration, as these are concurrent processes (Frankignoulle and others 1994).

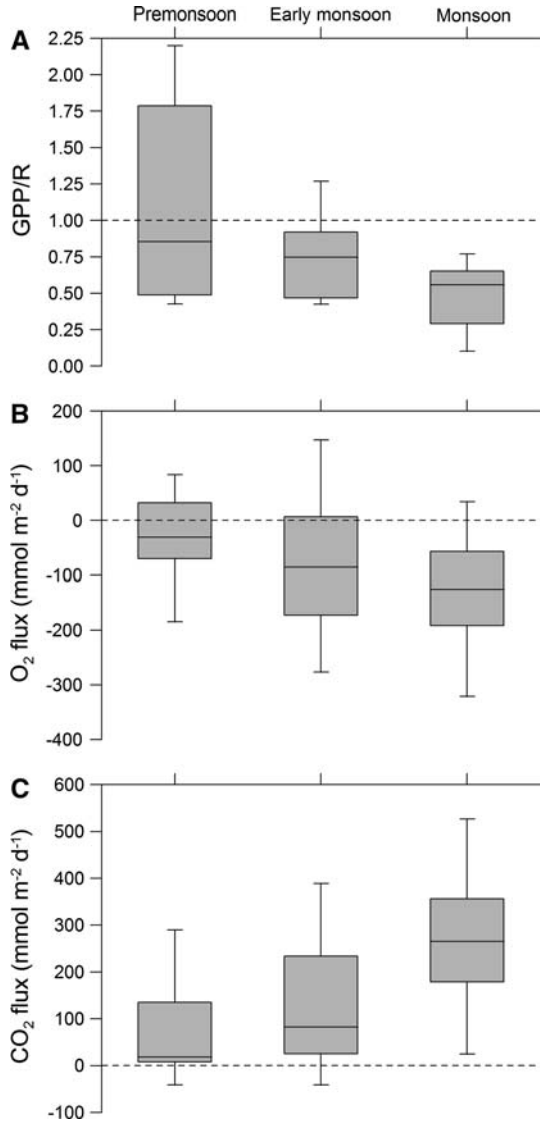

Figure 6. Seasonality in GPP/R ratios and fluxes of O_2 and CO_2. *Dotted line* in each panel represents GPP = R conditions. The trend of CO_2 flux mirrors the GPP/R ratio and O_2 flux reflecting the rise in heterotrophic intensity with change in season.

Apart from the seasonal changes, the observed inter-system variations in the metabolic rates (Figure 2) and CO_2 fluxes (Table 1) can be attributed to the different basin properties and the complex topography of the estuary. The fresh water fraction in the north is lower than the south estuary due to the varying influence of river inputs and tidal propagation (Balachandran and others 2008). The land-use pattern is also different, as the south estuary is influenced by agriculture, aquaculture and port activities, whereas numerous industries are concentrated in the north estuary. Thus, the varying quantities of wastes and their bio-availability are chiefly responsible for inter-system gradients.

It is now obvious that anthropogenic inputs are responsible for the net heterotrophy and CO_2 emissions from the CE. An interesting question here is what was the behavior of the CE before human impacts became widespread? Qasim and others (1969) from their study during August 1965–July 1966 in the lower reaches of the CE observed depth integrated GPP (767 ± 304 mgC m^{-2} d^{-1}) to be 3-fold higher than the respiration (261 ± 154 mgC m^{-2} d^{-1}). They also reported high GPP/R ratios during monsoon (4.0–5.7) and low ratios during premonsoon (2.1–2.8), indicating the system was net autotrophic. The decadal changes suggest that increased human interference has transformed the CE from an autotrophic system to a highly heterotrophic (CO_2 source) system. This change has probably induced shifts in the food chain with a consequent alteration in the tertiary fauna. An example for this can be observed in the abundance of an opportunistic fish 'Tilapia' (*Oryochromus mosambicus*) in the CE replacing an endemic and popular species such as 'Peal spot' (*Etroplus suratensis*) (Qasim 2003).

Conclusions

The net heterotrophic status of this system points to the growing stress in the Cochin estuary due to organic enrichment caused by diverse human activities. From the constructed total carbon budgets, the anthropogenic organic carbon fluxes exceeded the riverine fluxes, and their mineralization was mainly responsible for the increased heterotrophic activity and CO_2 supersaturation in the estuary. Consistently high bacterial respiration indicates rapid turnover of this organic matter supporting a dominant microbial loop in this ecosystem. Benthic respiration appears to contribute strongly to CO_2 supersaturation over pelagic respiration and defines the intensity of net ecosystem metabolism. Inter-system gradients are pronounced between the north and south estuaries due to the different flow regimes and varying quality and quantity of organic inputs from human activities. The Cochin estuary was found to be a sink for CO_2 four decades ago but widespread human impacts have transformed it to a potential source of CO_2. An increase in the export fluxes of carbon is significant because the southeastern Arabian Sea sustains negative NEP. Future studies should therefore focus on quantification of the organic loadings from various sources, their composition and bioavailability in the estuary and, export fluxes to ascertain their degree of impact on net ecosystem metabolism and food web dynamics in the southeastern Arabian Sea.

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