

**Transport of dissolved nutrients and chlorophyll-*a* in a tropical estuary,  
south west coast of India**

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**Abstract**

Intra-tidal variability in the water transport of materials through the Cochin estuary was studied over successive spring and neap tides to estimate the export fluxes of nutrients and chlorophyll *a* into the adjoining coastal zone. The results showed that there was a substantial increase in the fresh water flow into the estuary following heavy rains (~ 126 mm) prior to the spring tide observations. The estuary responded accordingly with a relatively larger export through the Cochin inlet during spring tide over neap tide. Despite an increased fresh water discharge during spring tide, the export fluxes of phosphate and ammonia were high during neap tide due to their input into the estuary through anthropogenic activities. The significance of this study is that the export fluxes from the Cochin estuary could be a major factor sustaining the spectacular monsoon fishery along the southwest coast of India.

**Keywords:** Cochin estuary. South-west coast of India. Coastal upwelling. Intra-tidal variations. Flux measurement. Nutrient fluxes. Spring-neap tides. Chlorophyll *a*

## Introduction

Estuaries are the intermediate zones of land-sea interactions contributing significantly to the nutrient fluxes in to the ocean on varying time scales (Simpson et al. 2001). The nutrient delivery is influenced by catchment hydrology, freshwater flow and tides, which eventually determine the productivity of an estuary (Pennock et al. 1994; Justic et al. 1995; Doval et al. 1997; Mackas & Harrison 1997). Due to complex circulation pattern and non-point sources, nutrient fluxes through estuaries are difficult to measure. Increased anthropogenic activities generally enhance nutrient levels in water bodies, leading to eutrophication and oxygen depletion (Beukema.1991; Parker & O'Reilly.1991). Estuaries are generally classified as matured systems when they sustain surplus nutrients (Dame et al. 1992; Dame and Allen 1996). Hence, transport measurements are important to study the nutrient economy and productivity patterns of coastal marine systems (Dehairs et al. 2000; McManus et al. 2001).

Cochin estuary is the second largest estuary along the west coast of India, spread over 250 km<sup>2</sup> and receiving a fresh water input of  $2 \times 10^{10}$  m<sup>3</sup>/y from six rivers (Srinivas et al. 2003). The estuary experiences mixed semidiurnal tides with clear variations from neap to spring phase. The tides at the inlet are ~1 m, which progressively attenuates towards upstream. The Cochin is the inlet (~450 m wide and 13.5 m deep), while there is another minor inlet at Azhikode, 25 km north of Cochin (Fig.1). The region receives a mean annual precipitation of 3200 mm, of which, >65% occurs during summer monsoon (Srinivas et al. 2004). Rapid industrialization and urbanization in the last few decades resulted in discharge of about  $1.04 \times 10^5$  m<sup>3</sup>d<sup>-1</sup> of effluents and 260 m<sup>3</sup>d<sup>-1</sup> of sewage into the estuary (Qasim 2003; Balachandran et al. 2005). In addition, there are several aquaculture (62 km<sup>2</sup>) and agriculture (80 km<sup>2</sup>) fields increasing the organic pollution in the estuary (Thomson 2002). These inputs through anthropogenic activities can alter the nutrient stoichiometry substantially (Martin et al. 2008). The clayey sediments in the lower estuary are often found to get re-suspended due to tidal activity (Sundaresan 1991). A considerable portion of the estuary has been reclaimed over the last 5 decades for urban growth (Gopalan et al. 1983). Earlier studies have reported that tides and freshwater flow are the main factors influencing the stratification and mixing characteristics of the estuary, which eventually regulate the nutrient availability and phytoplankton production (Joseph et al. 2007; Madhu et al. 2010; Shivaprasad et al. 2013). Although there are several studies delineating the environmental changes of the Cochin

estuary caused by anthropogenic activities (Menon et al. 2000; Martin et al. 2007), only a few studies have been accomplished (Naik et al. 2000) in quantifying the material transport across the estuary.

During southwest monsoon season, heavy rains and freshwater discharge bring in large amount of nutrients in to the estuary, a major portion of which is exported to the coastal sea. Thus, the estuary remains well coupled with the adjacent sea to complement the biogeochemistry of both systems. Fresh water input in to a tidal system can bring about substantial changes in the water quality (salinity, nutrients and plankton) even between successive spring and neap tides. In the present study, we measured the water flux through different locations in the Cochin estuary over successive spring and neap tidal cycles of a post monsoon season (6-7<sup>th</sup> and 13-14<sup>th</sup> October 2009). This is the first attempt to quantify the fluxes of nutrients from the Cochin estuary in to the sea.

## **Materials and methods**

A total of six stations were selected for the time-series measurements. They are; S<sub>1</sub> (minor inlet in the north), S<sub>3</sub> (major inlet at Cochin), S<sub>2</sub> (between S<sub>1</sub> and S<sub>3</sub>), S<sub>4</sub> (22 km south of S<sub>3</sub>), S<sub>5</sub> (43 km south near Thanneermukkom bund) and S<sub>6</sub> (21 km NE of S<sub>3</sub> river entrance) (Fig.1). Four rivers join to the south of S<sub>5</sub>, whereas River Periyar joins at S<sub>6</sub>. The region between S<sub>3</sub> and S<sub>4</sub> is quite dynamic due to the presence of strong rectilinear currents whereas the water movement is weak between S<sub>4</sub> and S<sub>5</sub> (Balachandran et al. 2008). Similarly, S<sub>2</sub> represents the stagnant north estuary caused by the entry of synchronous tides from the two inlets S<sub>1</sub> and S<sub>3</sub> (Ramamirtham and Muthusamy 1986). Hourly profiles of salinity and temperature were measured at S<sub>3</sub> and S<sub>4</sub> using a conductivity-temperature-depth profiler (CTD 19 plus, Seabird Electronics). Six Aanderaa current meters (RCM 9) were deployed at mid-depth of the channel at each location for 30 days to record the current speed and direction at ten minutes intervals. Considering the deep channel at Cochin inlet, two current meters were moored at the centre of the channel at 2 m and near bottom. Water sample were collected from the surface and bottom at 3 h intervals for 24 h on a successive spring and neap tides for analyzing the water quality variables. There was torrential rain (~126 mm) in the study area during the spring tide observation and there was little (~1mm) or no rain during neap observation (Indian Meteorological Department). This was well reflected in the daily mean discharge obtained from the Central Water Commission (CWC), Government of India. For spring phase, the daily mean discharge for 6/10/09 and 7/10/09 was 207m<sup>3</sup>s<sup>-1</sup> and 151m<sup>3</sup>s<sup>-1</sup>.

respectively. For neap phase, the daily mean discharge for 13/10/09 and 14/10/09 was  $80\text{m}^3\text{s}^{-1}$  and was  $94\text{m}^3\text{s}^{-1}$  respectively.

The pH was measured using a pH meter (ELICO LI610, accuracy  $\pm 0.01$ ). The samples for dissolved oxygen were fixed onboard and later analyzed according to Winkler's method (Grasshoff et al. 1983). Water samples were filtered and analyzed for nutrients using UV-VIS Spectrophotometer (Shimadzu 1650PC) following standard procedures (Grasshoff et al. 1983). For chlorophyll *a* estimation, 500 ml of water sample was passed through GF/F filter paper (pore size  $0.7\ \mu\text{m}$ ), the retained pigments were extracted in 90% acetone in dark for 24 h and the extinction was measured using a Spectrophotometer (Strickland and Parsons 1972).

**Flux computation:** The nutrient and chlorophyll *a* fluxes across the four sampling locations viz;  $S_1$  (minor inlet),  $S_3$  (Cochin inlet) and  $S_5$ ,  $S_6$  (river boundaries) were calculated (Table.1&2). The cross section transport,  $Q$  (kg/d) for each variable was obtained by integrating the instantaneous flux as:

$$Q = A' \int_{t_1}^{t_2} \bar{c} \bar{u} dt$$

where  $A'$  is the cross section area ( $\text{m}^2$ ),  $c$  is the concentration of the parameter ( $\text{kg}/\text{m}^3$ ), and  $\bar{u}$  is the current speed (m/s). The over bar denotes the average speed of water column. The net transport was calculated by integrating the 3 hourly transports over two tidal cycles. The positive values denote export fluxes and negative values, import fluxes. The cross-sectional areas of each location were calculated from the respective bathymetry data using Triangulated Irregular Network programme (Priyakant et al. 2003). A constant value was taken for each cross section area neglecting the tidal variations and the current velocity was corrected with respect to the channel orientation. In the present observations, the input fluxes were calculated as the sum of fluxes across  $S_5$  and  $S_6$ , whereas the export fluxes were calculated as the sum of fluxes across  $S_1$  and  $S_3$ .

## Results and Discussions

The variations in the currents and tides at  $S_3$  and  $S_4$  during spring and neap phases are furnished in Fig.2 and 3. The maximum spring and neap tidal amplitudes at  $S_3$  were 0.95 m and 0.57 m, whereas these were 0.48 m and 0.34 m respectively at  $S_4$  (Fig.2). The tidal amplitude and river flow were found to influence the current velocity on both locations. The average currents (depth average) at  $S_3$  were 0.35

m/s (spring) and 0.28 m/s (neap). The currents were weak at S<sub>4</sub> during spring (0.26 m/s) and neap (0.21 m/s) phases respectively (Fig.3). Ebb currents were generally stronger (0.84 m/s) than the flood currents (0.41 m/s) at S<sub>3</sub>. At S<sub>4</sub>, the maximum ebb and flood currents during spring and neap were 0.51 m/s and 0.34 m/s respectively.

The spring and neap variations in the physico-chemical variables at surface and bottom along the channel S<sub>1</sub>-S<sub>5</sub> are furnished in Figs 4-7. While the surface waters of the entire estuary remained warm (31-33.3°C), there was an incursion of cold (24- 26°C) high saline waters from S<sub>3</sub> to S<sub>1</sub> and S<sub>4</sub> during neap flood period. The variation in salinity was in accordance with tides and fresh water discharge, with a maximum during flood tide (34.9). It is evident from Fig.4b that from spring to neap phase, the bottom salinity at S<sub>3</sub> was reduced from 33.4 to 3.4. The water column at S<sub>3</sub> was stratified during spring flood. During neap tide, the stratification was limited only for a short period (flood), while well mixed conditions prevailed for the next 12 h. The freshwater flow ( $15.5 \times 10^6 \text{m}^3 \text{d}^{-1}$ ) during spring tide was relatively high as compared to that ( $7.5 \times 10^6 \text{m}^3 \text{d}^{-1}$ ) during neap tide. Vertical mixing was observed between S<sub>1</sub> and S<sub>4</sub> during neap tide, while stations S<sub>5</sub> and S<sub>6</sub> remained fresh water dominated during both observations. The pH increased with tide and varied in the range 6.21 -7.71 (spring) and 6.4 -7.18 (neap).

During spring flood period, the S<sub>3</sub> subsurface was found to be relatively cool (24- 26°C), high saline (34.9) and oxygen deficient (0.53 - 0.55 mg/l), indicating the presence of upwelling (Fig. 4c). The oxygen levels at other stations remained fairly saturated (3.7 - 7.5 mg/l) during both observations. However, the bottom oxygen deficiency continued during neap tide also, as there was intrusion of this low oxygen waters (1.15 - 1.74 mg/l) up to S<sub>4</sub>, when river flow was diminished. The summer monsoon upwelling is a well-studied process, when oxygen deficient, cold and nutrient rich subsurface waters rises to the surface along the southwest coast of India (Naqvi et al. 2000; Habeebrehman et al. 2008). As the upwelled waters advanced in to the estuary, it was further depleted in oxygen due to the increased demand for the oxidation of organic matter (Naqvi et al., 2000). A similar observation of hypoxic waters (DO < 1.51 mg/l) in the bottom during peak summer monsoon (July) has been reported in the Cochin estuary by Shivaprasad et al. (2013). The present observation has further delineated the extent and intensity of these hypoxic waters towards the inner estuary. Prolonged stratification in an ecosystem can result in the development of subsurface hypoxia and even anoxia (Rabalais and Gibert, 2009), which will severely affect the biological organisms, especially their composition and diversity at community levels

(Zhang et al., 2010). Another factor that can contribute to the oxygen deficiency is the dominant bacterial respiration in Cochin estuary, which contributes 65% of total respiration during summer monsoon (Shoji et al. 2008). Dissolved oxygen concentration  $< 2\text{mg/l}$  will induce stress on many aquatic organisms. However, it can be seen from Fig (4c) that due to the dynamic nature of the estuary, the oxygen saturation was quickly regained.

#### Dissolved inorganic nutrients and chlorophyll *a*

The major fraction of dissolved inorganic nitrogen (DIN =  $\text{NO}_3 + \text{NO}_2 + \text{NH}_4$ ) at all stations was nitrate except at  $S_2$ , where ammonia contributed  $>76\%$  of DIN. Regeneration and excretion are the sources of ammonia into the estuary apart from industrial wastes (Balls 1992; Page et al. 1995; Montani et al. 1998). Inorganic phosphate varied from 0.18 to 3.2  $\mu\text{M}$  during spring and from 0.17 to 3.9  $\mu\text{M}$  during neap phase. There was phosphate enrichment at  $S_2$  (3.9  $\mu\text{M}$ ),  $S_1$  (2.5  $\mu\text{M}$ ) and  $S_3$  (2.0  $\mu\text{M}$ ) during neap tide. The variation in the phosphate concentration, especially at  $S_2$  could be due to increased re-suspension or industrial discharge. The desorption of phosphorus at higher salinity has been reported for the Cochin backwaters (Rajagopala et al. 1974; Martin et al. 2007). There are several aquaculture fields near  $S_2$ , where ammonia and phosphorus compounds are used to destroy the predators (Kantha and Nair, 1987). As a result, the N/P ratio in this region was low ( $<10$ ) compared to its average estuarine value of 25.

The chlorophyll *a* biomass was consistently high at  $S_2$  (18.6  $\text{mg/m}^3$  during spring and 9.4  $\text{mg/m}^3$  during neap), whereas it remained  $< 5 \text{mg/m}^3$  in other regions. During spring tide, chlorophyll *a* was high at  $S_2$  and nitrate was low, indicating a productive belt associated with optimum nutrients. During neap phase, the high biomass of chlorophyll *a* was found spread out from  $S_3$  (22.5  $\text{mg/m}^3$ ) to  $S_4$  (9.7  $\text{mg/m}^3$ ). The upstream regions ( $S_5$  and  $S_6$ ) remained always fresh water dominated with little variations in the nutrient concentration. The dissolved oxygen in these regions also remained fairly saturated.

Fluxes of nutrients and chlorophyll *a* across the 4 locations (2 upstream and 2 inlets) were computed. The flux estimates indicate that export fluxes of nitrate was high during spring tide, whereas that of ammonia, phosphate and chlorophyll *a* were high during neap tide. This is because while the nitrate is mainly a river source, all other constituents have several external sources in the estuary. The results show that during the spring tide, the Cochin estuary received  $516 \times 10^3 \text{ kg/d}$  of DIN,  $4149.9 \times 10^3 \text{ kg/d}$  of  $\text{SiO}_4$ ,  $22 \times 10^3 \text{ kg/d}$  of  $\text{PO}_4$  and  $6.19 \times 10^3 \text{ kg/d}$  of Chl *a* and exported  $592 \times 10^3 \text{ kg/d}$  of DIN,  $3922$

$\times 10^3$  kg/d of  $\text{SiO}_4$ ,  $85.5 \times 10^3$  kg/d of  $\text{PO}_4$  and  $7.83 \times 10^3$  kg/d of  $\text{Chla}$  into the sea. Similarly, the neap tide input and export fluxes of the estuary varied from  $383 \times 10^3$ - $468 \times 10^3$  kg/d DIN,  $3109 \times 10^3$ - $2476 \times 10^3$  kg/d  $\text{SiO}_4$ ,  $11 \times 10^3$ - $97 \times 10^3$  kg/d  $\text{PO}_4$  and  $6.5 \times 10^3$ - $36.8 \times 10^3$  kg/d  $\text{Chla}$ . It is evident that between successive spring and neap tides, there was an increase in the net fluxes of phosphate ( $63.3 \times 10^3$  to  $86.6 \times 10^3$  kg/d), ammonia ( $25.8 \times 10^3$  to  $43.1 \times 10^3$  kg/d), DIN ( $76.4 \times 10^3$  to  $85.8 \times 10^3$  kg/d) and  $\text{Chla}$  ( $1.6 \times 10^3$  to  $30.3 \times 10^3$  kg/d), whereas nitrate flux showed a reduction ( $41.7 \times 10^3$  -  $35.8 \times 10^3$  kg/d). Silicate showed a more interesting feature in the estuary, as it was substantially removed during spring ( $-227 \times 10^3$  kg/d) as well as neap ( $-633 \times 10^3$  kg/d) phases (Table. 1, 2).

During spring phase, the stratification was present throughout the estuary due to high river flow, when nitrate flux remained high. However, the exports of  $\text{PO}_4$ ,  $\text{NH}_4$  and  $\text{Chla}$  were high during neap phase even when freshwater flow diminished, following an increase in their ambient concentrations in the estuary. The water column during neap phase was vertically mixed at the Cochin inlet, which increased the export of phosphate, ammonia and chlorophyll *a*. The increase in the chlorophyll *a* biomass at the Cochin inlet, concomitant to a reduction in the nitrate concentration during the neap flood was probably associated with the invasion of marine phytoplankton into the estuary. The phytoplankton collected at  $S_3$  during neap flood period was mostly marine species, which was subsequently exported ( $30.3 \times 10^3$  kg/d) to the sea by strong ebb currents, indicating an ebb-dominance in the estuary (Mckee et al. 2000). The export fluxes of the Cochin estuary during the present study are high compared to its previous years (Naik et al., 2000), as well as the fluxes from Camboriu estuary, Brazil (Pereira et al., 2001), Richmond estuary, Australia (Mckee et al., 2000) and Beypore estuary, India (Xavier et al., 2005).

## **Conclusion**

The present study shows that the hydrography of the Cochin estuary is very sensitive to the fresh water discharge. The rivers are the primary source of nitrogenous materials into the estuary, whereas there are numerous non-point sources leading to the enrichment of phosphate and ammonia. The import-export fluxes of phosphate and silicate are influenced by the estuarine processes such as tides, salinity and re-suspension. Irrespective of the freshwater discharge, the lower estuary remained consistently productive due to the availability of surplus nutrients. Even during the summer monsoon, a reduction in the fresh water flow (during neap tide) could favor the migration and growth of marine phytoplankton in the estuary. During the observation period, the Cochin estuary appeared to be a matured system, since it

exported substantial amount of nutrients and phytoplankton in to the sea. The significance of this study is that the export fluxes from the Cochin estuary could be a major factor sustaining the spectacular monsoon fishery along the southwest coast of India.

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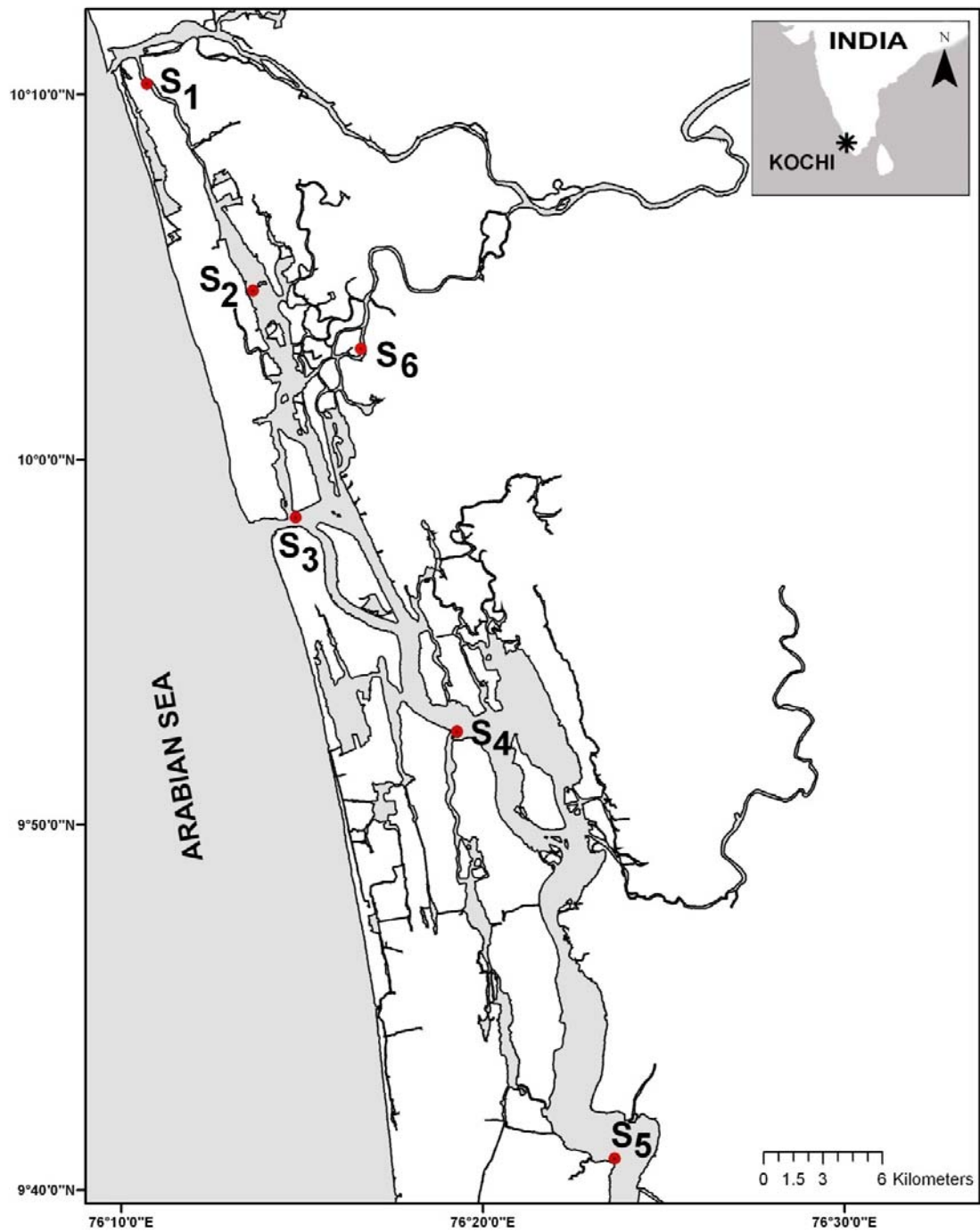
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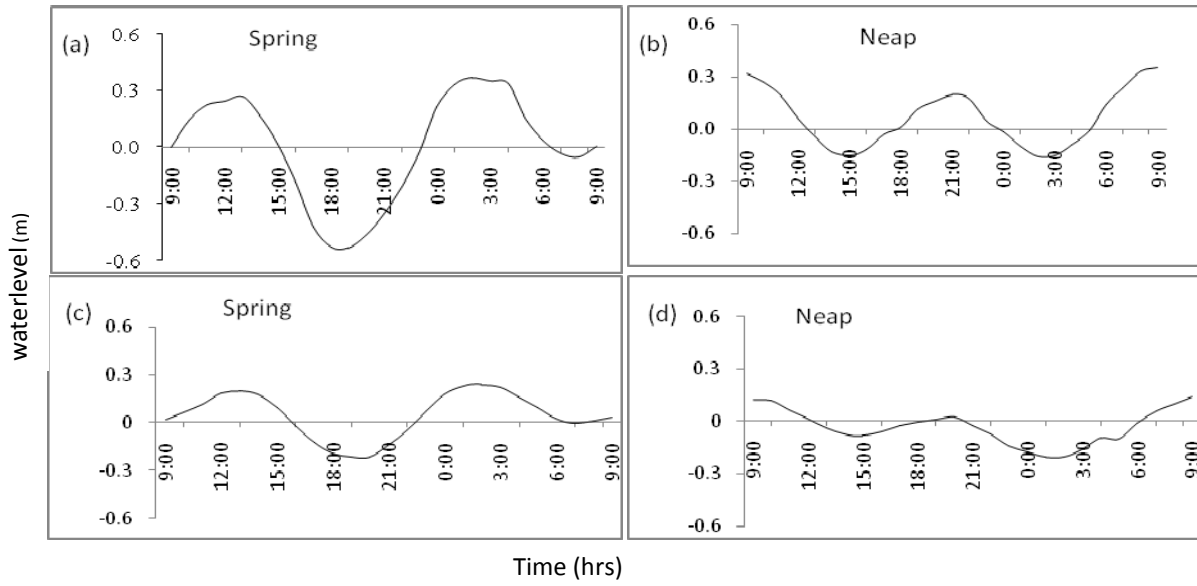
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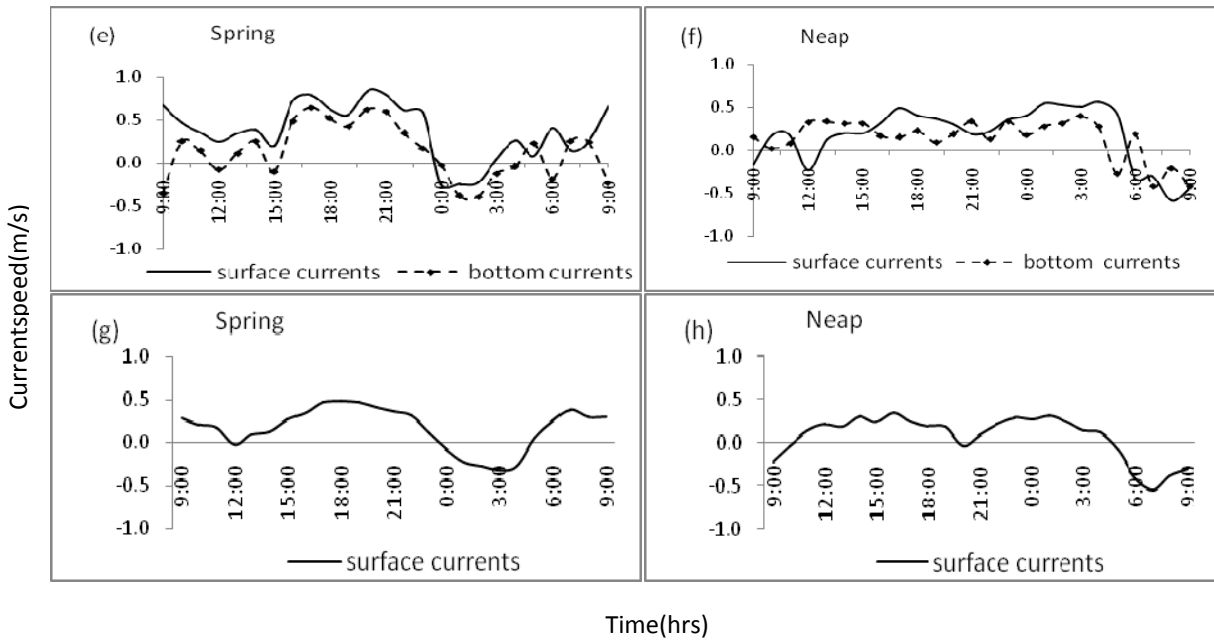
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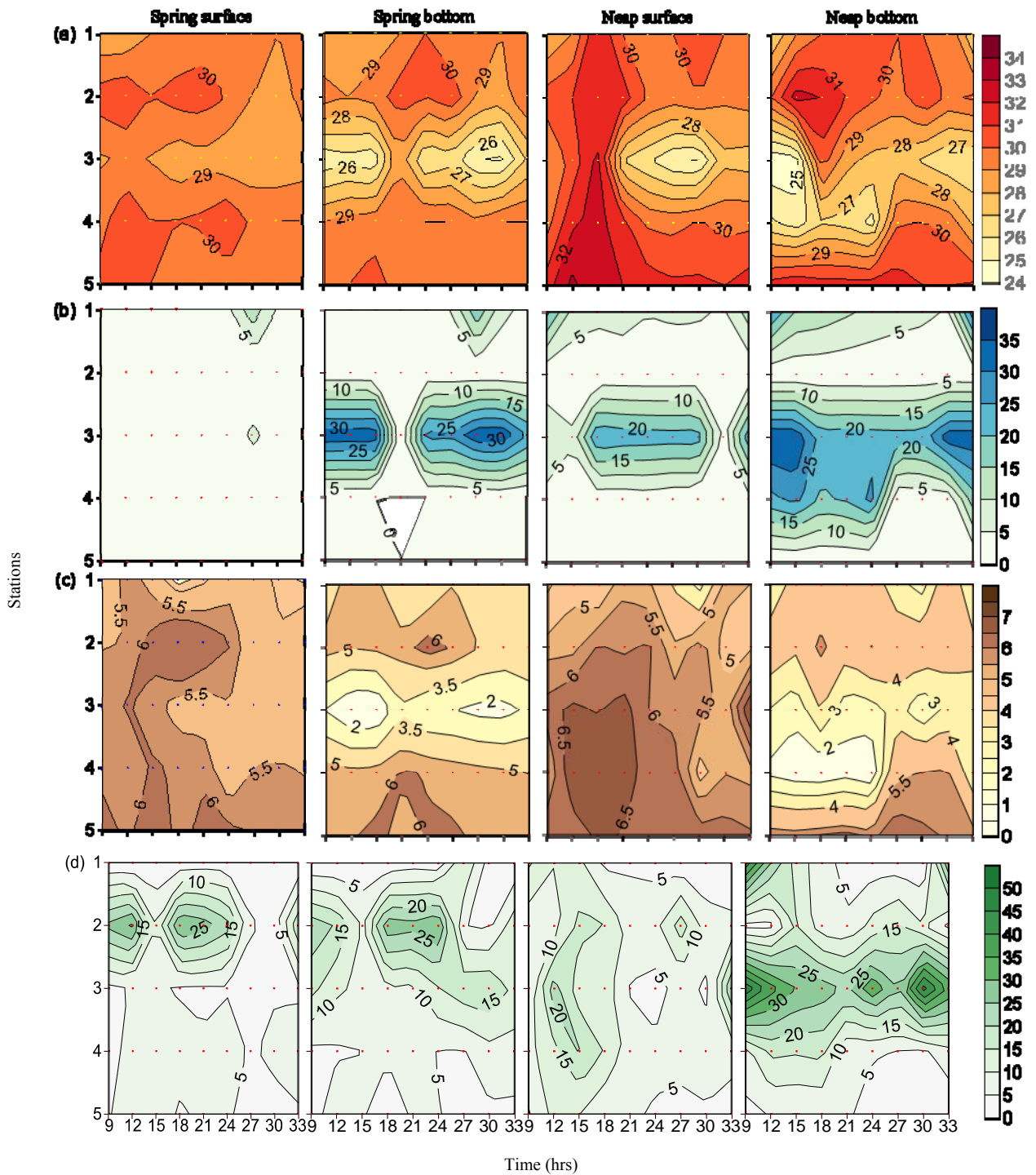
**Fig. 1** Study region in the Cochin backwaters showing the station locations for the time-series observation



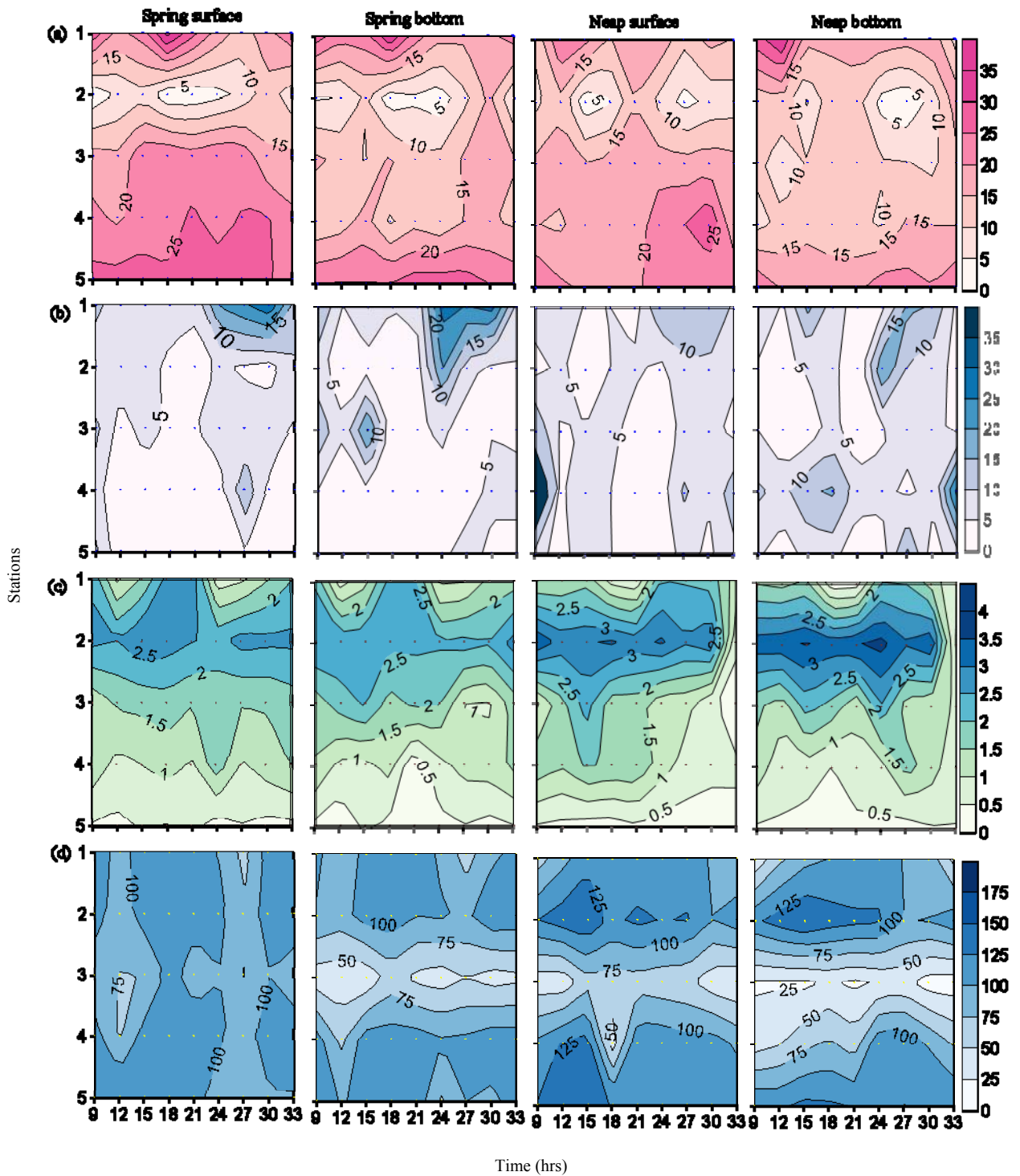
**Fig.2** Variation in the water levels (m) at S<sub>3</sub> (a, b) and S<sub>4</sub> (c,d) during the spring and neap tides



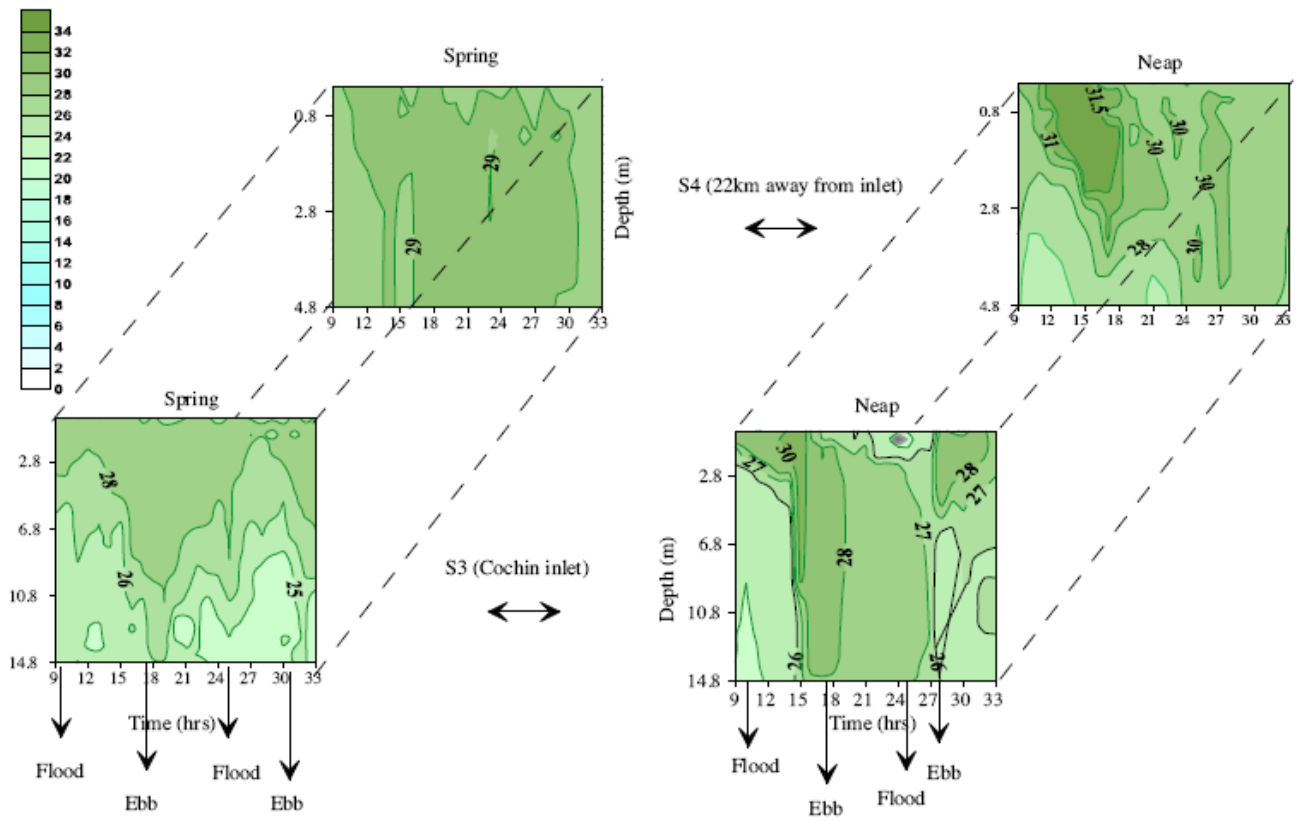
**Fig.3** Variation of currents (m/s) at S<sub>3</sub> (e, f) and S<sub>4</sub> (g, h) during the spring and neap tides



**Fig. 4** Time-series variations in (a) water temperature (°C), (b) salinity, (c) DO (mg/l), and (d) chlorophyll a (mg/m<sup>3</sup>) at surface and bottom waters of Cochin estuary along S<sub>1</sub>-S<sub>5</sub> (1-5) during spring and neap tides.

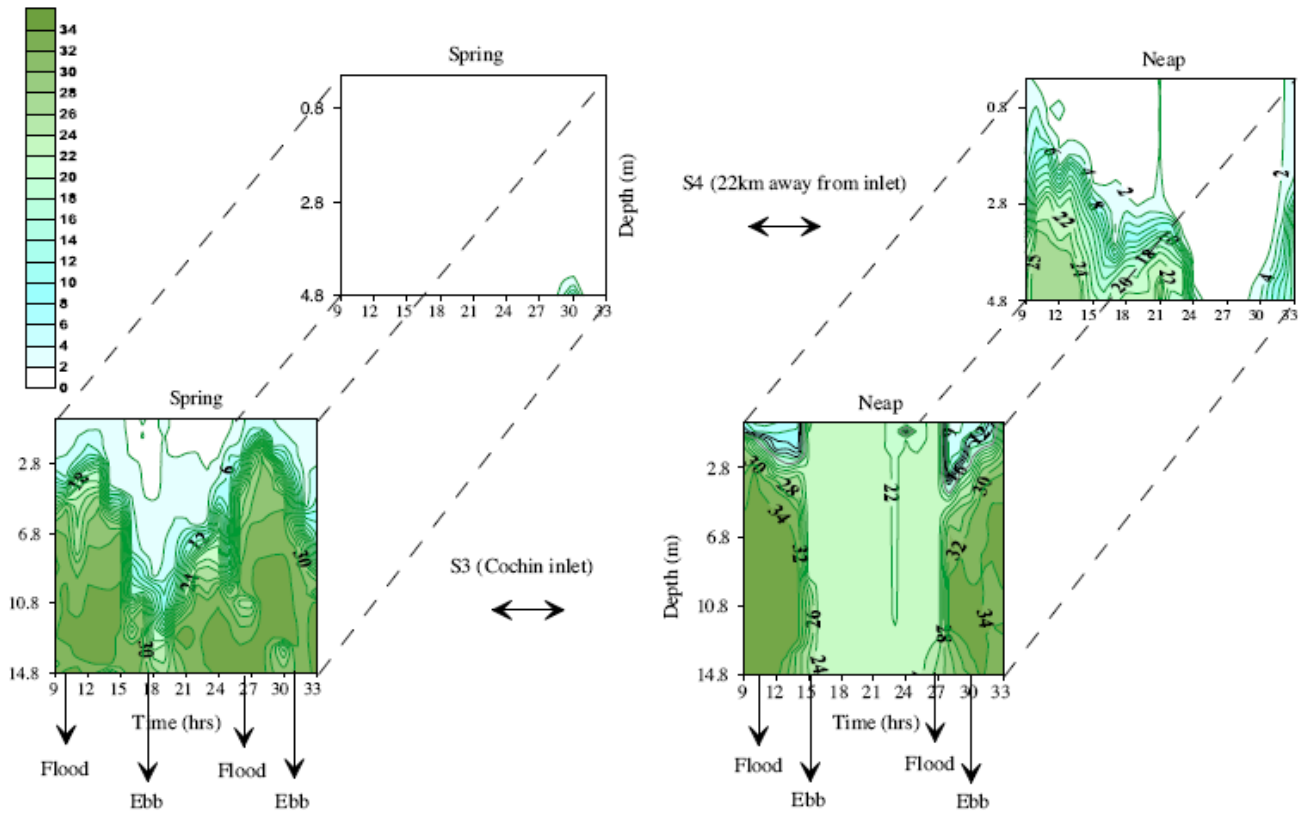


**Fig.5** Time-series variations in (a) nitrate, (b) ammonia, (c) phosphate, and (d) silicate at surface and bottom (all in  $\mu\text{M}$ ) waters of Cochin estuary along  $S_1$ - $S_5$  (1-5) during spring and neap tides.



**Fig. 6** Distribution of water temperature (CTD data) at S<sub>3</sub> and S<sub>4</sub> during the spring and neap tide





**Fig. 7** Distribution of Salinity (CTD data) at S<sub>3</sub> and S<sub>4</sub> during the spring and neap tide

**Table 1** Mass transport (kg/d) in to the estuary ( $S_5$ ,  $S_6$ ) and out of the estuary ( $S_1$ ,  $S_3$ ) during spring phase

Variables	$S_5$ (upstream)	$S_6$ (upstream)	$S_1$ (minor inlet)	$S_3$ (major inlet)	$S_5+S_6$ Input flux	$S_1+S_3$ Export	Net flux
$\text{NO}_3\text{-N}$	$370 \times 10^3$	$74 \times 10^3$	$26 \times 10^3$	$459 \times 10^3$	$444 \times 10^3$	$485 \times 10^3$	$41.7 \times 10^3$
$\text{NO}_2\text{N}$	$6.08 \times 10^3$	$1.64 \times 10^3$	$0.61 \times 10^3$	$16.0 \times 10^3$	$7.7 \times 10^3$	$16.6 \times 10^3$	$8.9 \times 10^3$
$\text{NH}_4\text{-N}$	$49.11 \times 10^3$	$15.5 \times 10^3$	$5.0 \times 10^3$	$85.37 \times 10^3$	$64.6 \times 10^3$	$90.4 \times 10^3$	$25.8 \times 10^3$
DIN	$425.2 \times 10^3$	$91.14 \times 10^3$	$31.7 \times 10^3$	$560.2 \times 10^3$	$516 \times 10^3$	$592 \times 10^3$	$76 \times 10^3$
$\text{SiO}_4$	$3513 \times 10^3$	$636.1 \times 10^3$	$173.0 \times 10^3$	$3749.8 \times 10^3$	$4149 \times 10^3$	$3923 \times 10^3$	$-227 \times 10^3$
Chl <i>a</i>	$6.09 \times 10^3$	$0.11 \times 10^3$	$0.02 \times 10^3$	$7.8 \times 10^3$	$6.19 \times 10^3$	$7.83 \times 10^3$	$1.6 \times 10^3$
$\text{PO}_4$	$15.18 \times 10^3$	$7.0 \times 10^3$	$5.0 \times 10^3$	$81 \times 10^3$	$22.2 \times 10^3$	$85.5 \times 10^3$	$63. \times 10^3$

**Table 2** Mass transport (kg/d) in to the estuary ( $S_5$ ,  $S_6$ ) and out of the estuary ( $S_1$ ,  $S_3$ ) during neap phase

Variables	$S_5$ (upstream)	$S_6$ (upstream)	$S_1$ (minor inlet)	$S_3$ (major inlet)	$S_5+S_6$ Input flux	$S_1+S_3$ Export	Net flux
$\text{NO}_3\text{-N}$	$22 \times 10^3$	$55 \times 10^3$	$8.28 \times 10^3$	$308.12 \times 10^3$	$280.6 \times 10^3$	$316.4 \times 10^3$	$35.8 \times 10^3$
$\text{NO}_2\text{-N}$	$3.1 \times 10^3$	$1.06 \times 10^3$	$0.26 \times 10^3$	$10.8 \times 10^3$	$4.14 \times 10^3$	$11.1 \times 10^3$	$6.9 \times 10^3$
$\text{NH}_4\text{-N}$	$73.1 \times 10^3$	$24.60 \times 10^3$	$6.5 \times 10^3$	$134.3 \times 10^3$	$97.7 \times 10^3$	$140.8 \times 10^3$	$43.1 \times 10^3$
DIN	$302.2 \times 10^3$	$80.7 \times 10^3$	$15.04 \times 10^3$	$453.22 \times 10^3$	$468 \times 10^3$	$382.9 \times 10^3$	$85 \times 10^3$
$\text{SiO}_4$	$2810.8 \times 10^3$	$298.8 \times 10^3$	$78.5 \times 10^3$	$2398.1 \times 10^3$	$3109 \times 10^3$	$2476 \times 10^3$	$-633 \times 10^3$
Chl <i>a</i>	$4.09 \times 10^3$	$2.41 \times 10^3$	$0.17 \times 10^3$	$36.6 \times 10^3$	$6.50 \times 10^3$	$36.8 \times 10^3$	$30.3 \times 10^3$
$\text{PO}_4$	$7.2 \times 10^3$	$3.9 \times 10^3$	$1.04 \times 10^3$	$96.7 \times 10^3$	$11.1 \times 10^3$	$97.7 \times 10^3$	$86.6 \times 10^3$