

## **Influence of net ecosystem metabolism in transferring riverine organic carbon to atmospheric CO<sub>2</sub> in a tropical coastal lagoon (Chilka Lake, India)**

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## Abstract

Studies on biogeochemical cycling of carbon in the Chilka Lake, Asia's largest brackish lagoon on the east coast of India, revealed, for the first time, strong seasonal and spatial variability associated with salinity distribution. The lake was studied twice during May 2005 (premonsoon) and August 2005 (monsoon). It exchanges waters with the sea (Bay of Bengal) and several rivers open into the lake. The lake showed contrasting levels of dissolved inorganic carbon (DIC) and organic carbon (DOC) in different seasons; DIC was higher by ~22% and DOC was lower by ~36% in premonsoon than in monsoon due to seasonal variations in their supply from rivers and in situ production/mineralisation. The DIC/DOC ratios in the lake during monsoon were influenced by physical mixing of end member water masses and by intense respiration of organic carbon. A strong relationship between excess DIC and apparent oxygen utilization showed significant control of biological processes over CO<sub>2</sub> production in the lake. Surface partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>), calculated using pH-DIC couple according to Cai and Wang (Limnol and Oceanogr 43:657-668, 1998), exhibited discernable gradients during monsoon through northern (1033-6522  $\mu$ atm), central (391-2573  $\mu$ atm) and southern (102-718  $\mu$ atm) lake. The distribution pattern of pCO<sub>2</sub> in the lake seems to be governed by pCO<sub>2</sub> levels in rivers and their discharge rates, which were several folds higher during monsoon than premonsoon. The net CO<sub>2</sub> efflux, based on gas transfer velocity parameterization of Borges et al. (Limnol and Oceanogr 49(5):1630-1641, 2004), from entire lake during monsoon (141 mmolC m<sup>-2</sup> d<sup>-1</sup> equivalent to 2.64 GgC d<sup>-1</sup> at basin scale) was higher by 44 times than during premonsoon (9.8 mmolC m<sup>-2</sup> d<sup>-1</sup> | 0.06 GgC d<sup>-1</sup>). 15% of CO<sub>2</sub> efflux from lake in monsoon was contributed by its supply from rivers and the rest was contributed by in situ heterotrophic activity. Based on oxygen and total carbon mass

balance, net ecosystem production (NEP) of lake ( $-308 \text{ mmolC m}^{-2} \text{ d}^{-1}$  |  $-3.77 \text{ GgC d}^{-1}$ ) was found to be almost in consistent with the total riverine organic carbon trapped in the lake ( $229 \text{ mmolC m}^{-2} \text{ d}^{-1}$  |  $2.80 \text{ GgC d}^{-1}$ ) suggesting that the strong heterotrophy in the lake is mainly responsible for elevated fluxes of  $\text{CO}_2$  during monsoon. Further, the pelagic net community production represented 92% of NEP and benthic compartment plays only a minor role. This suggests that Chilka lake is an important region in biological transformation of organic carbon to inorganic carbon and its export to the atmosphere.

*Keywords:* Rivers discharge, Dissolved Carbon, Heterotrophy, Net Ecosystem Production,  $\text{CO}_2$  flux.

## Introduction

Global warming is now most widely addressing issue and greenhouse gases viz. CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, etc. and their insulating (greenhouse) effect on the atmosphere are well recognized (Mitchell 1989; IPCC 2001). It is believed that rising levels of these gases in the earth's atmosphere caused a rise in global temperature as well as changes in precipitation patterns (IMBER 2005). CO<sub>2</sub>, being a major greenhouse gas, has drawn greater attention all over the world and its involvement in biogeochemistry of coastal and open sea regions (Kumar et al. 1996; Sarma et al. 1998, 2001, 2003; Frankignoulle and Borges 2001a; Takahashi et al. 2002; Borges and Frankignoulle 2003; Borges 2005; Borges et al. 2005). Coastal zone fluxes, however, seem to represent the largest among the unknown CO<sub>2</sub> balance and, they are excluded from the global data set on climatology dealing with CO<sub>2</sub> exchange between atmosphere and the sea due to lack of enough data from this region (Takahashi et al. 2002). Eventhough they are small, coastal seas seem to play a disproportionately important role in the overall ocean biogeochemical cycle (Gattuso et al. 1998). Despite huge impingement of terrigenous sediment and carbon fluxes into the Bay of Bengal by rivers such as the Ganges, Brahmaputra and Godavari along the northeast shelf of India (Subramanian et al. 1985; Somayajulu et al. 1993; Gupta et al. 1997; Sarin et al. 2002), studies on carbon biogeochemistry from this part of the world remained scarce at least until recently. Contemporary investigations on neighbouring estuarine and mangrove systems indicated that they are potential source regions for atmospheric CO<sub>2</sub> (Sarma et al. 2001; Mukhopadhyay et al. 2002; Borges et al. 2003; Bouillon et al. 2003; Biswas et al. 2004).

Globally, CO<sub>2</sub> levels in lakes vary enormously from highly under saturated

conditions to supersaturation, less than 10% of samples examined being within  $\pm 20\%$  of equilibrium with atmosphere (Cole et al. 1994, 2007) and mean  $p\text{CO}_2$  from lakes around the world was at  $1287 \pm 41 \mu\text{atm}$  (Sobek et al. 2005), indicating that they are a net source of  $\text{CO}_2$ . Spread over enormous area ( $2 \times 10^6 \text{ km}^2$ ), the  $\text{CO}_2$  efflux from these lakes was estimated to be  $0.14 \text{ Pg C yr}^{-1}$  (Cole et al. 1994) which is 30% of total export of organic and inorganic carbon from rivers to sea (Schlünz and Schneider 2000). Net heterotrophy, a characteristic feature of these ecosystems, has been attributed to bacterial degradation of organic carbon imported from catchments, which often dominates the community respiration (del Giorgio and Peters 1993; Jansson et al. 1999) and is responsible for excess  $\text{CO}_2$  (Kling et al. 1991; Hope et al. 1996; Sobek et al. 2005). Lakes with dissolved organic carbon (DOC) levels of  $4\text{--}6 \text{ mg L}^{-1}$  are generally net heterotrophic (Prairie et al. 2002; Sobek et al. 2005) and the shift from net autotrophy to net heterotrophy occurs in this DOC interval (Jansson et al. 2000). Apart from lakes, heterotrophic estuarine ecosystems were also found to be significant sources of  $\text{CO}_2$  to the atmosphere where total respiration exceeds gross primary production (Frankignoulle et al. 1998; Gattuso et al. 1998; Bouillon et al. 2003, 2007; Abril and Borges 2004; Biswas et al. 2004; Hopkinson and Smith 2005; Zhai et al. 2005) and also for the fact that river waters entering estuaries have  $p\text{CO}_2$  generally higher than the atmosphere due to organic carbon mineralisation in soils, river waters and sediments (Cole and Coraco 2001; Sarma et al. 2001; Richey et al. 2002; Ferguson et al. 2003; Gazeau et al. 2004; Hopkinson and Smith 2005; Kortelainen et al. 2006; Cole et al. 2007), UV photodegradation of DOC (Granéli et al. 1996; Bertilsson and Tranvik 1998), inflow of groundwater (Kling et al. 1991; Striegl and Michmerhuizen 1998) and surface water (Dillon and Molot 1997) rich in inorganic carbon. However, Borges et al. (2006) have shown that when residence time

of estuaries is longer the contribution of CO<sub>2</sub> from rivers to its emission from estuaries is relatively minor. Indeed, estuaries around the world were estimated to emit 0.43 Pg C yr<sup>-1</sup> of CO<sub>2</sub> to the atmosphere (Borges 2005; Borges et al. 2005), nearly three times more potential than world lakes.

Macrophyte vegetation, seagrasses and macroalgae are also known to have a profound influence on the carbon pool of aquatic ecosystems. Plankton production is a low-biomass, fast turnover process for carbon, therefore, it does not generally induce a large reduction of CO<sub>2</sub>. On the contrary, macrophyte production can induce large local changes in pCO<sub>2</sub>, because the turnover rate of carbon from macrophytes is slow due to its accumulation in biomass (Smith 1981). On the other hand, Gazeau et al. (2005a) have shown that the impact of *Posidonia oceanica*, one of the most productive macrophyte system, on seawater pCO<sub>2</sub> is low and argued that it is regulated more by hydrodynamics like water column depth and residence time. Primary production by algae in lakes is determined by interactions among a variety of factors that include nutrient loadings and food web structure, the latter is often determined by the dominant feeding modes of predatory fishes and has the potential to regulate carbon fluxes between lakes and the atmosphere (Schindler et al. 1997). Recently Lennon et al. (2006) have found that phytoplankton in lakes increase their use of heterotrophically respired CO<sub>2</sub> with increasing concentrations of terrestrially derived DOC. They have also found the signature of this CO<sub>2</sub> recycling in the stable isotope composition of crustacean zooplankton and suggested that the direct transfer of terrestrial DOC inputs to higher trophic levels is relatively inefficient.

Lakes/Estuaries are thus small in area compared to oceans but are potential

zones for transferring terrestrial carbon sources to atmosphere. Chilka Lake, Asia's largest brackish water lake and a Ramsar site in India, went into prominence recently owing to catchments modification and creation of a new mouth in September 2000 to augment exchange with the sea (Bay of Bengal). This has considerably altered the Lake's ecological character resulting in what has been apparently a gross shift from limnetic eutrophy (excessive weed growth) to subdued phytoplankton activity. The present study held during premonsoon and monsoon, was intended to focus on CO<sub>2</sub> fluxes in the lake as a consequence of prevailing environmental conditions and mechanisms maintaining the system known for its extreme vulnerability to anthropogenic interventions and impacts over the years.

## **Materials and Methods**

### Site Description

Chilka Lake, a shallow (~2 m) brackish water lagoon on the east coast of India, is situated about 350 km south of Kolkata (Fig. 1). The lake is pearshaped and covers a total area of about 1000 km<sup>2</sup> during monsoon (August-October), which is reduced by nearly 60% during premonsoon (April-May) when evaporation far exceeds precipitation. The lake is surrounded by numerous fishing hamlets and hundreds of acres of agriculture land that impinge themselves on biogeochemistry of lake. Topographically, Chilka lake can be divided into a south sector (also known as Rambha Bay), a central and a north sector, and the connection to the sea (Bay of Bengal) is through a long (32 km) narrow channel. In September 2000 as a part of its management endeavour the local authority had opened a new mouth at Satpada (see Fig. 1) to facilitate efficient tidal mixing between the lake and the sea. Prior to this

(1996-'97) salinity in the lake was low (mean <10 ), which favoured intense growth of (invasive) macrophytic vegetation (e.g. *Potamogeton*, *Halophila*, *Gracilaria*, *Ruppia* etc.) and the effect is the greatest in the northern most part of the lake with intense (freshwater) weeds mainly *Eichornia*, *Hydrilla*, *Chara* etc. (Satyanarayana 1999). As a consequence, the weeded area had increased from 20 km<sup>2</sup> in 1972 to 685 km<sup>2</sup> by 2000 ([www.chilika.com](http://www.chilika.com)). The creation of a new mouth, considered historical and the most successful hydrological intervention, appeared to have brought in its wake large-scale changes in the Lake such as reduction in weeded area, and rise in salinity, flushing rate and seagrass cover, etc.

Seawater exchange takes place predominantly through outer channel although there is a discrete connection (through Palur canal) further south in Rambha Bay. The lake has huge catchments, nearly 4146 km<sup>2</sup>, with an average rainfall of 1238 mm (in 72 rainy days) lasting through June-September (southwest or summer monsoon) and November-December (northeast or winter monsoon); nearly 75% of it occurs during southwest monsoon with peak intensity during August. Inter -annual variability in rainfall is quite distinct for this region as with the summer monsoon of 2006, which proved aggressive relative to previous years. 52 rivers/rivulets drain enormous freshwater into the lake together with significant loads of nutrients and suspended matter resulting in appreciable changes in hydrological conditions seasonally and annually. While the north-east rivers (e.g. Bhargavi, Daya, Nuna, Makara) representing the Mahanadi system contribute 60 -80% of total freshwater discharge, the western rivers (e.g. Kansari, Kusumi, Janjira, Tarimi, etc.) account for the rest. During summer, there is practically no discharge from these rivers except Makara.



## Sampling and Analysis

Two independent observations were carried out during 21 -31<sup>st</sup> May (premonsoon) and 24<sup>th</sup> August to 3<sup>rd</sup> September, 2005 (monsoon) covering a spread of 36 hydrologically differing locations representing the south, central, and northern lake and the outer channel (Fig. 1). Simultaneously, 18 major rivers/rivulets, which drain into Chilka lake, were also sampled. Time-series observations for 24 h were also made at stations 23, 29 and 36 with a sampling frequency of 2 h during monsoon. While it was not always possible to cover the entire lake (~60 x 30 km) in one day, samples were collected in 10 days during each season assuming steady state conditions during sampling period as the tidal amplitude inside the lake is negligible (<0.07 m). Indian Remote Sensing data (LISS -III, 24.5 m resolution) and ERDAS software were used to estimate water spread area. ArcGIS through Tin model and Surfer software coupled with observed depth records have been used to estimate lake volume. Briefly, the lake was divided into 99 cells, each of 3.5 x 3.5 km in size and surface area of each cell was computed. Depth data was interpolated using Kriging method to a grid size of 1 x 1 km. Grid data points in each cell were averaged and multiplied with its area to compute its volume. Total lake surface area and volume were computed by adding all the cells surface area and volume.

River discharge observations were made at all rivers/rivulets as well as at the mouth of the lake. During May (summer) 2005, there was hardly any inflow except for three northeast rivers (Makara, Daya and Nuna). Current speed was measured by deploying self-recording Current Meter (Nortek, USA) for 15 minutes at each (river) location and discharge computed by measuring its cross-section area. The estimated rivers discharge was linearly extrapolated to daily scale assuming that their qualitative

and quantitative variations in a day are insignificant. At lake mouth (st.36), the Current Meter was deployed for 24 h (covering two complete tidal cycles) at 10 minute recording interval; its cross-section area measured every 2 h and net discharge computed. These discharge rates were then cumulated to obtain net water exchange flux per day at the sea. In addition, time-series current/tide data (Valeport Tide Gauge, UK) were obtained for selected locations (sts.12, 16, 17, 29 and 36) during premonsoon.

Surface water samples were collected using a 5 L Niskin bottle. In-situ temperature was recorded using thermometer (1-51°C range within  $\pm 0.1^\circ\text{C}$ ; Brannan, UK). Salinity was measured by argentimetry and nutrients were estimated following Grasshoff et al. (1999).  $\text{O}_2$  was measured using Winkler's method (Grasshoff et al. 1999) and its solubility was computed following Garcia and Gordon (1992). Suspended particulate matter (SPM) was measured by filtering a known volume of water through 0.45  $\mu\text{m}$  cellulose acetate membrane filters (Millipore), rinsed with copious Milli-Q water and by taking the difference of initial and final weights of filter. For determination of Chlorophyll *a* (Chl *a*), 1 L of water was filtered onto 47 mm Whatman GF/F filter, extracted in 90% acetone for 12 h, and estimated spectrophotometrically (Parsons et al. 1984).

Samples for dissolved organic carbon (DOC) and particulate organic carbon (POC) were collected in glass bottles (precombusted at 450°C for 4 h) and were preserved on ice in dark in the field. In the field lab, known volume of samples were filtered through 25 mm Whatman GF/F filters (0.7  $\mu\text{m}$  pore size; precombusted at 450°C for 4 h), oven dried at 60°C for 12 h and stored at -20°C until analysis of POC.

The filtrates were acidified to pH 3-4 using 1% Phosphoric acid and stored in precombusted 10 ml air-tight glass tubes at  $\sim 10^{\circ}\text{C}$  till the analysis. DOC in these samples was measured using a TOC analyzer (Shimadzu TOC-V<sub>CPH</sub>) following high temperature catalytic oxidation method. The accuracy of DOC measurements was checked once in every five samples with Certified Reference Material supplied by Dr.D. Hansell, University of Miami, USA (Batch 5 FS) and internal standards prepared using potassium hydrogen phthalate (10 and 20 mg L<sup>-1</sup>), and were within  $\pm 1\%$ . POC in the filters (decarbonated by HCl fumes) were analysed using Elemental Analyser (Thermo Finnigan, Flash EA1112) using L-Cystine as standard and precision of analysis was checked against NIST 1941b and found to be at  $\pm 0.1\%$ .

Samples for pH and dissolved inorganic carbon (DIC) were collected in 100 ml glass bottles, poisoned with 100  $\mu\text{l}$  of saturated mercuric chloride and sealed air-tight. pH was measured using a ROSS combination glass electrode (ORION 8102U) and pH meter (ORION 555A) calibrated on the NBS scale as described by Frankignoulle and Borges (2001b). The pH values on NBS scale were first converted to the pH in situ and then to total scale. DIC was measured using a Coulometer (UIC Inc., USA; Model CM 140-02). Analytical precision for pH of fresh water samples was  $\pm 0.008$  and for the rest  $\pm 0.005$ . DIC accuracy was found to be 1.5-2.0% from the Certified Reference Material (Batch No.67) supplied by Dr.A.G. Dickson of Scripps Institution of Oceanography, USA and internal standards prepared using sodium carbonate (500 and 1000  $\mu\text{mol kg}^{-1}$ ), and appropriate corrections were made to the data. All the analyses were done within 12 h of sample collection except DIC, DOC, and POC, these samples were brought to the laboratory in Chennai and analysis were completed within 20 days of collection. The  $\text{pCO}_2$  was computed from pH and DIC

couple using the carbonic acid dissociation constants for the whole range salinity derived by Cai and Wang (1998) with a precision of 9-13  $\mu\text{atm}$ . Recently Millero et al. (2006) have also reported different set of carbonic acid dissociation constants for 0-50 salinity and temperature range and we made an attempt to compare  $\text{pCO}_2$  obtained from both the constants.  $\text{CO}_2\text{SYS.XLS}$  (version 14) program developed by Pelletier et al. (2007), an updated version of original  $\text{CO}_2\text{SYS.EXE}$  (Lewis and Wallace, 1998) with dissociation constants of Cai and Wang (1998) and Millero et al. (2006), was used for computing  $\text{pCO}_2$ .  $\text{CO}_2$  fluxes across the air-water interface were computed according to:

$$F = \alpha.k.\Delta\text{pCO}_2 \quad (1)$$

where  $F$  is the air-water  $\text{CO}_2$  flux ( $\text{mmol m}^{-2} \text{d}^{-1}$ ),  $\alpha$  is the  $\text{CO}_2$  solubility coefficient according to Weiss (1974),  $k$  is the gas transfer velocity of  $\text{pCO}_2$  ( $\text{m d}^{-1}$ ) and  $\Delta\text{pCO}_2$  is the difference of  $\text{pCO}_2$  between water and air. The average atmospheric  $\text{pCO}_2$  value (for dry air) for the periods of survey were taken from a monitoring station in India ( $15.08^\circ\text{N}$ ;  $73.83^\circ\text{E}$ ) which is closest to Chilka region (GLOBALVIEW- $\text{CO}_2$ , 2007) and were corrected for water vapor using the algorithms proposed by Weiss and Price (1980). Accordingly, the atmospheric  $\text{pCO}_2$  in wet air was 377.3 and 378.1  $\mu\text{atm}$  respectively for premonsoon and monsoon. Recently Zappa et al. (2003) and Borges et al. (2004) have established that tidal currents apart from wind speeds strongly contribute to water turbulence and gas transfer velocity in estuarine environment. Accordingly  $k$  was computed as a parameterization as a function of wind speed, water current and water column depth:

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

where  $k_{600}$  is the gas transfer velocity of  $\text{CO}_2$  normalised to a Schmidt number ( $Sc$ ) of 600 in  $\text{m d}^{-1}$ ,  $w$  is the water current ( $\text{cm s}^{-1}$ ),  $h$  is the water column depth (m) and  $u_{10}$  is the wind speed ( $\text{m s}^{-1}$ ). Wind speed data for premonsoon was collected from self-recording weather station (R.M.Young, USA; Model 05106) installed on the west shore of the lake. Daily averaged wind data from Quicksat was used for monsoon (<http://poet.jpl.nasa.gov>). Water currents measured at specific stations during premonsoon were interpolated to all the stations whereas modelled water currents for monsoon were taken from Jayaraman et al. (2007). A generic  $k$ -wind parameterization proposed by Raymond and Cole (2001) for estuarine environments has also been considered for  $\text{CO}_2$  flux estimation and comparison of fluxes between both the  $k$  parameterizations has been made.

Air-water fluxes of oxygen were also computed according to:

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

where  $k$  is the gas transfer velocity of  $\text{O}_2$  ( $\text{m d}^{-1}$ ) that was estimated as mentioned above (eq.2) and  $\Delta O_2$  is the difference of  $\text{O}_2$  observed and its solubility. Schmidt number ( $Sc$ ) was taken from Wanninkhof (1992).

$$k = \frac{k_{600}}{(Sc / 600)^{-0.5}} \quad (4)$$

The in and out fluxes of carbon and  $\text{O}_2$  through rivers and sea were computed by multiplying the water discharge (rivers) and exchange (sea) rates with parameter concentration at the boundaries. Their exchange flux at the mouth was calculated in a similar way as estimated for net water exchange flux. Total gas fluxes from surface water were estimated in a similar way as volume of lake was calculated by replacing

depth with surface gas flux data. Total carbon and O<sub>2</sub> budgets were constructed by mass balancing their various sources and sinks in the lake.

Benthic O<sub>2</sub> fluxes in the lake were estimated through benthic chamber (30 cm height x 29 cm diameter) incubations at one location close to station 10, which is habitated with dense vegetation of macrophytes (Fig. 1), only once during 14-15 March 2007. The chamber was designed to leak proof with a provision to replace the withdrawn sample volume from surrounding environmental water through a side port. The chamber waters were gently mixed mechanically once in every 10 minutes and samples for analysis of O<sub>2</sub> were drawn from top of the chamber through tygon tubing at 50 ml per minute at 3 h interval using a peristaltic pump. Care was taken avoid trapping of air bubbles while sampling and volume equivalent to tygon tube used for sample drawing was rejected before actual sampling.

#### Estimation of Net Ecosystem Production using O<sub>2</sub> mass balance model

Net ecosystem production (NEP) was computed according to Sarma (2004) considering O<sub>2</sub> mass balance between total influx and outflux to the lake from different source and sink regions. The O<sub>2</sub> concentrations in the lake are controlled by its (i) advection from rivers, and sea, (ii) exchange at air-sea and sediment-water interfaces, and (iii) NEP.

$$\frac{\partial}{\partial t} \int_D^0 [O_2]_z = BP - R - O_{2h} - O_{2v} - O_{2r} - O_{2f} \quad (5)$$

where subscripts h, v, r, and f represent fluxes of O<sub>2</sub> through horizontal advection

from sea, vertical mixing at sediment-water interface, mixing with river water and air-sea interface boundary to the water column, BP, and R represents the biological production and respiration integrated to water column depth (D).

The mass balance equation for O<sub>2</sub> at steady state can be expressed as:

$$\frac{\partial}{\partial t} \int_D^0 [I_h + I_v + I_r + I_{BP}] = O_h + O_v + O_R + O_f = 0 \quad (6)$$

where I and O denotes influx and outflux respectively while subscripts h, v, r, f, BP and R are same as in equation (5). In case of biological production is equal to respiration [I<sub>BP</sub> = O<sub>R</sub>], the O<sub>2</sub> influx should be balanced by its outflux. Therefore, the equation for the NEP integrating both pelagic and benthic compartments can be written as:

$$[I_{BP} - O_R] \text{ or NEP} = \int_t^0 \int_D^0 [O_h + O_r + O_f] - [I_h + I_r + I_f] \quad (7)$$

If NEP is positive, the system is said to be net autotrophic (i.e., biological production is higher than respiration) otherwise it is called as net heterotrophy (i.e., biological production is less than respiration).

The entire lake is considered as a single box assuming steady-state conditions and negligible material inputs and outputs from precipitation and evaporation. The distribution of salinity in the lake during monsoon exhibited a strong horizontal stratification between central and southern sectors (Fig. 2b, see results for details), and we thus expect least exchange of water/material mass between these two sectors. The construction of single box model encompassing the entire lake is inevitable in absence of cross-sectoral exchange fluxes, which are essentially required for multiple

box modelling. Estimation of cross-sectoral fluxes for such a wide lake (~25 km in central lake, Fig. 1) can only be possible through hydrodynamic modelling studies. Although Jayaraman et al. (2007) have made numerical simulation of circulation and salinity for Chilka lake for the months January and July 2002, this model for the other seasons is under construction. Finally, NEP is computed using in and out fluxes of O<sub>2</sub> through rivers and sea, its air-water fluxes in the lake.

## Results

### Hydrodynamic characteristics of the lake

Based on the comprehensive (physico-chemical) data, it was possible to classify the lake into south (stns.1-14), central (stns.15-21, 23), north sectors (stns.22, 24-33) and, the outer channel (stns.34-36) (Fig. 1). There was a significant increase in water depth between May ( $1.66 \pm 0.77$  m) and August ( $2.18 \pm 0.78$  m); the northern and southern parts remained most shallow and deep in both the seasons respectively (Table 1). The wetland area ( $704 \text{ km}^2$ ) and volume ( $977 \times 10^6 \text{ m}^3$ ) were both low during premonsoon but witnessed a 1-2 fold rise in monsoon. During monsoon, the northern sector (because of heavy inflows) alone contributed up to 43% of total volume although there was no such significant disparity during premonsoon. Wind forcing was stronger during wet season ( $4.45 - 7.02 \text{ m s}^{-1}$ ) than dry season ( $0.97 - 3.89 \text{ m s}^{-1}$ ).

During premonsoon, tidal amplitude at stn.36 (mouth) measured 0.7 m and remained consistent with a semi-diurnal cycle. Currents were east-west oriented, and flood currents were relatively stronger ( $28.3 \pm 13.1 \text{ cm s}^{-1}$ ) than ebb currents ( $26.2 \pm 10.5 \text{ cm s}^{-1}$ ). Currents at stn.17 (central lake) were also east-west oriented due to tidal



influence from the outer channel. The flood current in the central lake was stronger than ebb, but its magnitude was less ( $11.0 \pm 4.6 \text{ cm s}^{-1}$ ) than that at mouth. At stn.12 (between central and southern lake), current velocities were comparable to stn.17 and directed N-NE during falling tide and S-SW during rising tide, the later being stronger than former. Currents at stn.29 (northern sector) were weak ( $1.2 \pm 0.7 \text{ cm s}^{-1}$ ) and highly scattered in direction. Currents in Palur Canal directed N-S and oscillated according to tides. While there was considerable tidal propagation from the sea to central lake and then up to some distance towards south, the northern lake remains relatively a shadow zone. Non-tidal forces such as wind and freshwater inflow from rivers appeared more important for the northern lake. Overall, local bathymetry and topographic variations have also influenced the circulation pattern.

Jayaraman et al. (2007) presented post-intervention lake circulation model meant for southwest monsoon and noticed an increase in current velocities from northern lake ( $5\text{-}10 \text{ cm s}^{-1}$ ), to central ( $10\text{-}30 \text{ cm s}^{-1}$ ) and further to mouth ( $95\text{-}110 \text{ cm s}^{-1}$ ). Current velocities in the southern lake during monsoon and premonsoon were comparable and varied from  $5$  to  $10 \text{ cm s}^{-1}$ . Overall, currents during monsoon were stronger and mostly unidirectional towards outer channel attributable to heavy inflow from northeast rivers.

### Water and Salt Budget

The lake is a mixing zone for freshwater entering through several spatially distributed rivers along its west and north periphery, and tide propagated seawater through the lake mouth (Fig. 1). While the overall freshwater discharge into the lake was a mere  $3.1 \times 10^6 \text{ m}^3 \text{ d}^{-1}$  during premonsoon, it was as high as  $166.8 \times 10^6 \text{ m}^3 \text{ d}^{-1}$

during monsoon (Table 2). It is noteworthy that the inflow during premonsoon was solely due to northeast rivers since all other sources dried. During monsoon the discharge from northeast rivers was strongest and accounted to about 80% of the total inflow; river Makara alone contributed up to 63% of the overall discharge from northeast rivers and 50% of all other sources put together. The diel observations made for 24 h at station 36 (mouth) during monsoon revealed that the flood current lasted for only 7 h and was quite weak ( $\sim 0.2 \text{ m s}^{-1}$ ) relative to ebb current ( $\sim 0.7 \text{ m s}^{-1}$ ). Salinity varied mostly between 4.5 and 9.0 with exceptional high values (25.8 -26.4) only once at surface and twice at the bottom during flood phase, suggesting weak stratification and strong net outflow of freshwater. The estimated water fluxes showed that ebb flux ( $204.7 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ ) was stronger than flood flux ( $87.9 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ ) but salt flux was higher during flood phase ( $1262 \times 10^9 \text{ g d}^{-1}$ ) relative to ebb phase ( $1223 \times 10^9 \text{ g d}^{-1}$ ) (Fig. 2). Salt influx from rivers was estimated at  $44 \times 10^9 \text{ g d}^{-1}$ . Water loss due to evaporation from entire lake in this season was estimated using Meyer's formula and observed average water temperature ( $32.4^\circ\text{C}$ ), atmospheric temperature ( $32^\circ\text{C}$ ), wind speed ( $5.6 \text{ m s}^{-1}$ ) and relative humidity (65%). The estimated evaporative outflow ( $6.4 \times 10^6 \text{ m}^3 \text{ d}^{-1}$ ) accounts only to 0.31% of lake volume and is insignificant. Precipitation data was not available and assumed to be negligible. Considering the total inflows and outflows, lake displayed a net positive water balance equivalent to  $43.6 \times 10^6 \text{ m}^3 \text{ d}^{-1}$  in monsoon. The corresponding salt accumulation was at  $79 \times 10^9 \text{ g d}^{-1}$  and taking into account the lake volume of  $2060 \times 10^6 \text{ m}^3$  (Table 1) this rises water salinity by a meagre 0.04 per day. Thus the balance of water and salt budgets for monsoon appears to be highly reasonable in the Chilka lake.

Water residence time (R) in the lake was estimated according to

$$R = \frac{\text{Volume of lake}}{\text{Total influx of water}} \quad (8)$$

During premonsoon, the total influx of water is calculated as a sum of rivers discharge and net sea water exchange flux at the mouth whereas it is only due to fresh water discharge from rivers during monsoon (Table 2). Accordingly water residence time of lake was estimated at 127 and 12.3 days during premonsoon and monsoon respectively.

#### Distribution of Temperature and Salinity

Temperature of lake water in premonsoon ( $31.8 \pm 0.9^\circ\text{C}$ ) and monsoon ( $32.4 \pm 1.9^\circ\text{C}$ ) did not show any significant seasonal and spatial variation. The distribution of salinity in premonsoon showed existence of low saline (0-5) waters in the northeast lake indicating the importance of freshwater supply through northeast rivers whereas salinity in other regions in the lake ranged between 15-30 (Fig. 3a). Drastic changes, however, ensued during monsoon when freshwater conditions prevailed in the northern lake and its effect extended up to the central sector (salinity 1-5) (Fig. 3b). Simultaneously, however, the southern lake continued to remain relatively saline ( $16.9 \pm 6.5$ ) with a marginal difference from premonsoon salinity ( $20.2 \pm 6.0$ ).

#### Distribution of SPM, O<sub>2</sub> and Chl *a*

During premonsoon (low river discharge), photic (secchi) depth in the central lake was relatively high (Table 1) and associated with low SPM (Fig. 3a). The

southern lake was, however, highly turbid during this season ( $\text{SPM } 140 \pm 81 \text{ mg L}^{-1}$ ) and had shallowest photic depth caused by wind-induced turbulence (speed  $3\text{-}4 \text{ m s}^{-1}$ ) and bottom scouring. During monsoon, heavy suspended loads brought by rivers (Table 2) resulted in brown turbid waters in the northern lake and as a result photic depth was greatly reduced to  $0\text{-}0.25 \text{ m}$  while the southern lake was relatively free from such effects and displayed deeper photic depths to  $1.0\text{-}1.75 \text{ m}$ . Waters are found to be supersaturated with respect to  $\text{O}_2$  during premonsoon with exceptional levels at stations 20 (132%) and 21 (153%) in the central lake. Station 31 exhibited highest supersaturation of  $\text{O}_2$  (160%) in premonsoon where dense floating vegetation was observed. Contrastingly, undersaturation of  $\text{O}_2$  was noticed in most parts of the lake during monsoon. Chl *a* decreased between premonsoon ( $9.55 \pm 7.88 \text{ } \mu\text{g L}^{-1}$ ) and monsoon ( $8.53 \pm 5.26 \text{ } \mu\text{g L}^{-1}$ ), with highest values ( $35 \text{ } \mu\text{g L}^{-1}$  and  $24 \text{ } \mu\text{g L}^{-1}$  in the respective seasons) in the northeast lake. The Chl *a* for southern lake during premonsoon ( $9.56 \pm 5.16 \text{ } \mu\text{g L}^{-1}$ ) was nearly twice as high as monsoon ( $5.29 \pm 3.50 \text{ } \mu\text{g L}^{-1}$ ).

#### Distribution of pH, DIC, DOC and POC

The pH, DIC and DOC in the lake were lower by  $0.1\text{-}0.7$ ,  $300\text{-}600 \text{ } \mu\text{mol kg}^{-1}$  and  $100\text{-}600 \text{ } \mu\text{mol kg}^{-1}$  respectively, during monsoon than premonsoon (Fig. 4). However, their seasonal variability was much larger in the northern lake where the influence of freshwater was high during monsoon. High pH ( $8.1\text{-}8.3$ ), low DIC ( $1500\text{-}1700 \text{ } \mu\text{mol kg}^{-1}$ ) and DOC ( $315\text{-}530 \text{ } \mu\text{mol kg}^{-1}$ ) in the central lake during premonsoon were associated with high salinity conditions (Fig. 3a) advected through tides. The observed DIC at the mouth ( $1849\text{-}1906 \text{ } \mu\text{mol kg}^{-1}$ ) is consistent with values recorded from adjoining coastal waters (Bay of Bengal) during premonsoon ( $1850 \text{ } \mu\text{mol kg}^{-1}$ ;

Kumar et al. 1996). The lake pH, DIC, DOC and POC showed distinct non-conservative behaviour in both the seasons (Fig. 5). DOC concentrations in the lake were relatively higher than fresh and seawater end stations during premonsoon (Fig. 5c) suggesting its significant in situ production. On the other hand, DOC and POC during monsoon displayed exponential decrease with salinity (Figs. 5c,d) suggesting their significant contribution through river runoff and subsequent consumption or sink in the lake. The distribution of POC (Fig. 4) corroborates the distribution of SPM (Fig. 3) and was high in the south during premonsoon and in the north during monsoon. DIC contributed on average 76% and 64% to total carbon pool in the water column during premonsoon and monsoon respectively. DOC comprised the dominant form of total water column organic carbon with (avg.) 79% and 82% in the respective seasons.

Spatial distribution of carbon variables in the lake were in agreement with their concentrations in different rivers draining to lake. For example, the northern rivers were acidic (6.090-6.930) with high DOC (669-2815  $\mu\text{mol kg}^{-1}$ ) and low DIC (412-1168  $\mu\text{mol kg}^{-1}$ ) which is in strong contrast to central and southern rivers (Table 2), their variations in river inputs reflected in their spatial concentrations in the lake. The DIC of rivers, especially northern rivers, was lower than reported for Godavari river (>2000  $\mu\text{mol kg}^{-1}$ ; Sarin et al. 2002; Bouillon et al. 2003) but higher than Mandovi-Zuari rivers (~500  $\mu\text{mol kg}^{-1}$ ; Sarma et al. 2001) and Periyar river (~200  $\mu\text{mol kg}^{-1}$ ; own unpublished data) in India. It is equally noteworthy that DOC in river water entering Chilka was appreciably high compared to other Indian rivers viz. Godavari (100-300  $\mu\text{mol kg}^{-1}$ ; Sarin et al. 2002; Bouillon et al. 2003), Ganges and Brahmaputra (260-380  $\mu\text{mol kg}^{-1}$ ; Spitzy and Leenheer 1991), and Periyar (<200  $\mu\text{mol kg}^{-1}$ ; our unpublished data). We therefore contend that the rivers draining into

Chilka lake carry appreciable dissolved carbon (both organic and inorganic) rendering it as a repository or a hub for export to either atmosphere or coastal reaches in the Bay of Bengal.

#### Distribution of surface pCO<sub>2</sub>

A comparison of pCO<sub>2</sub> values computed from different constants showed that those derived according to Cai and Wang (1998) were lower than that from Millero et al. (2006) for salinities <9 (Table 3) and the difference is highest for 0-1 salinity (-28 ± 4.5%) followed by 1-3 salinity (-18 ± 4.5%) and 3-8 salinity (-4.5 ± 2.0%). But for salinities between 9 and 36 the pCO<sub>2</sub> from former constants were higher by 5.5 ± 2.1% compared to latter constants. Although magnitude varies, pCO<sub>2</sub> values derived from both the constants showed systematic variations both with space and time. Unless specified, we used pCO<sub>2</sub> and, in turn, CO<sub>2</sub> fluxes derived according to Cai and Wang (1998) for interpreting the results. However the basic conclusion drawn in this study will not be changed on use of Millero et al. (2006) constants.

The pCO<sub>2</sub> showed a pronounced gradient between north (1033-6522 μatm) and central lake (391-2573 μatm) during monsoon (Fig. 4b) which is consistent with pCO<sub>2</sub> in the discharging rivers, and their flux to lake (Table 2). For instance, pCO<sub>2</sub> in the northeast rivers was as high as 4615 to 7922 μatm, followed by northwest (5495-7352 μatm), central (3912-7482 μatm) and south rivers (6166-6420 μatm). Also, the pCO<sub>2</sub> levels in the north and central lake was several folds higher during monsoon than premonsoon (Table 3) because of enormous freshwater influx from rivers (Table 2). In contrast, the southern lake average pCO<sub>2</sub> during premonsoon (677 μatm) was higher by about 1.7 times of monsoon (401 μatm). Station 33, under the direct

influence of north-east rivers, recorded the highest  $p\text{CO}_2$  in both premonsoon (3231  $\mu\text{atm}$ ) and monsoon (9135  $\mu\text{atm}$ ). Excluding stn.33, the lake  $p\text{CO}_2$  varied between 83  $\mu\text{atm}$  (stn.31) and 1097  $\mu\text{atm}$  (stn.11) in the premonsoon and 102  $\mu\text{atm}$  (stn.5) and 6522  $\mu\text{atm}$  (stn.30) in monsoon. These seasonal maxima differed significantly from that observed in Mandovi-Zuari estuarine systems (monsoon:  $\sim 2250$   $\mu\text{atm}$ , non-monsoon:  $\sim 2600$   $\mu\text{atm}$ ; Sarma et al. 2001) but are in the same range as observed in the mangrove creeks of Godavari estuary (500-6500  $\mu\text{atm}$ , Borges et al. 2003; Bouillon et al. 2003). The  $\text{CO}_2$  in the entire central lake and few stations in the northern lake (24, 25, 27 and 31) during premonsoon were under-saturated (Fig. 4a) compared to atmospheric levels. Similarly  $p\text{CO}_2$  in the southeastern lake during monsoon was under-saturated (Fig. 4b). Overall, the lake exhibited supersaturation of  $\text{CO}_2$  in both seasons.

#### $\text{CO}_2$ air-water flux

Unless specified, we used  $\text{CO}_2$  fluxes estimated using gas transfer velocity ( $k$ ) parameterization proposed by Borges et al. (2004) for discussion.  $\text{CO}_2$  fluxes were lowest in the outer channel during premonsoon ( $-1$  to  $5$   $\text{mmol m}^{-2} \text{d}^{-1}$ ) and highest in the northern lake during monsoon ( $81$  to  $861$   $\text{mmol m}^{-2} \text{d}^{-1}$ ) (Table 3). Strong seasonal gradients persisted in the northern lake where monsoon evasion rates were about 58 times higher than premonsoon. The estimated maximum fluxes were higher than that reported from other ecosystems of India (Sarma et al. 2001; Mukhopadhyay et al. 2002; Bouillon et al. 2003; Biswas et al. 2004) and elsewhere (Frankignoulle et al. 1998; Abril et al. 2003; Bouillon et al. 2007).

$\text{CO}_2$  fluxes computed from  $p\text{CO}_2$  calculated from the Cai and Wang (1998)

have showed large differences, on higher side, compared to those calculated from Millero et al. (2006). The difference in fluxes between these constants was less in premonsoon (13%) when high saline conditions prevailed and high in monsoon (28%) when most of the lake is occupied by low saline waters (Table 3). These disparities in fluxes were in agreement with those observed for  $p\text{CO}_2$  levels for different salinity ranges i.e. low salinity in monsoon displayed large variation in  $p\text{CO}_2$  and in turn  $\text{CO}_2$  flux, and vice versa in premonsoon.

### Carbon budget

For a quantitative and convincing estimate of system metabolism, concurrent data collected using different approaches such as production-respiration, net  $\text{O}_2$  and  $\text{CO}_2$  gas flux, etc. (Cole et al. 2000) or mass balance using water column integrated methods (Gazeau et al. 2005b) are necessary. Dissolved inorganic nitrogen mass balance is related to its complex cycle that can not be worked out from a box model because of too many unknowns. Budgeting of dissolved inorganic phosphorus through LOICZ model has limitation that abiotic processes (adsorption/desorption from suspended particles and sediment) strongly influence it. Therefore,  $\text{O}_2$  and  $\text{CO}_2$  are good variables for computing net ecosystem production (NEP). However, such studies were not adequately addressed in tropical ecosystems. We constructed a carbon budget at the basin scale to address whole lake metabolism and to estimate NEP.

Carbon import and export fluxes of lake were several folds higher during monsoon than premonsoon. DIC influx from rivers during monsoon was  $2.03 \text{ GgC d}^{-1}$  ( $1 \text{ Gg} = 10^9$  grams) and 90% of it was lost to the sea ( $1.82 \text{ GgC d}^{-1}$ ). The influx of



riverine DOC ( $2.88 \text{ GgC d}^{-1}$ ) was higher than DIC and POC ( $0.36 \text{ GgC d}^{-1}$ ), and only 10% of DOC and 42% of POC influxes were exported to the sea. Fluxes for premonsoon could not be estimated as we lost river samples for DO, DOC and POC.

The total  $\text{CO}_2$  fluxes in both the seasons showed that lake is a net source of  $\text{CO}_2$  to atmosphere. Its net flux, computed from  $\text{pCO}_2$  calculated from Cai and Wang (1998), was estimated at  $0.06 \text{ GgC d}^{-1}$  during premonsoon and the corresponding evasion flux for monsoon was  $2.64 \text{ GgC d}^{-1}$  which is about 44 times higher than premonsoon efflux (Table 3). The higher evasion fluxes of  $\text{CO}_2$  during monsoon can be related to higher influxes of DIC, DOC and POC from rivers in this season. However, the flux computed from  $\text{pCO}_2$  calculated from Millero et al. (2006) was found to be marginally lower in premonsoon ( $0.05 \text{ GgC d}^{-1}$ ) but high in monsoon ( $3.38 \text{ GgC d}^{-1}$ ). Interestingly, central sector displayed a net sink of  $\text{CO}_2$  in premonsoon with both Cai and Wang (1998) and Millero et al. (2006) constants. On the contrary, fluxes derived from  $\text{pCO}_2$  calculated from Millero et al. (2006) displayed net sink in outer channel during premonsoon which is otherwise displayed as net sources using Cai and Wang (1998) constants. A comparison of  $\text{CO}_2$  fluxes estimated using  $k$  parameterization proposed by both Raymond and Cole (2001) and Borges et al. (2004) showed large differences with fluxes from former parameterization were lower by 66% in premonsoon and 82% in monsoon compared to latter parameterization (Table 3).

## Discussion

Potential mechanisms for supersaturation of  $\text{CO}_2$  in the lake

During premonsoon (lean flow conditions), the influx of seawater resulted in

high salinity and water column transparency (1.0-1.5 m) across most parts in the central lake favouring photosynthetic production by phytoplankton, microphytobenthos and macrophytes resulting in CO<sub>2</sub> undersaturation (Fig. 4a) and supersaturation of oxygen (106-154%). At stn. 31, CO<sub>2</sub> remained heavily undersaturated (129 μatm) with high oxygen (160%) apparently as a result of photosynthetic activity of floating vegetation. Wind induced bottom churning leads to highest SPM, POC, DOC and DIC in the southern sector (Fig. 4a) and the respiration of this organic carbon pool might be the potential mechanism responsible for elevated pCO<sub>2</sub> levels in this sector. In contrast, the southern lake displayed undersaturation with respect to CO<sub>2</sub> on its east (200-350 μatm) and marginal supersaturation on its west (~500 μatm) during monsoon (Fig. 4b). Such a disparity is mainly driven by low SPM (23-56 mg L<sup>-1</sup>) and high photic depth (1.0-2.25 m) enabling more intense photosynthesis by submerged macroalgae on the eastern side.

Following heavy freshwater influx during monsoon, the northern lake witnessed a drop in pH (6.853-7.635) resulting in high pCO<sub>2</sub> (1168-7373 μatm). It also brought in its wake several alterations in pCO<sub>2</sub> in the central lake from undersaturation during premonsoon (210-578 μatm) to supersaturation (487-2776 μatm).

#### *CO<sub>2</sub> supply from rivers*

The rivers drain freshwater in to Chilka lake carry elevated levels of both inorganic and organic carbon and their CO<sub>2</sub> concentrations are supersaturated by 10-21 times with respect to atmospheric levels (Table 2). Studies in the past have shown that a fraction of this riverine DIC is present as 'excess CO<sub>2</sub>' (Abril et al. 2000, 2003)

which mainly results from community respiration in the soil/sediment and water (Cole and Caraco 2001; Richey et al. 2002) and this can either escape as CO<sub>2</sub> to atmosphere or can be transported to downstream systems. We estimated this excess DIC fraction in the rivers and lake as a difference between in situ DIC and a theoretical DIC at atmospheric equilibrium, the latter was calculated according to Abril et al. (2000) by resolving the inorganic carbon system with the estimated total alkalinity according to Cai and Wang (1998) [Millero et al. (2006)] and atmospheric pCO<sub>2</sub>. The excess CO<sub>2</sub> in the rivers during monsoon represent  $19 \pm 7\%$  ( $24 \pm 9\%$ ) of observed DIC concentrations and its flux to lake was  $0.42 \text{ GgC d}^{-1}$  ( $0.51 \text{ GgC d}^{-1}$ ) which accounts to 20% (25%) of total DIC influx. Raw domestic sewage from few small settlements, runoff from agricultural fields along the rivers, etc. release organic matter and its decomposition might be responsible for excess CO<sub>2</sub> in these rivers. Consequent to the river waters mixing in the lake, excess CO<sub>2</sub> (DIC) decreased exponentially along the salinity gradient (Fig. 6) suggesting its rapid ventilation to the atmosphere in the low saline regions, i.e. northern lake. This is in agreement with the earlier studies that physical ventilation of riverine excess CO<sub>2</sub> occurs rapidly in the low saline regions of estuary (Frankignoulle et al. 1998; Abril et al. 2000). Despite this, the excess CO<sub>2</sub> flux transported by rivers represents only 15-16% of total CO<sub>2</sub> ventilated to atmosphere from entire lake ( $2.64\text{-}3.38 \text{ GgC d}^{-1}$ , Fig. 10) which is consistent with the findings of Borges et al. (2006) that CO<sub>2</sub> supply from rivers play only a minor role compared to its emission from estuaries. Therefore understanding lake processes that leads to large in situ production of CO<sub>2</sub> are vital.

#### *Respiration of organic matter*

There was a disparity in the relative contributions of riverine DIC and DOC to

total dissolved carbon (DC=DIC+DOC) pool during monsoon. DIC constituted 70% of DC from south and central rivers, and 25 to 50% in the northern rivers. Overall, DOC contributed to 60% of total DC pool from all rivers during monsoon. Contrastingly, the DOC constituted 33% and 10% of DC pool in the lake and seawater (mouth) respectively. The fluxes of these parameters also showed similar trends. In order to examine the processes responsible for the fate of DC in the lake, we constructed mixing model for different carbon fraction ratios between end members. In view of multiple rivers opening into the lake, one major river representative of each sector was considered. It was found that the average DIC/DOC ratio of northern rivers (0.36-0.70) was lower relative to central (2.10) or south rivers (2.52) and even seawater (4.49) whereas lake ratios (0.81 -4.36) were intermediate between the rivers and seawater. The model showed a general increase of DIC/DOC ratios with salinity albeit with a large scatter in the points (Fig. 7a), suggesting that these ratios are not only influenced by physical mixing of end member water masses but also affected significantly either by DOC respiration and/or its conversion to POC. The rise in DOC/POC ratios (Fig. 7b) and drop in POC/SPM ratios (Fig. 7c) along the salinity gradient indicated that POC in riverine SPM is getting desorbed after entering the lake and the converted DOC together with unaffected POC is respired in the system. Further, the northern lake is highly dominated by fresh water with high SPM (Fig. 3b) and absolutely zero transparency (Table 1). O<sub>2</sub> saturation was lowest (78 ± 2%) and consistent with low pH and DOC, and high DIC and pCO<sub>2</sub> (Fig. 4b). The time-series observations made at st. 29 (in the north) for 24 h (figure not shown) did not show any clear diel signals but the concentrations of these variables varied only narrowly. In spite of high Chl *a* in the northern lake (Fig. 3b) the dense turbid cloud in this part can hamper phytoplankton production, hence, community respiration is expected to

exceed its production. Bacterial degradation of organic matter in water through unimpeded supply from rivers (Jansson et al. 1999, 2000) and respiration of sediment organic carbon (Jonsson et al. 2001; Sarma et al. 2001) are expected to be high under such conditions. This is supported by our observations that sediment organic carbon ( $1.5 \pm 0.7\%$ ) and net community respiration ( $203 \pm 70 \text{ mgC m}^{-2} \text{ h}^{-1}$ ) (estimated by dark incubation of  $\text{O}_2$  in dark bottles for 3 h) are high in the northern lake during monsoon. Significant positive correlation ( $P > 0.001$ ) between excess DIC and apparent oxygen utilisation (Fig. 8) further supports that there is a strong biological control over  $\text{CO}_2$  production in the lake. Their strong relationship also showed that intense respiration of organic matter in the rivers is extended up to northern lake and weakened towards central lake and outer channel, therefore, the former regions are considered to be potential zones for  $\text{CO}_2$  production (Table 3).

#### *Community respiration of macrophytes*

St. 23 is heavily vegetated and has deeper photic depth (1.5 m). Despite high  $\text{pCO}_2$  through rivers Kansari (R6) and Badashanka (R7) (Fig. 1; Table 2), diel observations (Fig. 9) showed high pH ( $7.951 \pm 0.058$ ) and supersaturation of  $\text{O}_2$  ( $105 \pm 6\%$ ) associated with low DIC ( $1651 \pm 11 \text{ } \mu\text{mol kg}^{-1}$ ) and  $\text{pCO}_2$  ( $705 \pm 92 \text{ } \mu\text{atm}$ ) during day hours. The conditions however reversed ( $\text{O}_2$ :  $92 \pm 13\%$ ; pH:  $7.823 \pm 0.163$ ; DIC:  $1731 \pm 53 \text{ } \mu\text{mol kg}^{-1}$ ;  $\text{pCO}_2$ :  $1040 \pm 444 \text{ } \mu\text{atm}$ ) by night, suggesting a significant role of the macrophyte community on inorganic carbon system in the lake. A rise in salinity from 3 to 5 between 15:00 h and 19:00 h, attributed to drop in proximate rivers flow, corresponds to a rise in DIC. Interestingly, despite constant salinity from 19:00 h onwards, DIC steadily increased from 17:00 h to 05:00 h on the next day (for 12 h) by  $\sim 155 \text{ } \mu\text{mol kg}^{-1}$ . The net community respiration (estimated by

O<sub>2</sub> incubation in dark bottles at in situ conditions for 24 h) at this station was found to be 3.67 gC m<sup>-3</sup> d<sup>-1</sup> (although nitrification consumes some amount of oxygen during incubation, we expect its intensity is highly insignificant compared to respiration) that corresponds to production of DIC by 153 μmol kg<sup>-1</sup> in 12 h, which is in agreement with its observed increase in DIC (~155 μmol kg<sup>-1</sup>), and strongly suggests enhanced pCO<sub>2</sub> levels in the night was caused by intense community respiration.

#### *Net Ecosystem Production (NEP)*

It is imperative from Table 2 that the lake receives huge amount of carbon via rivers during monsoon. In order to find out its relative influence over system metabolic balance and CO<sub>2</sub> effluxes from lake we estimated NEP, integrating both pelagic and benthic compartments, through oxygen mass balance model (Fig. 10a). During monsoon, the oxygen influx to lake from all the rivers is estimated to be 0.96 Gg O<sub>2</sub> d<sup>-1</sup> (29.9 x 10<sup>6</sup> mmol O<sub>2</sub> d<sup>-1</sup>) and its outflux to sea is 0.74 Gg O<sub>2</sub> d<sup>-1</sup> (23.1 x 10<sup>6</sup> mmol O<sub>2</sub> d<sup>-1</sup>) ie. 0.22 Gg O<sub>2</sub> d<sup>-1</sup> (6.9 x 10<sup>6</sup> mmol O<sub>2</sub> d<sup>-1</sup>) equivalent to 23% of influx is utilized in the lake. Air-water oxygen flux (average 119 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup> corresponds to -3.88 Gg O<sub>2</sub> d<sup>-1</sup> at basin scale) is found to be the largest source which is 4 fold higher than riverine flux. Thus NEP, derived as a difference between total sinks (outflux to sea) and sources (rivers and atmosphere), is estimated at -4.10 GgO<sub>2</sub> d<sup>-1</sup> (128 mmol O<sub>2</sub> m<sup>-2</sup> d<sup>-1</sup>) during monsoon showing that the lake is strongly heterotrophic. Applying the observed DIC/O<sub>2</sub> ratio (slope) of 0.92, carbon produced due to NEP is equivalent to -3.77 GgC d<sup>-1</sup> (308 mmolC m<sup>-2</sup> d<sup>-1</sup>). This is consistent with the total carbon trapped (246 mmolC m<sup>-2</sup> d<sup>-1</sup> or 3.01 GgC d<sup>-1</sup>) in the lake and also with CO<sub>2</sub> efflux to atmosphere from lake (2.64-3.38 GgC d<sup>-1</sup>; Fig. 10b). Therefore, the carbon mass balance in the system is appeared to be biased between the computations

made using the carbonic acid dissociation constants of Cai and Wang (1998) and Millero et al. (2006) through  $k$  parameterization of Borges et al. (2004) (Fig. 10b).

Sediment oxygen demand (SOD) in the lake estimated through benthic chamber experiment revealed that in the first three hours  $O_2$  in the chamber was decreased by  $0.14 \text{ mg L}^{-1}$  equivalent to  $0.34 \text{ g m}^{-2} \text{ d}^{-1}$  ( $10.6 \text{ mmol } O_2 \text{ m}^{-2} \text{ d}^{-1}$ ) by community respiration on the surface sediment which is highly clayey (based on our physical observation) and expected to have high organic carbon in it. We linearly extrapolated this chamber result to the entire lake area under the simplifying assumption that the environmental settings at the experimental station is representative for most parts of the lake. Accordingly, SOD for the entire lake during monsoon was estimated at  $-0.34 \text{ GgO}_2 \text{ d}^{-1}$  which is equivalent to  $-0.31 \text{ GgC d}^{-1}$  (by applying DIC/ $O_2$  ratio). Care must be taken as this value may be either over or underestimated. Thus benthic respiration represents only 8% of NEP suggesting sediment carbon storage is only a minor pathway for the carbon inputs at least during monsoon and remaining 92% ( $-3.46 \text{ GgC d}^{-1}$ ) is contributed by pelagic net community production.

The carbon mass balance strongly suggests that 93% of total riverine carbon trapped in the river is represented by organic carbon (DOC+POC) which together with sediment organic carbon is respired in the lake through heterotrophic activity and respired carbon is released mostly in the form of  $CO_2$ . This heterotrophic respiration has occurred mainly in the north and central lake as supported by strong relationship between excess DIC and apparent oxygen utilisation in these regions (Fig. 8). The released  $CO_2$  is driven out to atmosphere through wind forcing and water currents

instead of transported to sea. The insignificant fluxes from the outer channel ( $0.003 \text{ GgC d}^{-1}$ ) relative to the lake proper in particular north ( $2.32 \text{ GgC d}^{-1}$ ) and central lake ( $0.31 \text{ GgC d}^{-1}$ ) suggest that Chilka lake is a source of  $\text{CO}_2$  to the atmosphere driven by strong heterotrophic activity via transforming riverine organic carbon to  $\text{CO}_2$ . Thus Chilka lake is yet another coastal ecosystem where heterotrophic activity of system is a highly dominant process contributed to emission of  $\text{CO}_2$  fluxes compared to physical ventilation of riverine  $\text{CO}_2$  in the system during monsoon.

The monsoon budgets clearly showed that rivers supply high flux of DOC, apart from excess DIC, which is mineralised in the lake and elevated the  $\text{pCO}_2$  levels. Although budgets for premonsoon could not be constructed, low  $\text{pCO}_2$  levels in this season are regulated by negligible river discharge that leads to poor supply of terrestrial DOC. Owing to high residence time of water and, in turn, nutrients the photosynthetic efficiency is very high during calm periods that facilitates sink of atmospheric  $\text{CO}_2$  as was seen in the central sector. But during the windy periods, the production is masked by high sediment resuspension that reduces the light penetration depth. In addition to this additional  $\text{CO}_2$  adds to the water column from the sediments that leads to supersaturation of  $\text{CO}_2$  as seen in the southern sector. Despite the influence of various processes, the net  $\text{CO}_2$  flux at basin scale in premonsoon remain several fold lower compared to monsoon.

## Conclusions

Chilka lake is another coastal ecosystem that can be concluded as net source of  $\text{CO}_2$ , a net heterotrophic during the periods of observation.  $\text{CO}_2$  efflux during monsoon are very strong and excess  $\text{CO}_2$  transported by rivers represented only 15-



16% of total efflux from lake. Net ecosystem production ( $-3.77 \text{ GgC d}^{-1}$ ) derived through mass balancing of  $\text{O}_2$  and total carbon revealed that large flux of trapped organic carbon from rivers ( $2.80 \text{ GgC d}^{-1}$ ) is biologically respired in the lake and converted  $\text{CO}_2$  is pumped out to the atmosphere ( $2.64\text{-}3.38 \text{ GgC d}^{-1}$ ) instead of exporting to the sea. We contend that such evasion rates could be a characteristic feature for lakes/lagoons of large dimensions even elsewhere and coastal lagoons can then develop into environmental 'hot spots' in terms of regional carbon budgets.

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## Legend to Figures

- Figure 1. Map of Chilka Lake with station locations. The dotted lines represent imaginary boundaries of different sectors of lake.
- Figure 2. Water and Salt budgets of the lake during monsoon. Values in black shaded boxes are water flows ( $10^6 \text{ m}^3 \text{ d}^{-1}$ ) and others are salt flux ( $10^9 \text{ g d}^{-1}$ ). Precipitation was assumed to be negligible.
- Figure 3. Distribution of different variables in the lake during (a) premonsoon and (b) monsoon.
- Figure 4. Distribution of carbon variables in the lake during (a) premonsoon and (b) monsoon.  $\text{pCO}_2$  values are according to Cai and Wang (1998).
- Figure 5. Seasonal distribution of (a) pH, (b) DIC, (c) DOC, (d) POC, and (e)  $\text{pCO}_2$  along the salinity gradient.  $\text{pCO}_2$  values are according to Cai and Wang (1998).
- Figure 6. Seasonal distribution of excess DIC (calculated from Cai and Wang (1998)) along salinity gradient.
- Figure 7. Mixing models of different ratios along salinity gradient during monsoon. (a) DIC/DOC, (b) DOC/POC, and (c) POC/SPM. Mixing lines are drawn between different river waters and seawater.
- Figure 8. Relationship of excess DIC (calculated according to Cai and Wang (1998)) vs apparent oxygen utilisation (AOU) in the lake during monsoon. It is highly pronounced in the rivers and north where the respiration of organic matter is appeared to be strong and leads to elevated  $\text{CO}_2$  levels in these regions.
- Figure 9. Diel variations at station 23 (macrophyte vegetated) during monsoon.  $\text{pCO}_2$  values are according to Cai and Wang (1998).
- Figure 10. Total influx, outflux and net fluxes of (a) Oxygen ( $\text{GgO}_2 \text{ d}^{-1}$ ) and (b) Total Carbon ( $\text{GgC d}^{-1}$ ) in Chilka Lake during monsoon.  $\text{CO}_2$  air-water flux is computed from  $\text{pCO}_2$  calculated from Cai and Wang (1998) and the parenthesis value is calculated from Millero et al. (2006).



Table 1. Physical properties of Chilka Lake (average values).

	Depth (m)		Area (km <sup>2</sup> )	Volume (10 <sup>6</sup> m <sup>3</sup> )	
	Water Column	Photic Zone		Water Column	Photic Zone
<u>Premonsoon</u>					
North	1.03	0.48	269	295.6	124.6
Centre	1.64	0.86	236	344.8	198.1
South	1.85	0.22	182	308.2	39.3
Outer Channel	2.42	0.78	17	28.6	8.3
Total	1.61	0.49	704	977.2	370.3
<u>Monsoon</u>					
North	1.83	0.06	478	874.3	23.9
Centre	2.08	1.09	299	622.6	326.2
South	2.29	1.23	225	516.4	270.6
Outer Channel	2.58	1.08	18	46.4	19.4
Total	2.13	0.84	1020	2059.7	640.1

Table 2. Characteristics of major inflow/outflow waters into Chilka Lake during monsoon (parenthesis values correspond to premonsoon).

River code	Location/ River name	Discharge ( $10^6 \text{ m}^3 \text{ d}^{-1}$ )	SPM ( $\text{mg L}^{-1}$ )	pH	O <sub>2</sub> ( $\text{mg L}^{-1}$ )	DOC ( $\mu\text{mol kg}^{-1}$ )	DIC ( $\mu\text{mol kg}^{-1}$ )	POC ( $\mu\text{mol kg}^{-1}$ )	pCO <sub>2</sub> <sup>s</sup> ( $\mu\text{atm}$ )
<u>Southern Rivers</u>									
R3	Ghat road	--	66.8	7.273	3.77	--	2868	132	6420
R4	Langaleshwar	2.76	80.3	7.310	5.80	1156	2918	231	6166
	<i>Sub-total</i>	2.76							
<u>Central Rivers</u>									
R5	Janjira	1.04	77.1	7.006	4.64	674	1896	201	7482
R6	Kansari	4.67	100.8	7.102	4.64	650	1784	244	5512
R7	Badashanka	0.52	48.4	7.385	7.25	764	2612	216	3912
	<i>Sub-total</i>	6.23							
<u>Northwestern Rivers</u>									
R8	Kusumi	1.94	301.2	6.514	5.80	669	650	313	6223
R9	Kantabani	2.42	213.2	6.542	4.30	954	608	337	5854
R10	Sananai	1.56	133.2	6.517	8.70	1356	671	286	6865
R11	Tarimi	0.54	97.5	6.490	8.70	1296	574	291	6017
R12	Mangalajodi	0.98	57.5	6.090	5.80	734	412	448	7352
R13	Malguni	16.24	171.8	6.655	5.80	2203	800	206	6092
	Gidigia	1.77	221.6	6.564	6.38	1186	604	262	5495
	<i>Sub-total</i>	25.45							

contd...

River code	Location/ River name	Discharge (10 <sup>6</sup> m <sup>3</sup> d <sup>-1</sup> )	SPM (mg L <sup>-1</sup> )	pH	O <sub>2</sub> (mg L <sup>-1</sup> )	DOC (μmol kg <sup>-1</sup> )	DIC (μmol kg <sup>-1</sup> )	POC (μmol kg <sup>-1</sup> )	pCO <sub>2</sub> <sup>§</sup> (μatm)
<u>Northeastern Rivers</u>									
R14	Makara	83.98 (2.68)	104.4	6.604 (7.043)	5.80	1300	947 (1458)	171	7922 (7735)
R15	Daya	10.80 (0.04)	158.2	6.649 (7.434)	6.09	2815	989 (1412)	221	7668 (3397)
R16	Nuna	21.60 (0.38)	50.8	6.826 (6.889)	4.35	1302	1168 (1983)	81	6393 (14640)
R17	Bhargavi	10.58	232.2	6.930	7.25	1065	1000	271	4615
R18	Thodasnai	5.40	--	6.713	4.64	1636	981	77	6784
	<i>Sub-total</i>	132.36 (3.11)							
	<u>Total</u>	166.80 (3.11)							
Stn. 36	Mouth	116.80 (-4.58) <sup>#</sup>	45.6 (27.0)	8.043* (8.234)	5.51* (7.40)	412* (202)	1849* (1906)	52* (36)	436* (375)

§ pCO<sub>2</sub> values according to Cai and Wang (1998).

\* for maximum salinity (26 ) recorded over 24 h time scale.

# -ve sign indicates the net flow towards lake.

Table 3. pCO<sub>2</sub> levels in the Chilka Lake according to dissociation constants of carbonic acid proposed by different authors (stn.33 data is excluded as it falls in dredged channel, an extension of northeastern rivers confluence into the lake). CO<sub>2</sub> fluxes were given according to *k* parameterization of Borges et al. (2004) and parenthesis values were based on *k* parameterization suggested by Raymond and Cole (2001). 1 MgC = 10<sup>6</sup> gC.

	pCO <sub>2</sub> (µatm)		CO <sub>2</sub> flux (mmol m <sup>-2</sup> d <sup>-1</sup> )		Sectoral CO <sub>2</sub> flux (MgC d <sup>-1</sup> )
	Range	Mean	Range	Mean	
<u>Cai and Wang (1998)</u>					
<u>Premonsoon</u>					
North	83- 939	487	-15.7-35.9	7.03	22.7
Centre	138- 615	293	-14.3- 9.9	-4.83	-13.7
South	421-1097	677	3.1-56.0	23.00	50.3
Outer Channel	367- 438	393	-1.0- 5.0	1.28	0.3
Total	83-1097	506	-15.7-56.0	9.82	59.5 (20.5)
<u>Monsoon</u>					
North	1033-6522	3222	81.0-861.4	405.11	2322.4
Centre	391-2573	940	1.9-327.5	84.30	302.8
South	102- 718	401	-27.5- 46.4	3.43	9.3
Outer Channel	382- 626	466	0.6- 36.0	12.84	2.8
Total	102-6522	1363	-27.5-861.4	141.43	2637.3 (473.5)
<u>Millero et al. (2006)</u>					
<u>Premonsoon</u>					
North	76-1101	490	-16.1-49.5	7.47	24.1
Centre	127- 596	275	-14.9- 9.1	-5.87	-16.6
South	392-1071	646	1.0-54.0	20.54	44.9
Outer Channel	339- 405	364	-3.8- 2.3	-1.42	-0.3
Total	76-1101	488	-16.1-54.0	8.55	52.1 (17.7)
<u>Monsoon</u>					
North	1077-7878	4036	86.4-1051.4	521.52	2989.8
Centre	410-3292	1089	-4.6- 434.7	106.86	383.8
South	95- 697	395	-28.2- 43.5	2.73	7.4
Outer Channel	395- 666	485	2.4- 41.9	15.68	3.4
Total	95-7878	1637	-28.2-1051.4	180.96	3384.4 (607.5)

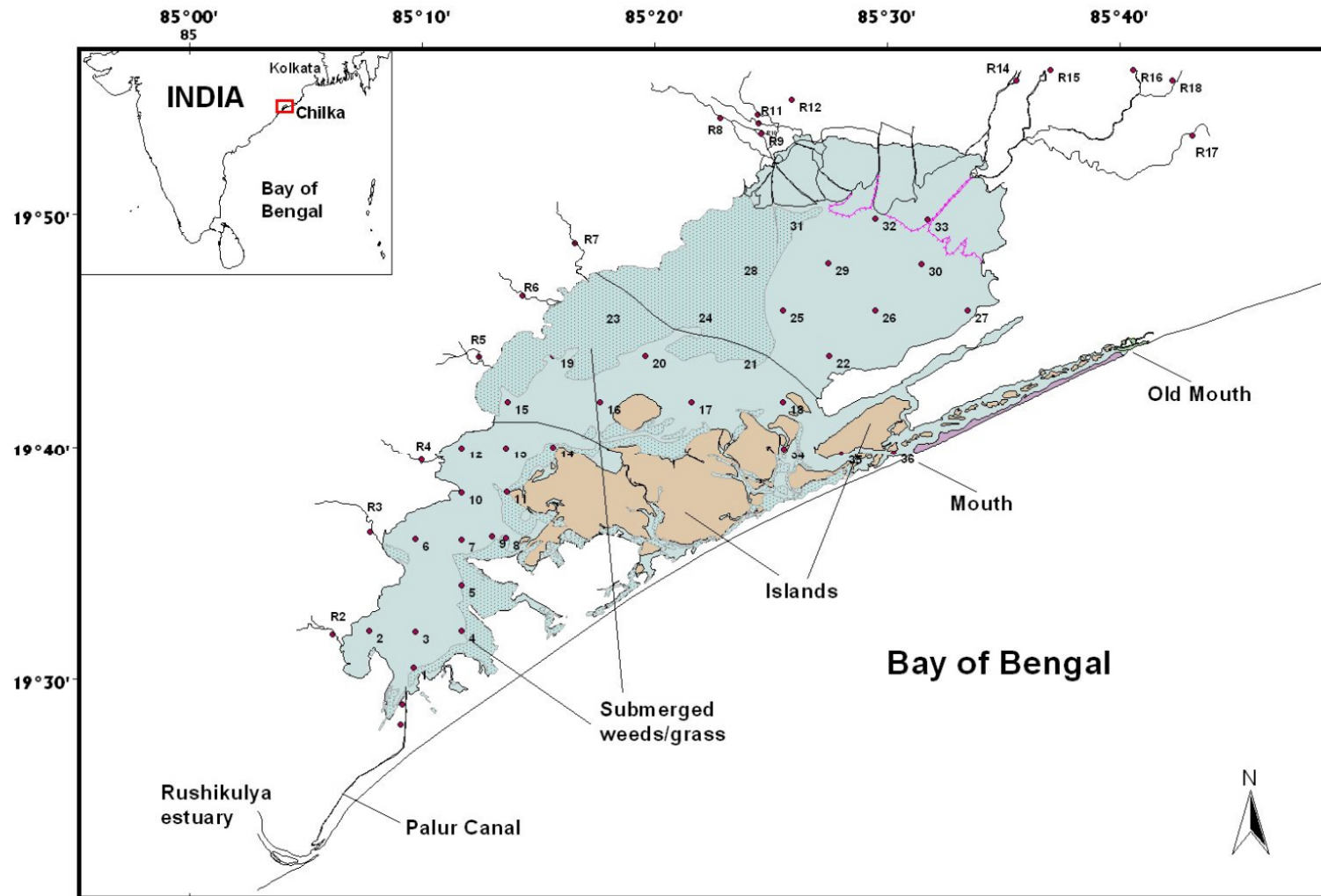


Fig. 1

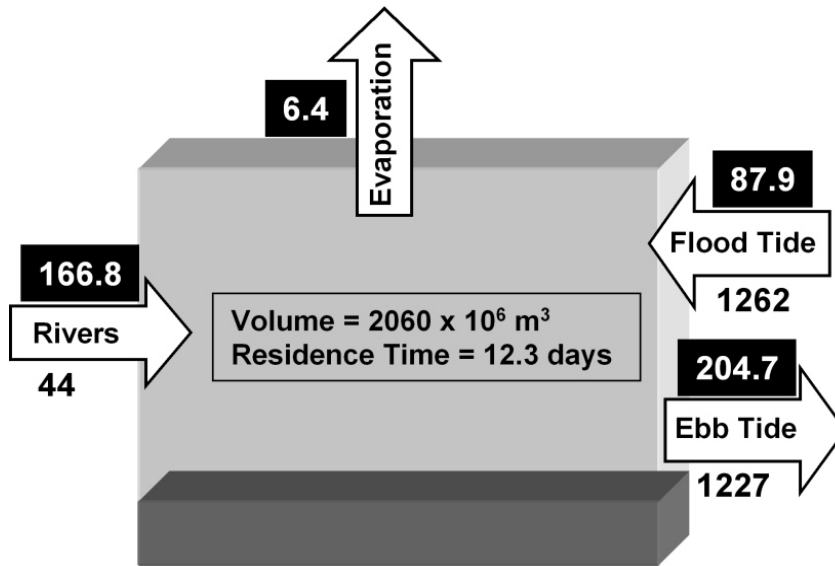
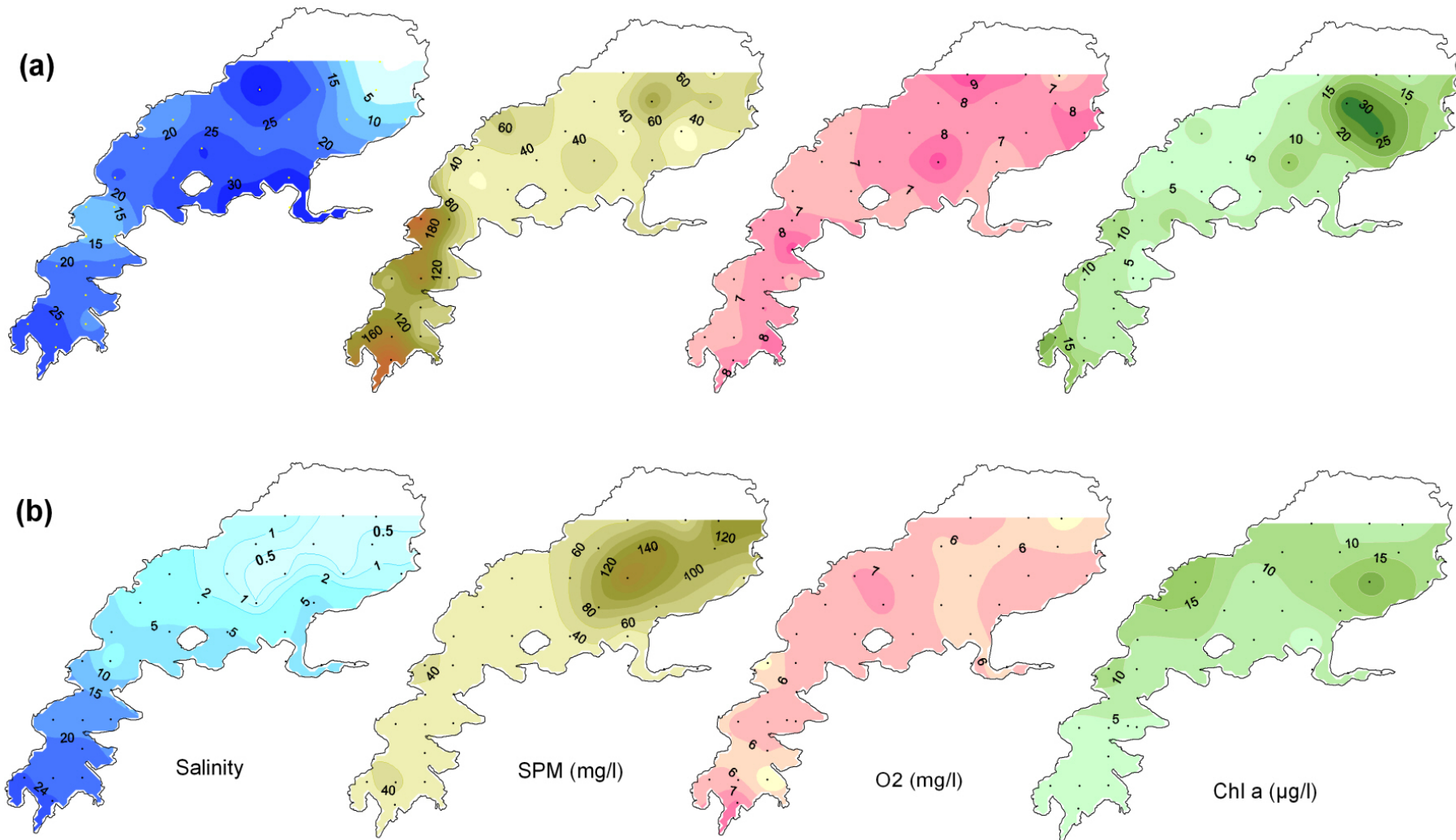


Fig.2



**Fig.3**

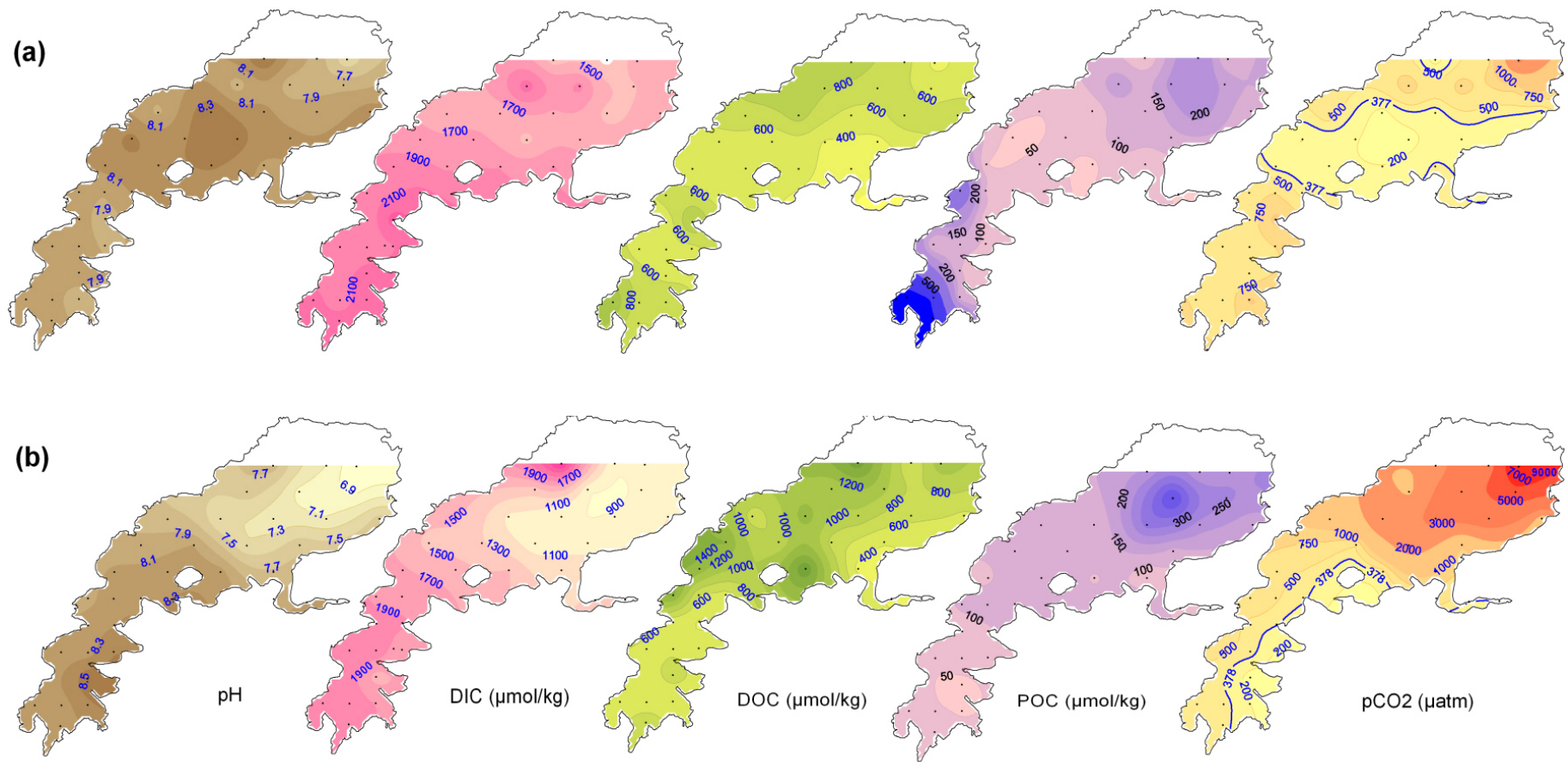


Fig.4



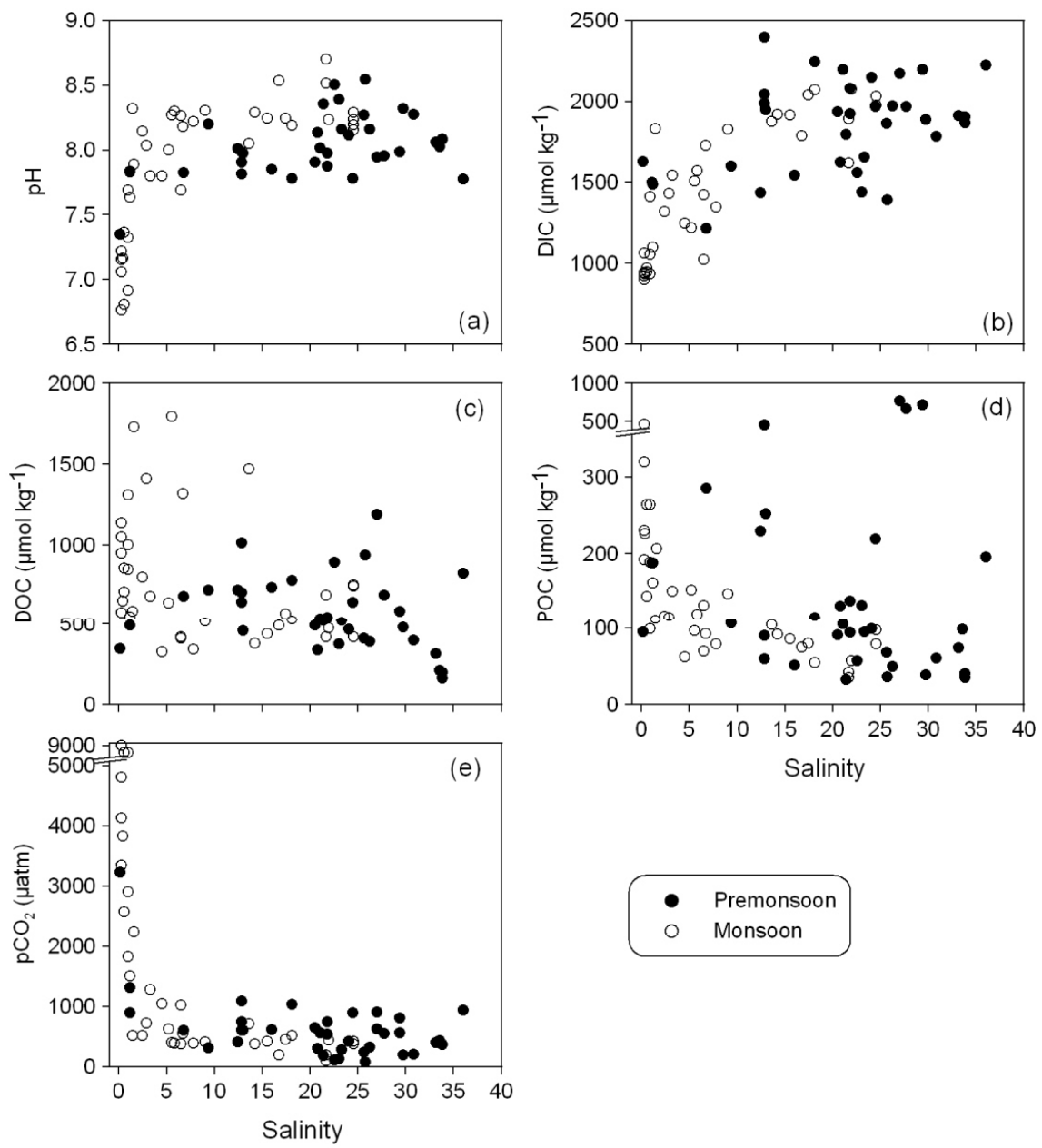
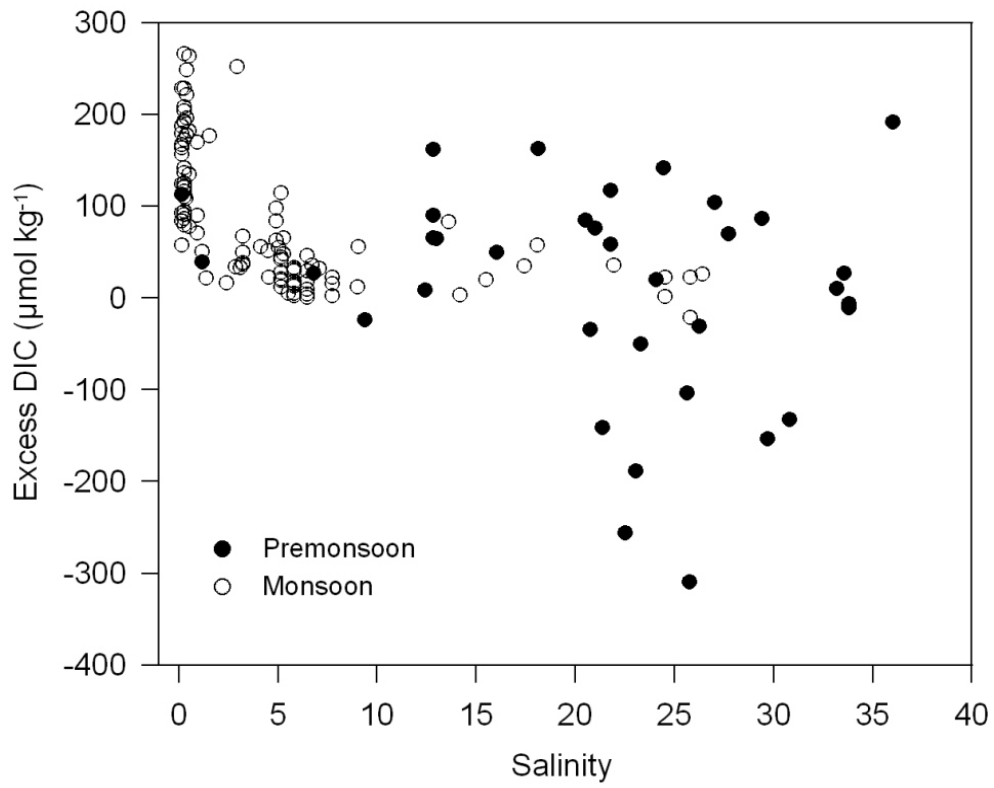


Fig.5



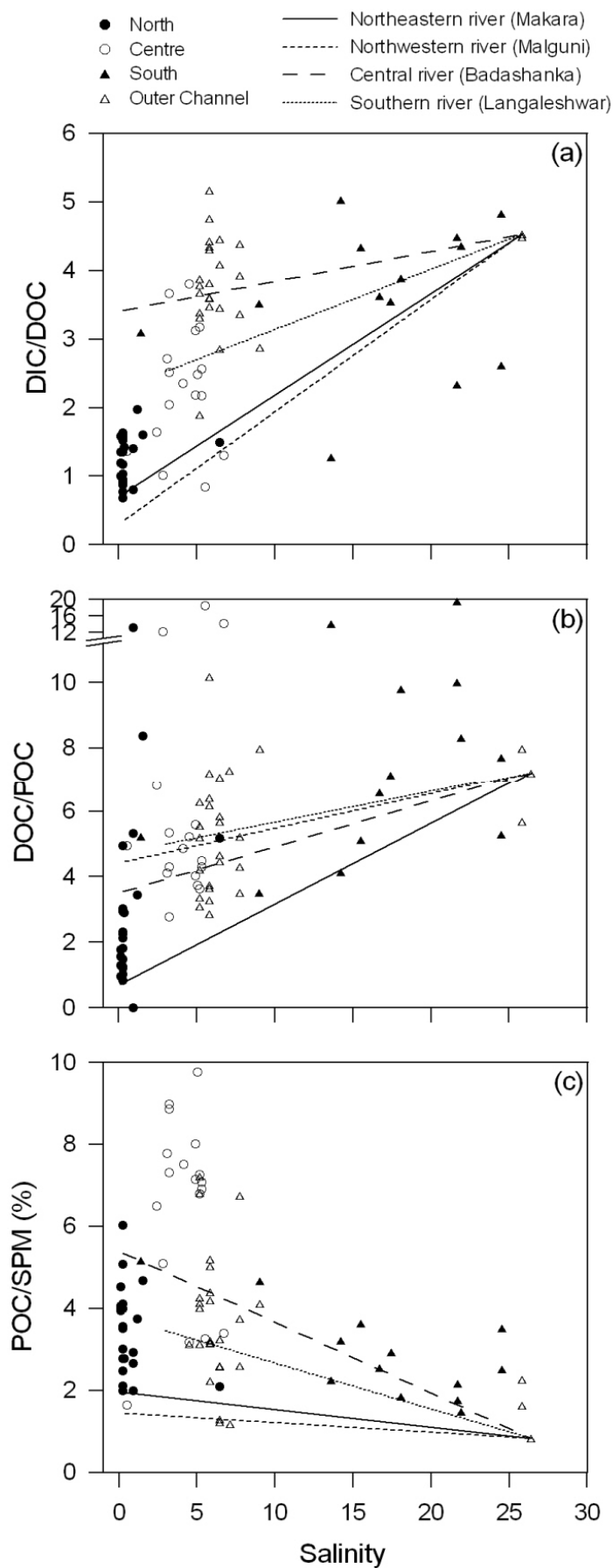


Fig. 7.

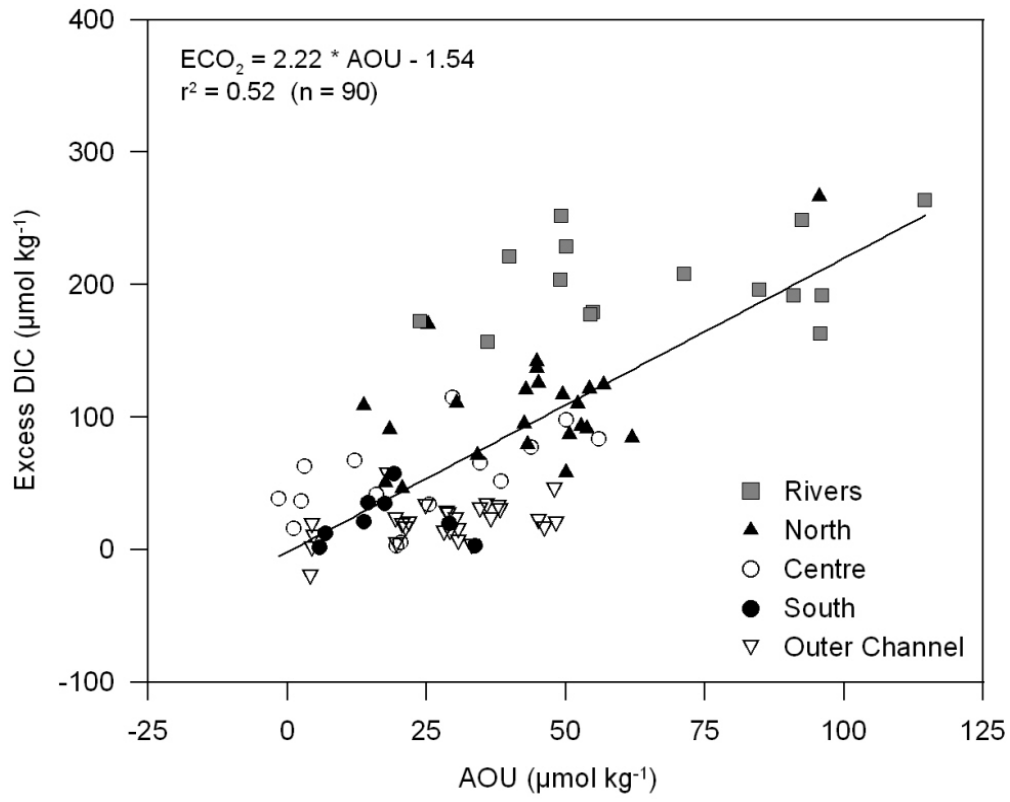


Fig.8

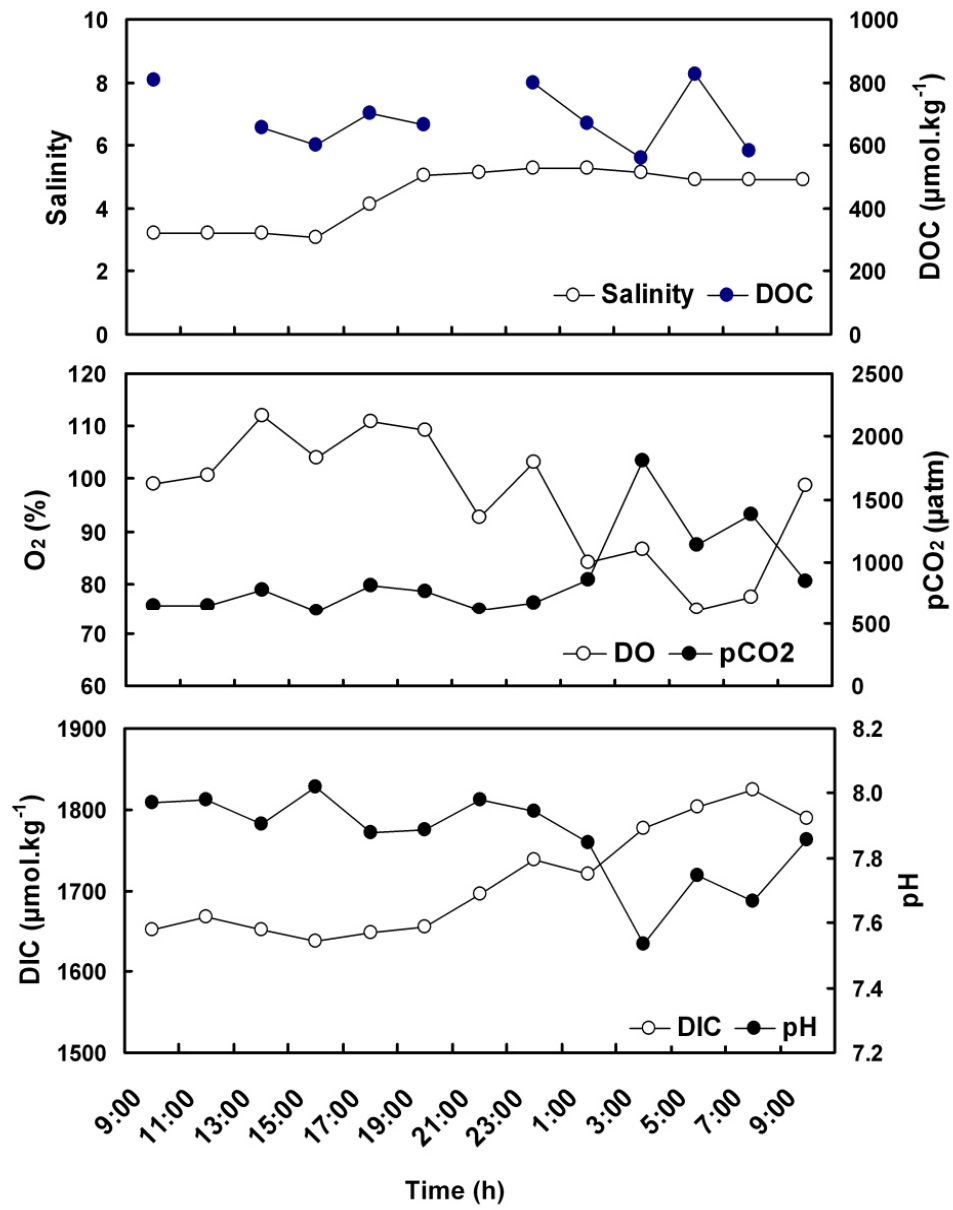


Fig.9

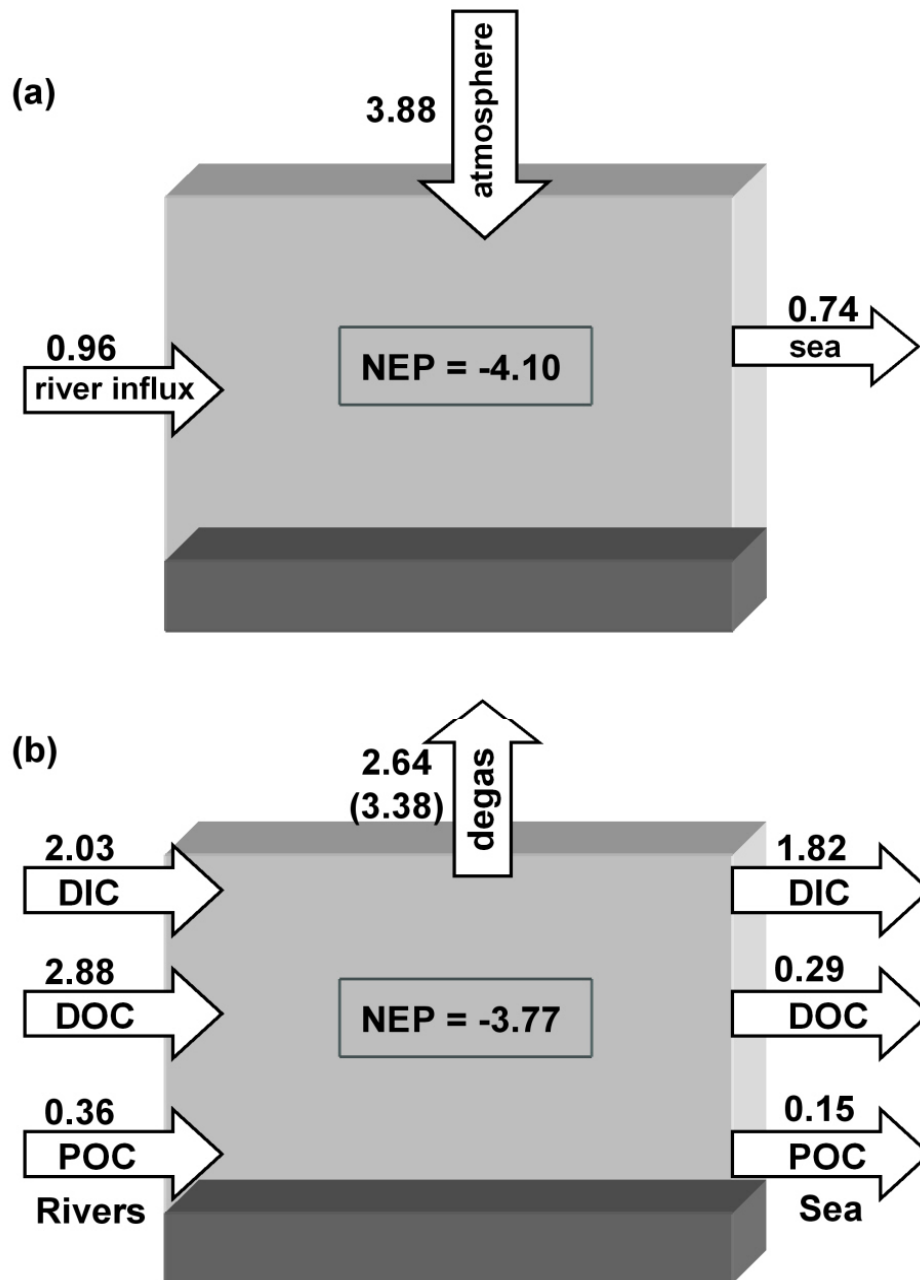


Fig.10