

Seasonal variations in the water quality of six tropical micro and meso-tidal estuaries, central west coast of India

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Abstract

The seasonal nutrient dynamics were investigated in four rivers having micro-tidal range (Terekhol, Chapora, Sal, Talpona) and compared with two rivers of meso-tidal range (Zuari and Mandovi), along the central west coast of India. The rainfall and freshwater discharge, during the wet season, led to salinity stratification of the water columns at these river mouths. The nutrient concentrations in all the rivers were higher during the wet season as compared to the dry season due to considerable land runoff. Based on the estuarine mixing diagrams of the nutrient with respect to the salinity, the meso-tidal rivers showed greater flushing capacity and acted as corridors for the nutrient passage between the estuary and the open ocean. On the other hand, amongst the micro-tidal rivers, the Terekhol and Chapora seemed to retain the nutrients, while the Talpona R. did not show the presence of nutrient sink or source. The Sal R. was observed to be eutrophic with high nutrients and acted as a source of phosphorus and nitrogen. Thus, the present study clearly illustrates the important role played by minor river estuaries in modifying the nutrient concentrations during their transport from the rivers to the coastal waters and vice versa.

Keyword: nutrients, rivers, conservative behavior, stratification, sand bars

Introduction

Estuaries, present at the interface of freshwater and marine environments, have fragile ecosystems. The increasing pressures from the catchment and coastal processes are a cause of concern for the future health of the estuary. The Nutrient concentrations (Nitrate, Nitrite, Ammonium, Phosphate and Silicate) are dependent on the estuarine flushing characteristics which are a function of the river flow, individual catchment, tidal range and seasons (Balls 1994). Increased nutrient loads can lead to eutrophication and influence the biotic activity in the estuaries and the coastal seas, cause changes in food web structure, produce harmful or nuisance algal blooms which can deplete the dissolved oxygen (hypoxia) critical for the aquatic life (Sawidis and Tsekos 2004; Wolanski 2007). Hence, nutrients may be considered as one of the key indicators of the water quality. The nutrient dynamics in estuaries strongly depend on the suspended particle-water interactions, which can lead to the addition/removal of dissolved constituents and result in non-conservative mixing (Balls 1994). This approach is often represented in the form of Theoretical dilution Line (TDL) diagrams. Amongst the many studies carried out to evaluate the conservative and non-conservative behaviour of nutrients in the estuarine environments (Morris *et al.* 1981; Eyre 1994; Billen and Garnier 2007), salinity has often been used as an indicator of conservative mixing. The constituent that exhibits a linear relationship with it is assumed to be conserved. Rapidly flushed estuaries of low turbidity exhibit least effects of the suspended particle-water interactions (conservative behavior) while it is greatest in turbid sluggishly flushed estuaries (non-conservative behavior).

The estuaries, being at the center of human habitation, are sensitive to the nutrient pollution (Valiela *et al.* 1997; Nixon *et al.* 2001). Therefore, it is important to know the estuarine processes taking place in such regions and the conditions that sustain them. In the present study, four micro and two meso-tidal estuaries are considered along the central west coast of India. The micro-tidal rivers remain closed by sand bars near the estuary mouths during the wet season and are open to the ocean during the dry season. On the other hand, the meso-tidal estuaries have insignificant effect of the sand bars but exhibit stratification due to high freshwater runoff during the wet season. While there is a large literature available on the nutrient and eutrophication status of estuaries (Sanders *et al.* 1997; Kim *et al.* 2006; Chew and Chong 2011), less of it covers estuaries with seasonally varying morphologies that influence the estuarine flushing characteristics (Rao *et al.* 2011; Priya *et al.* 2015). Thus, in this study, we explore the stratification and the degree to which the extent of connectivity of an estuary with the ocean influences the nutrient dynamics of the region.

Study area

Goa is a small state located on the central west coast of India. Out of the nine tidal rivers flowing within the state, the six rivers considered in this study include the rivers with basin area – the Terekhol- 71 km², Chapora- 255 km², Sal- 301 km², Talpona- 233 km², Mandovi- 1580 km² and Zuari- 973 km² (Fig. 1). The rivers Terekhol and Chapora originate in Maharashtra, the Mandovi and Zuari in Karnataka, the River Sal in the south Goa while the Talpona R. originates on the Sahayadri hills and drains into the Arabian Sea. The tides in the Mandovi and Zuari rivers are of semi-diurnal nature with a tidal range of about 2.3 and 1.5 m during the spring and neap tides, respectively. In the other rivers the tidal range is < 2m. The summer (dry) and monsoon (wet) are the two distinct seasons that determine the extent of saline and freshwater distribution in the region. A maximal runoff of about $2,190 \times 10^6$ m³ has been reported in the Mandovi R. during the southwest monsoon (Shetye *et al.* 2007; Suprit and Shankar 2008). The reported freshwater runoff in the Mandovi R. (surface area- 35 km², volume- 160×10^6 m³) is $\sim 3,580 \times 10^6$ m³ (mcm) while the Zuari R. (volume- 270×10^6 m³) exhibits $\sim 2,247 \times 10^6$ m³ (Vijith *et al.* 2009). The large freshwater discharge during the wet season results in a salinity gradient in the meso-tidal rivers while during the dry season with the reduced freshwater input, the salinity becomes more or less uniform throughout the estuary (Shetye *et al.* 1995). According to Shetye *et al.* (2007), the average runoff during the dry season (November–May) is only 3.4% of the annual average. The flushing time in the Mandovi estuary varies from 0.9 days (run-off induced) in the wet season to upto 3 days (tide driven) during the dry season (Vijith *et al.* 2009). On the other hand, the flushing time in the Zuari R. is estimated to be almost three times more than that of the Mandovi R. (Manoj 2008). The Suspended Particulate Matter (SPM) concentrations of the rivers are reported to be higher during the wet season (4.03-31.58 mg/l in meso-tidal, 0.05-23.27 mg/l in micro-tidal) as compared to the dry season (1.25-16.29 mg/l in meso-tidal and 1.42-13.81 mg/l in micro-tidal) with greater concentrations near the estuary mouths as compared to the rest of the river (Fernandes *et al.* 2017). The six rivers have convergent nature, i.e., their width and depth decrease rapidly from the mouth (few kms, 10 m) to head (~ a tenth of a km, ~1m) (Vijith *et al.* 2009). The Mandovi and Zuari rivers have wider (~5 km) and deeper mouths (~10 m) connecting to the ocean and are open to the sea throughout the year. In contrast, the other river estuaries have narrow (~1km) and shallow (~4 m) openings to the ocean which due to the high rainfall and the longshore currents during the wet season, develop sand bars across the estuary mouths further narrowing the mouths (~0.10-0.40 km). In the Sal and Talpona rivers, the sand bars can sometimes become sufficiently large to completely isolate the estuary from the ocean for a considerable period. The area and volume occupied by the sand bars are reported to vary over the

years due to changing wave strength and the rainfall pattern (Rajashekhar *et al.* 2014). During the dry season, the wave action is stronger while the river discharge is low resulting in either depletion of the sand bars or diversion from the river mouths either to the north or south. In the River Sal, the narrow mouth of the river hinders the transport of domestic wastes into the sea. As a consequence, the heavy metals and wastes from the industries settle along the banks of the river, producing an unsuitable environment for the various aquatic organisms. Furthermore, large inputs of nutrients from agricultural lands have made the Sal estuary highly eutrophic. In this paper, the spatial and seasonal distributions of nutrients and dissolved oxygen, in the six tidal estuaries are discussed.

Materials and methods

The sampling was carried out during the spring tide of the wet and the dry seasons in the six rivers. The water samples were collected at every 2 km distance from the estuary mouth to the upstream of the rivers using a hired fishing trawler. Around 12-14 stations were sampled in each of the rivers (Fig. 1). Wherever the depth was too shallow for the trawler entry, the samples were collected from the bridge nearest to the station (few meters from the fixed station locations). During the wet season, due to rough sea conditions, the mouth and the offshore stations could not be sampled. The surface waters were collected using a plastic bucket while the bottom waters were sampled using acid washed Niskin sampler. The Conductivity-Temperature-Depth (CTD) profiler (Sea-Bird Electronics 19plus) with chlorophyll sensor was used to obtain the vertical profiles of salinity and chlorophyll-fluorescence at the different locations. Soon after the water collection, the dissolved oxygen (D.O.) was fixed onboard using Winkler's reagents and the samples were analyzed for D.O. using the Winkler technique (Grasshoff *et al.* 1983). The Nutrients (nitrate, nitrite, ammonium, phosphate and silicate) were estimated using the Skalar autoanalyzer (Skalar Analytical, The Netherlands) setup following the standard photometric methods (Grasshoff *et al.* 1983). The rainfall and freshwater discharge data were obtained from the Water Resource Department, Goa (Table 1) with gauging stations located upstream (head) of each of the rivers.

Results

In the Sal and Talpona rivers, the CTD could not be deployed because of shallow depths so the data on vertical salinity and chlorophyll-fluorescence profiles are not available. The nutrient data for the Mandovi R. has been inferred from Maya *et al.* (2011) while the data for the Zuari R. has been obtained from Subha Anand *et al.* (2014).

Salinity and Dissolved oxygen

The range and average concentrations of the different parameters studied are summarized in Tables 1-3. The highest freshwater discharge was seen in the Mandovi River followed by the Talpona, Chapora, Zuari and Sal rivers during the wet season with similar values of rainfall in all the rivers. During the dry season with no rainfall, low to negligible river discharge was observed in all the rivers (Table 1, Fig. 2). Overall, the dry and wet seasons are not found to be affected by short-term fluctuations in the rainfall and river discharge that would affect the interpretations of the results. During both the seasons, the surface and bottom water salinity in all the rivers showed gradual decreasing trends from the sea to the river end (Fig. 2). The surface horizontal salinity gradient was large in the Terekhol R. during both the seasons and varied from 0.04 to 23.75 in the wet season and from 13.11-31.46 during the dry season. In the Chapora R., the surface salinity was almost similar during both the season, i.e., from 0.04 to 26.35 in the wet season and 0.08-28.13 in the dry season, respectively. On the other hand, in the Mandovi (0.03- 6.35), Zuari (0.03-8.04), Sal (0.03-0.49) and Talpona (0.03-2.86) rivers, the surface salinity gradient was narrow during the wet season but broader during the dry season and ranged from 7.80-34.09 in the Mandovi R., 0.16-34.67 in the Zuari R., 5.91-30.55 in the Sal R. and 0.09-33.53 in the Talpona R., respectively. In general, based on the seasonal observation, higher salinity variations were seen during the dry season as compared to the wet season (Table 2). The bottom water salinity profiles (Fig. 2) during the wet season had saline waters (>25) near the mouth in most of the rivers and low salinity (<1) towards the upstream ends, exhibiting freshwater conditions. Overall, significant salinity stratification was noticed during the wet season, with the incursion of high saline waters along the bottom and the freshwater on the surface in the Terekhol (9 km) and Zuari (15 km) rivers (Fig. 2). The salinities in all the rivers during the dry season remained at or close to that of seawater (35). Unlike the wet season, the dry season displayed homogenous mixing with similar salinity range (>30) between the surface and the bottom waters. The mean seasonal DO concentrations in the rivers underwent consistent seasonal changes, with the highest surface values occurring in the mesotidal river (7.72 mg/l- Mandovi R.) in the wet season and the microtidal river (6.16 mg/l- Chapora R.) during the dry period. The corresponding lowest DO values were seen in the Talpona R. (3.03 mg/l) and Mandovi R. (5.09 mg/l) during the wet and dry periods, respectively (Fig. 3). Interestingly, during the wet season, the DO concentration in the bottom waters decreased sharply at a salinity of ~29 (0.30-1.80 mg/l DO) in the Terekhol R. while the DO in the surface waters remained relatively constant (>2.4 mg/l) along the salinity gradient (Fig. 3a). During the wet season, in all the rivers except for the Sal R. ($r_{\text{Sal}} = 0.43$, $p < 0.005$), the DO correlated negatively with the salinity ($r^2 = -0.65_{\text{Terekhol}}$, -0.27_{Chapora} , -0.23_{Talpona} , -0.69_{Mandovi} , -

0.10_{Zuari} at $p < 0.005$). The surface and bottom waters showed similar DO values throughout the water column during the dry season in all the rivers (Fig. 3g-l).

Nutrients and chlorophyll-fluorescence

Figure 4 (see figures S1-S4 as supplementary material) depicts the dissolved Nitrite (NO_2), Nitrate (NO_3), Ammonium (NH_4), Phosphate (PO_4) and Silicate ($\text{Si}(\text{OH})_4$) distribution along the estuarine–coastal region. During the wet season, the mesotidal rivers showed the highest NO_2 and $\text{Si}(\text{OH})_4$ concentrations while the other nutrients were high in the microtidal rivers (NO_3 and NH_4 in the Sal R., PO_4 in Terekhol and Chapora rivers). The Talpona R. had the lowest nutrient concentration. Most of the nutrients showed high concentration near the head of the estuary with concentration decreasing towards the mouth. In the dry season, the Zuari R. had the highest concentration of NO_2 , NO_3 and $\text{Si}(\text{OH})_4$ while Sal R. had high NH_4 and PO_4 concentrations. Similar to the wet season, low values were seen near the mouth region as compared to the middle region or upstream of the estuary. In almost all the rivers the concentrations of most of the nutrients, except NH_4 and NO_2 , were higher in the wet season as compared to the dry season (Table 3). Each of the rivers exhibited similar NH_4 concentration during both the seasons. The highest variation in nutrient concentrations during the two seasons was seen in the Sal R. upto a factor of 60 for NO_3 and 7 for NO_2 , while Terekhol R. accounted for 9 and 7.5 times for PO_4 and $\text{Si}(\text{OH})_4$, respectively. However, the Zuari R. had similar nutrient concentration during both the seasons. Interestingly, the Dissolved Inorganic Nitrogen [$\text{DIN} = \text{NO}_3 + \text{NO}_2 + \text{NH}_4$] concentrations in the bottom waters of the Terekhol and Chapora rivers, especially near the estuary mouths, were higher than those of the surface waters during the wet season. In the Sal and Talpona rivers with shallow depths, the water column was well mixed in both the seasons and displayed no distinct variations in the nutrient profiles from the sea to the river end. The DIN/P ratios were higher in the dry season for Terekhol, Chapora and Mandovi rivers as compared with the wet season while in Talpona and Zuari rivers the values were similar in both the seasons (Table 4). The Sal R. had higher values in the wet season as compared to the dry season, with the DIN/P ratios almost an order of magnitude above the Redfield ratio at the upstream stations (Table 4a). On the other hand in the Terekhol (wet season), Mandovi (dry season), Chapora and Zuari (both seasons) rivers and near the mouth and the upstream of the Talpona R. (both seasons), the DIN/P ratios were below the Redfield ratio (Table 4a, b). In almost all the rivers, the estuarine mixing diagrams for nitrogen and phosphorus showed non-conservative behaviour for both the seasons with most of the points falling above or below the TDL (Fig. 5). The $\text{Si}(\text{OH})_4$, on the other hand, behaved conservatively throughout the estuary in all the rivers during both the seasons except for the Chapora R. which showed non-conservative behavior during the dry season (Fig. 5). In most

of the rivers during the wet season, the chlorophyll-fluorescence contours showed greater values near the estuary mouths as compared to the other parts of the rivers (Fig. 6). During the dry season, comparatively higher values were seen near the mouth of the Zuari R. and the upstream of the Terekhol R. than the other rivers.

In general, the salinity, chlorophyll-fluorescence and DO were found to be low during the wet season and high during the dry season with vice versa condition seen for the nutrients.

Discussion

Factors responsible for the river stratification

The extent of tidal incursion and the consequent seawater intrusion into the estuary depends on the magnitude/speed of river discharge (i.e., rainfall), geomorphology (permanent features or presence/absence of temporary coastal developments e.g., sand bars/pits). In high-precipitation regions, the addition of freshwater to the surface waters lowers the salinity, which enhances stratification, thereby causing hindrance in the vertical mixing of the water column. In the present study, the high rainfall and river discharge during the wet season (Table 1) caused a vertical stratification due to salinity gradient in almost all the rivers. During this period in the microtidal rivers, the longshore currents transport the sediments towards the narrow estuary mouths resulting in sand bar formations (Rajasekaran *et al.* 2014). Similar phenomena's are reported in wave dominated micro-tidal coastal environments due to high rainfall (Young and Potter 2002; Coates and Guo 2003; Baldock *et al.* 2004), low streamflow and/or high onshore or longshore sediment transport (Ranasinghe and Pattiaratchi 1998; 1999). The formation of sand bars decreases the width of the river mouth by almost 100 m in the Terekhol R., 150 m in the Chapora R. and 250 m in Talpona and Sal Rivers (google earth). The presence of these sand bars makes the estuary mouths shallow, affecting significantly the entry of seawater into the river. Further, the high bottom friction resulting from the shallow depth can decrease the tidal energy thus preventing considerable mixing between the lower layer saline waters and the upper layer freshwater. Therefore, in the micro-tidal rivers, the high riverine discharge and the sand bar formations during the wet season restricted the entry of seawater into the estuaries. The low average salinities (~10) seen during the wet season in Sal and Talpona as compared to the relatively higher salinity (>20) in the Terekhol and Chapora rivers, may be because the estuary mouths were completely closed by sand bars in the former rivers as compared to the latter rivers. Also, the depth at the estuary mouths in the Sal and Talpona rivers was less (<2 m) as compared to the other two rivers (~5 m). The meso-tidal rivers, i.e., the Mandovi and Zuari, have been extensively studied with respect to stratification due to salinity (Qasim and Sen Gupta

1981; Shetye *et al.* 1995; Sundar *et al.* 2015; Vijith *et al.* 2016) wherein tide-induced formations of salt wedge takes place (Sundar and Shetye 2005). The lower salinity seen in the Mandovi R. as compared to the Zuari R. is because the Mandovi receives a greater amount of freshwater discharge from larger tributary systems (Table 1). In both the rivers, shoal/sandbar formation occurs near the mouth, with the waterway in the Mandovi completely closed for the boat traffic. On the other hand in the Zuari R., the navigation system is not affected. After the withdrawal of the monsoon, the estuaries are reported to be partially mixed system governed by the tidal circulation (Shetye *et al.* 1995). Thus, in rivers with meso-tidal range, the water column stratification is significantly due to the high freshwater discharge while in the rivers with micro-tidal range, the freshwater discharge together with the sand bar formations at the estuary mouths resulted in the water column stratification.

Seasonal distribution of nutrients

Wet season

The nutrient status of estuaries is often dominated by their riverine input, the trapping and recycling of nutrients within the basin and the exchange with the ocean (Nixon 1995). Therefore, in the present study, the estuarine mixing diagrams using the nutrient and salinity parameters (Fig. 5) are employed to determine the nutrient status in the different estuaries. Due to the high freshwater flow and occurrence of sand bars at the estuary mouths in most of the rivers, the salinity across the estuary represents freshwater conditions in the Sal and Talpona (<3) rivers and to some extent in the Mandovi R. (<10). As a result, the seawater end member is not present or distinct in these rivers. The nitrogen and phosphorus data points lying above the TDL in the wet season suggest the addition of nutrients. The river water can contribute dissolved chemicals that are conservative as well as those that can be modified locally by biological or chemical processes and therefore act as non-conservative. The negative correlations between the nutrients and salinity (Fig. 5) suggest the riverine inputs as the main source of nutrients in the region (Sierra *et al.* 2002; Haralambidou *et al.* 2010). The high NO₃ content seen in all the rivers during the wet season may be from the organic matter (OM) in the catchment area (Das and Sahoo 1997). The estuaries of Goa are surrounded by mangrove-rich wetland systems, lying within the inter-tidal zones, and hence significant quantities of organic material enter the estuarine waters (Karuppasamy and Perumal 2000; Santhanam and Perumal 2003). The PO₄ being a large component of fertilizer run-off could explain its high addition throughout the estuary. The addition could also come from the sewage effluent of the nearby sewage plants. The silicate showed conservative behavior. The silicates are reported to behave both conservatively and non-conservatively depending on the biology and geology of the area, with the

seasonal variations of the $\text{Si}(\text{OH})_4$ concentrations resulting more from the seasonal variations in biological removal than the seasonal changes of fluvial loads (Fichez *et al.* 1992; Balls *et al.* 1995). However, in the present study, the source of $\text{Si}(\text{OH})_4$ input in all the rivers seem mainly from natural weathering of the source rocks and erosion, as the concentration decrease considerably during the dry season (Hessen 1999) which can be attributed to its low supply as well as from phytoplankton uptake.

The mixing and circulation of an estuary is significantly influenced by the exchange and interaction between the fluvial and oceanic processes. Thus, when the sand bar isolates the estuary from the ocean, the flushing mechanism can deteriorate affecting the water quality of the estuary (Ranasinghe and Pattiaratchi 1998). Such situation can be seen clearly in the River Sal. Here, the surface waters are found to exhibit high DIN (mostly NO_3) values probably washed down from the agricultural, rural or urban catchment areas, which can trigger eutrophication. The NO_3 values are on the order of $100 \mu\text{M}$, similar to the values encountered in the Mississippi River flowing into the famous “Dead Zone” of the Gulf of Mexico (Dagg *et al.* 2004). The river is a tourist hotspot, so the observed high PO_4 values may be due to the discharge of wastes directly into the river from the large number of hotels housed along its bank. The ammonium generally represents only a small fraction ($>10\%$) of the total inorganic nitrogen concentration in estuaries. However, in the case of the Sal R., a notable exception is seen where the ratio exceeds 50%. A similar observation was seen in the Han River in Korea, which was reported due to the application of inorganic N fertilizer (ammonium bicarbonate) in the drainage basins and wastewater discharge (Sheldrick *et al.* 2003; Cao *et al.* 2005). The low DIN/P values in all the rivers except for Sal R. may be due to the equally high NO_3 and PO_4 concentrations producing the low ratios. Therefore, the concentrations of nutrients have been seriously disturbed by the anthropogenic activities in the Sal R. In the Mandovi and Zuari rivers, the exchange of nutrients between the estuary and the open ocean is seen even during the wet season. However, the decrease in salinity due to the freshwater runoff has been reported to cause a shift in the net ecosystem productivity, producing a change in the dominance of the phytoplankton species (Ram *et al.* 2003). The N: P ratio that is required to sustain phytoplankton growth (the Redfield ratio) is 15:1 (N: P by atoms). However, as estuaries are closely connected with their catchments, the estuaries in agricultural regions predominantly have the N/P ratio correlating with the ratio of N and P fluxes from the agricultural land use (Arbuckle and Downing 2001). A ratio of below 5, seen in the Terekhol and Chapora rivers, essentially indicates a potential N-limiting condition for the phytoplankton growth (Obenosterer and Herndl 1995; Yin *et al.* 2001). The biological assimilation by the phytoplankton/benthic communities has been cited as a possible mechanism for the NO_3

removal from the water column (Johannes *et al.* 1994) in addition to the denitrifying bacteria. The closure of the river mouths in micro tidal rivers might have precluded the nutrient supply from the marine region. Interestingly, the higher NH_4 and NO_3 concentration near the estuarine mouths in the Terekhol and Chapora rivers may be due to the nitrification process (Peterson *et al.* 2001; Merriam *et al.* 2002).

Based on studies of nutrients (Falco *et al.* 2010; Haralambidou *et al.* 2010) and organic matter (Fuks *et al.* 1991; Legovic *et al.* 1994) in estuaries, the interface between the upper freshwater and the lower saline water is found to be significant in structuring the primary productivity (Muylaert and Sabbe 1999). During periods of persistent stratification, phytoplankton biomass is reported to increase rapidly as high levels of photodegradation or bleaching of fluorescent material, highest in river discharge, are kept at the surface where solar irradiance is highest (Del Vecchio and Blough 2002). In the Zuari, Terekhol and Chapora rivers, the high nutrient concentration observed at the bottom in the salt wedge zone (Fig. 4, S1-S4) may be because of OM mineralization produced from sinking phytoplanktons which undergo a saline shock upon encountering salinity of 4-7 (Kinne 1971; Vilicic *et al.* 1989; Sempere and Cauwet 1995). Further, the sinking OM may result in nutrient maxima if particulate matter is concentrated around a turbidity maximum. The Estuarine Turbidity Maximas (ETM), i.e., regions of high SPM concentration, present at the estuary mouths in all the three rivers (Fernandes *et al.* 2017) might be contributing to the observed high bottom nutrient content. There is also a possibility that the nutrients may be getting regenerated (released from the sediments) in the bottom waters as the water column becomes stratified (Wilson and Eliot 2000). This observation is well supported by the DO profiles. The OM remineralization process along with the isolation of the water from the atmosphere can result in oxygen consumption (aerobic decomposition) affecting the DO concentration in the salt-wedge. The hypoxia (DO values < 2 mg/l) observed in the salt wedge at the bottom stations (T3 to T9) of the Terekhol River (Fig. 3a) can restrict the nitrification process (Baird and Pereyra-lago 1992). The higher DIN seen in the bottom waters attest to this process indicating that the dynamics of DIN in the salt-wedge region is expected to change with the reductions in the DO (Table 2). Although hypoxic events at the river bottom promote sediment nutrient release, the stratification tends to restrict nutrient movement into the surface waters while the sand bars restrict the nutrients out of the estuary.

The decreases in the chlorophyll-fluorescence from the sea to the river end of the meso-tidal estuaries indicate the existence of a physical mechanism of flushing of the estuarine system. The catchment of the permanently-open Mandovi and Zuari rivers are large, and huge amounts of nutrients enter the basin of these estuaries via their tributaries (Qasim and Sen Gupta 1981). Surface

discharge comprising up to 90 % of the total freshwater discharge occurs during periods of heavy rainfall (Suprit and Shankar 2008; De Sousa *et al.* 1981). This large runoff (total seasonal runoff ~40 times the volume of the estuary; Vijith *et al.* 2009) causes flushing of substantial amounts of nutrients to the sea (flushing rate- 0.9 days). Subha Anand *et al.* (2014) noted that the NO₃ have remained at similar levels for the last four decades in the Zuari estuary suggesting its dilution or removal in the estuary. The high riverine discharge thus leads to reduced water residence time, with increased flushing of phytoplankton biomass out of the estuary (Devassy and Goes 1988; Lane *et al.* 2007), which can be seen from the inverse correlation between the chlorophyll-fluorescence concentration and the distance from the river head (Fig. 6). Also, during the wet season, the inflowing water is more turbid, restricting the light availability to the aquatic plants, including the phytoplankton. Overall, there is a good input of nutrients but lesser uptake. The higher chlorophyll-fluorescence concentration seen in the Mandovi R. is due to more dilution of seawater by the freshwater favouring the phytoplankton bloom in less saline waters (Qasim *et al.* 1972).

Dry season

During this season, with the negligible river discharge and the waning of the sand bars due to strong winds and waves (Aparna *et al.* 2005; Vethamony *et al.* 2009), the estuary mouths of the microtidal rivers were much wider than during the wet season. As a result, the estuarine waters were released into the ocean, and the oceanic water intruded into the estuaries, increasing the salinity (>30). Also, a concomitant decrease in the nutrient delivery was observed, which may be due to low river discharge, nutrient uptake by the phytoplankton (Wollast and De Broeu 1971; van Bennekom *et al.* 1974) or absorption to the suspended matter (Padmavathi and Satyanarayana 1999). The high NH₄ concentrations seen in the Sal and Talpona rivers may be linked to the presence of thick mangrove covers along the banks of both the rivers. The organic-rich mangrove sediments are reported to be an important source of NH₄ for estuaries (Sardessai and Sundar 2007; Pratihary *et al.* 2009). At the wider estuarine mouths sans the sand bars, the water column oxygenation improved, with the DO concentrations higher than that under the salt-wedge regime and the disappearance of the bottom hypoxic zone. Homogenous concentrations of nutrients in both the surface and the bottom waters was also seen in all the rivers except the Terekhol and Zuari rivers which showed signatures of high nutrient concentration at the bottom as compared to the surface waters. Here, the notable increase in the DIN values in the bottom water may be due to the NH₄ release from the sediments. In well-oxygenated seawater, the NO₃ is the thermodynamically most stable form of inorganic nitrogen. The increased nitrogen-fixing activity of organisms might have caused the concentration of the NO₃ to increase steadily. However, its contribution to photosynthesis can be limited in the presence of high

nitrogenous source such as NH_4 . Also, the longer residence time of the water can favour in the removal of the NO_3 by denitrification (Seitzinger *et al.* 2006) by photoautotrophic/heterotrophic organisms through biological consumption (Peterson *et al.* 2001). The higher NO_2 in the dry season as compared to the wet season is because the well mixed oxygenated estuarine water column are reported to favour the NO_2 production through assimilatory reduction of the NO_3 by the phytoplankton (Naqvi *et al.* 2006a, b). A study carried out by Maya *et al.* (2011) in the Mandovi estuary reported that the in situ NO_2 production during the dry season was controlled largely by the internal cycling (mostly phytoplankton production) rather than the external sources such as precipitation and freshwater runoff. Similar processes must also be taking place in the other estuaries of the present study.

Based on the TDL diagrams, the nitrogen and phosphorus are either added or removed from the system. Some studies have reported the release of phosphate from suspended particles induced by the seaward increase of pH and salinity (Fox *et al.* 1985). In addition to the presence of ETM near the mouths in all the rivers (Fernandes *et al.* 2017), some other factors may also be responsible for the present observation. Sanders *et al.* (1997) observed similar phenomena in the Humber estuary and explained it due to: (1) nitrifying bacteria converting ammonia to nitrate; (2) some ammonia sticking to particles; (3) potentially some recycling of nitrate by denitrifying bacteria; and (4) phosphate sticking to particles and/or co-precipitated with the iron oxides. Therefore, the nitrogen and phosphorus can be assumed were removed or added by a complex series of biogeochemical reactions. In most of the rivers $\text{Si}(\text{OH})_4$ showed a conservative behaviour. However, in the case of the Chapora estuary, the seawater end member showed non-conservative behavior indicating its slight removal within this area. This behaviour could be due to a higher bloom of phytoplankton stripping away some of the nutrients in the high salinity region. However, this is contrary to the observation of silica uptake by diatoms in the Chesapeake Bay (D'Elia *et al.* 1983), and the Amazon estuary (Milliman and Boyle 1975) which occurs in the low-salinity regions. Therefore, the ETM near the estuarine mouth might be causing removal through sorption onto the suspended matter. The high chlorophyll-fluorescence at the upstream station in the Terekhol R. (T10) might be due to two reasons; SPM accumulation and input of waters from a small rivulet leading to the high chlorophyll. On the other hand in the Zuari R., relatively high chlorophyll-fluorescence near the estuary mouth and low values immediate to it are seen in the channel (stations Z4 to Z8). A study carried out by Rao *et al.* (2011), reported that the channel becomes the major depositional center (40-80% of SPM) compared to the bay part (stations Z0 to Z3). Since the phytoplankton populations are highly dynamic, when the conditions are favourable (the bay region with less turbidity) they are capable of

explosive growth. Occurrences of mixed-species blooms of the diatoms and dinoflagellates have been reported by Patil and Anil (2011) associated with high salinity in the Zuari R. The relatively high chlorophyll-fluorescence seen during the dry season as compared to the wet season may be related to less freshwater discharge, high salinity and the longer residence time of water (Maya *et al.* 2011; Patil and Anil 2015). Ram *et al.* (2003) reported that the mean ratio of Primary Production /Respiration were low in the Mandovi and Zuari rivers (0.28-0.67) during the wet season, and high (1.49–2.53) in the dry season, with the prevalence of net autotrophic conditions. They suggested of a temporary shift in the status of the coastal ecosystem from net heterotrophic to net autotrophic.

Therefore, we can summarize that the processes affecting the behaviour of nutrients in the estuarine waters were found to be strongly dependent on the seasonal conditions. During the wet season, in the micro-tidal rivers, the salinity stratification together with the presence of sand bars restricted their ability to flush the excess salt and nutrients out to sea. This condition caused the storage of nutrients within the estuarine regions. On the other hand, during the dry season with the fading of the sand bars and better mixing of the water column, the nutrients were abundantly present in the estuary supplied by the marine environment. For the meso-tidal rivers, although significant stratification was seen due to salinity during the wet season, the formation of the sand bars was less prominent. Here, the nutrients showed non-conservative behavior during both the seasons with the estuarine region acting as a corridor for the nutrient passage. As a result, nutrients were transported from the estuaries to the coastal waters and vice versa.

Conclusion

The seasonal changes in the coastal geomorphology of six rivers, with different tidal ranges along the Goa coast, significantly affected the water quality of the estuaries. During the wet season, the water column was stratified near the estuary mouths due to increased freshwater inputs in the meso-tidal rivers and by the sand bar formations in the micro-tidal rivers. On the other hand, during the dry period, the waning of the sand bars and the intrusion of saline waters made the water column well mixed. The nutrient concentrations showed a clear seasonal trend with high values in the wet season and low values during the dry season with a vice versa condition seen for the chlorophyll-fluorescence. The microtidal estuaries played a vital role in the nutrient sequestration during the wet season, by retaining the land-derived and bottom-regenerated nutrients within the system. Here, the sandbars controlled the river hydrodynamic behaviour which in turn influenced the river hydrochemistry and helped in sustaining the nutrient requirements of the system. Therefore, for effective management of the water quality in the estuaries, understanding the dynamics of the sand bars is required. The management of the estuary should prevent artificial breaching of the sand bars

through dredging, which can impart a negative impact on the prevailing nutrient cycles and productivity of the coastal zone and have social as well as environmental implications.

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Conflicts of Interest

The authors declare no conflicts of interest.

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Figure legend

Fig. 1. Sampling locations in the Terekhol, Chapora, Sal, Talpona, Mandovi and Zuari rivers.

Fig. 2. Vertical Salinity distribution in the waters of the microtidal (Terekhol, Chapora) and mesotidal (Mandovi and Zuari) rivers of Goa. (Inset- Bar plots of monthly river discharge and rainfall in the microtidal and mesotidal rivers).

Fig. 3. Seasonal distribution of Dissolved oxygen in the surface and bottom waters of micro-tidal and meso-tidal rivers of Goa.

Fig. 4. Seasonal distribution of Nitrite in the surface and bottom waters of the Terekhol, Chapora, Sal, Talpona, Mandovi and Zuari rivers.

Fig. 5. Plots of Nutrients vs. Salinity in the (a) Terekhol, Chapora, Sal and Talpona rivers (b) Mandovi and Zuari rivers. The units for the nutrients are in $\mu\text{mol/l}$.

Fig. 6. Vertical profile of Chlorophyll-fluorescence in the Terekhol, Chapora, Mandovi and Zuari rivers.

Supplementary Figures

Fig. S. Seasonal distribution of (1) Nitrate, (2) Ammonia, (3) Phosphate and (4) Silicate in the surface and bottom waters of the Terekhol, Chapora, Sal, Talpona, Mandovi and Zuari rivers.

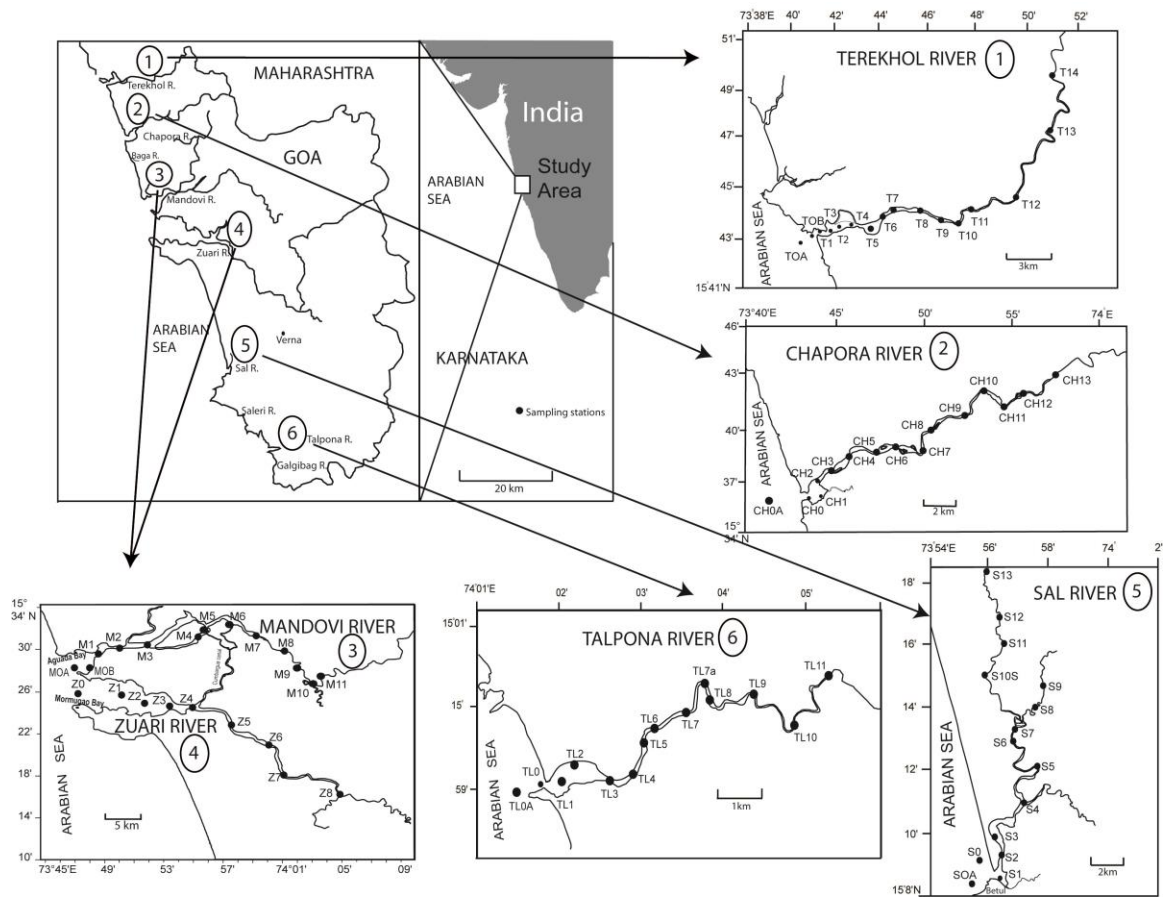


Fig. 1.

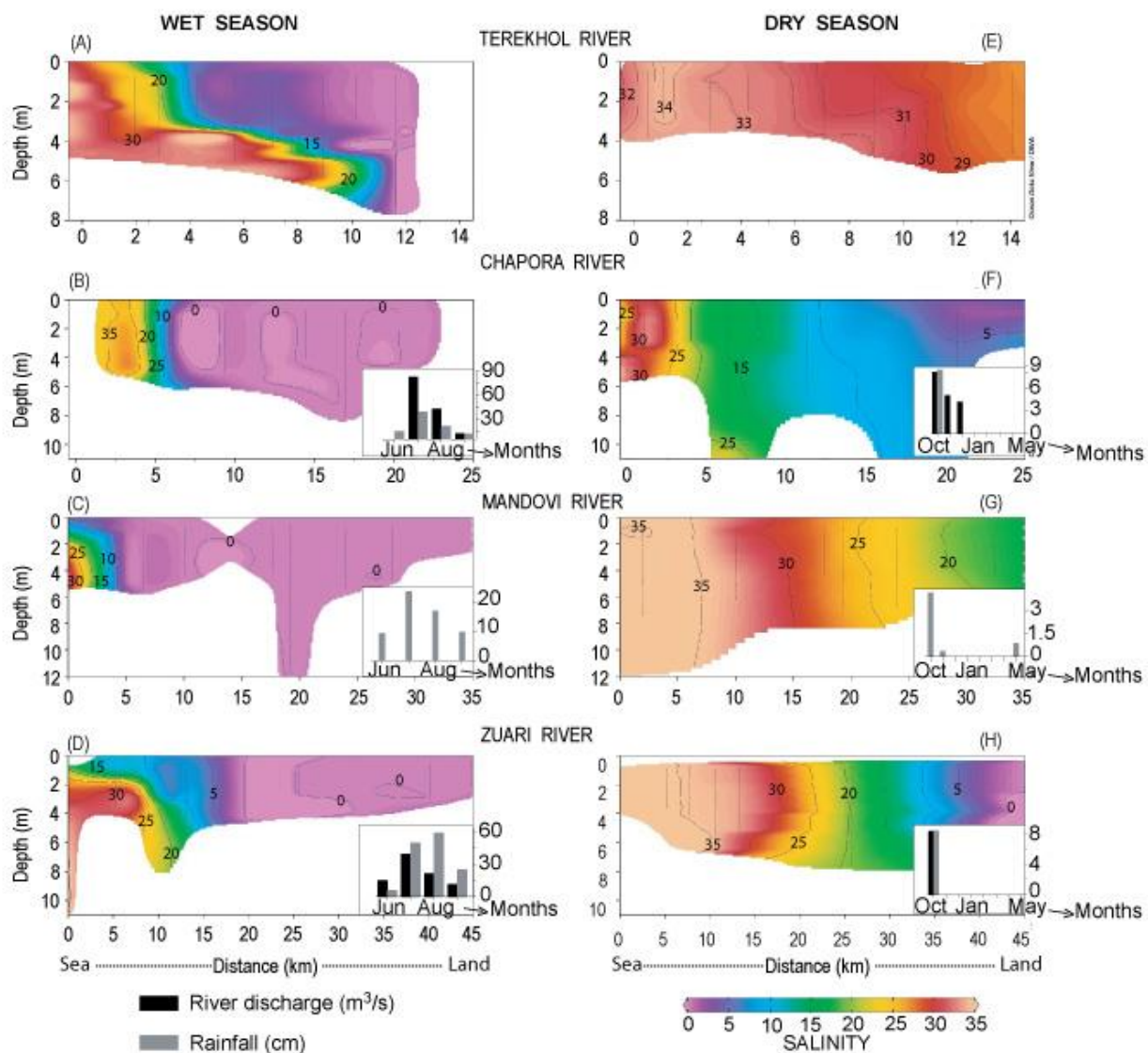


Fig. 2.

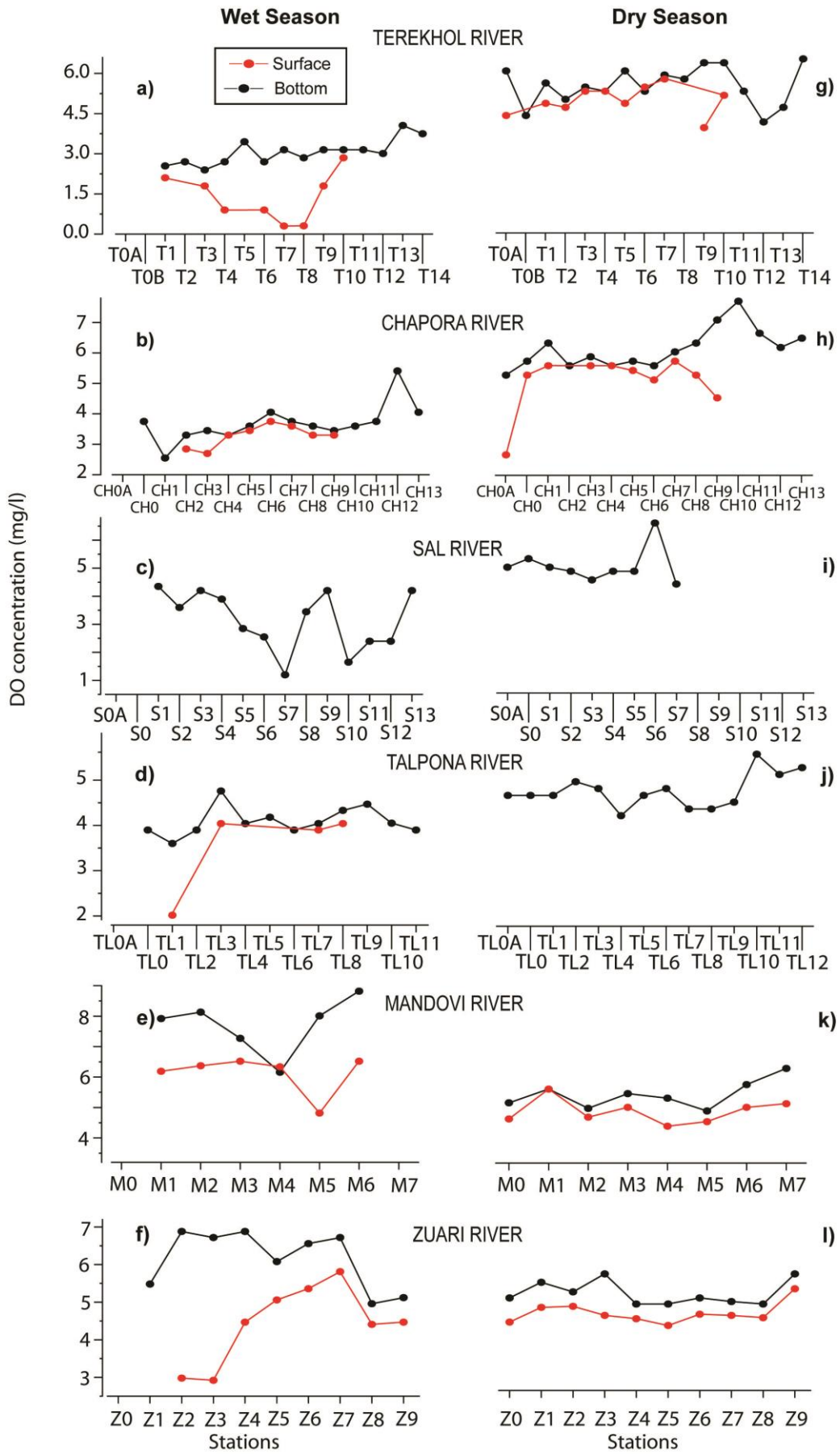


Fig. 3

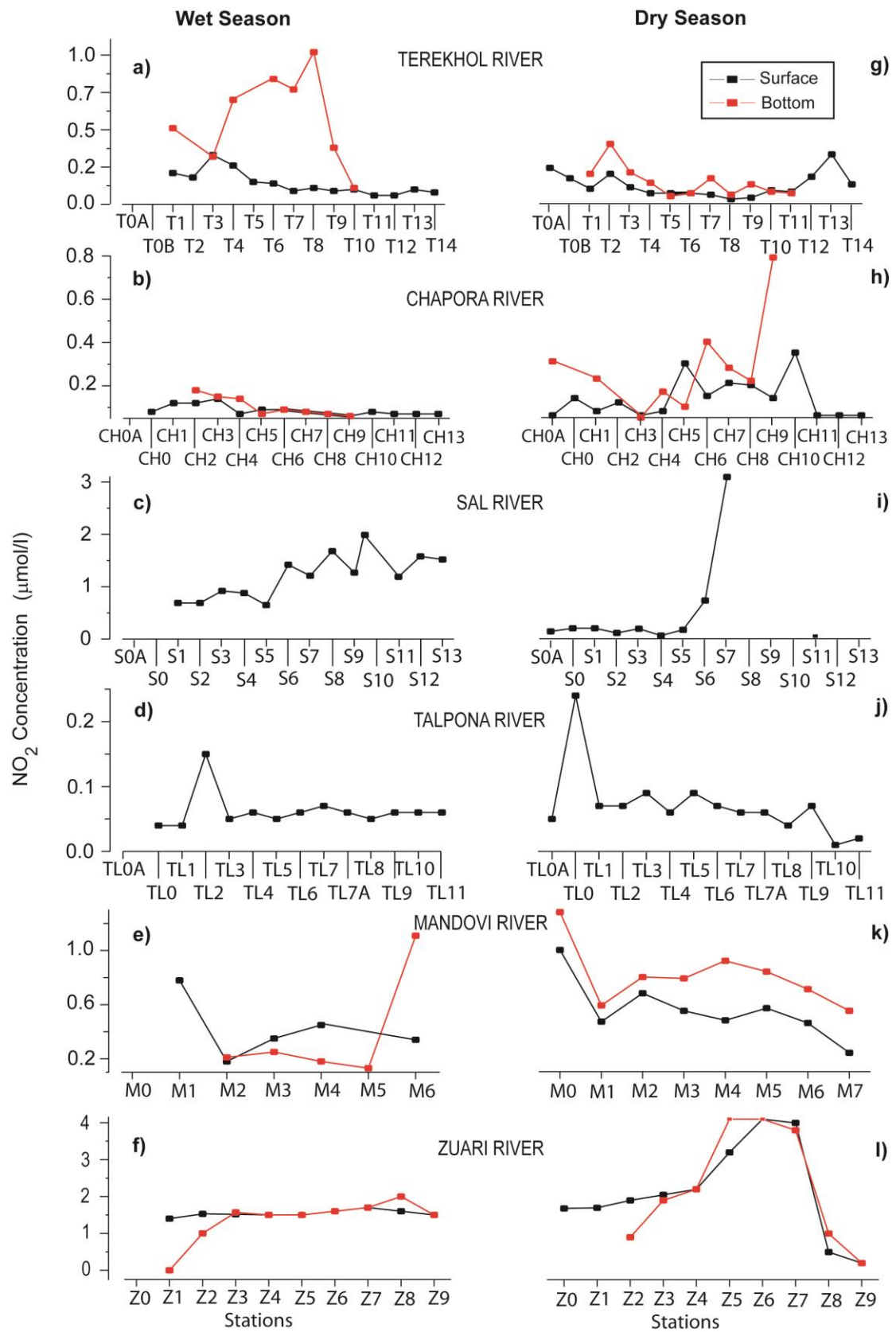


Fig. 4

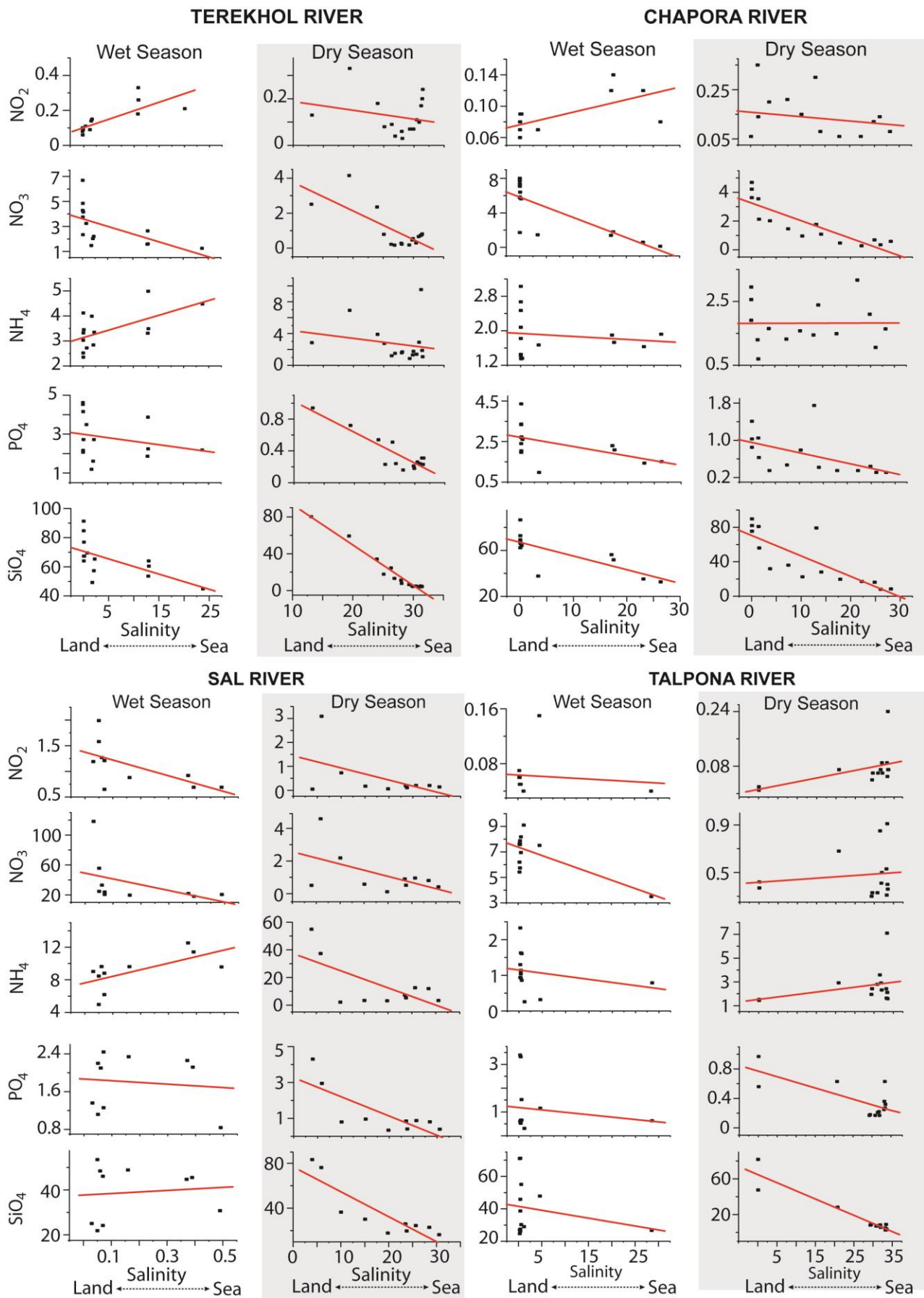


Fig. 5a

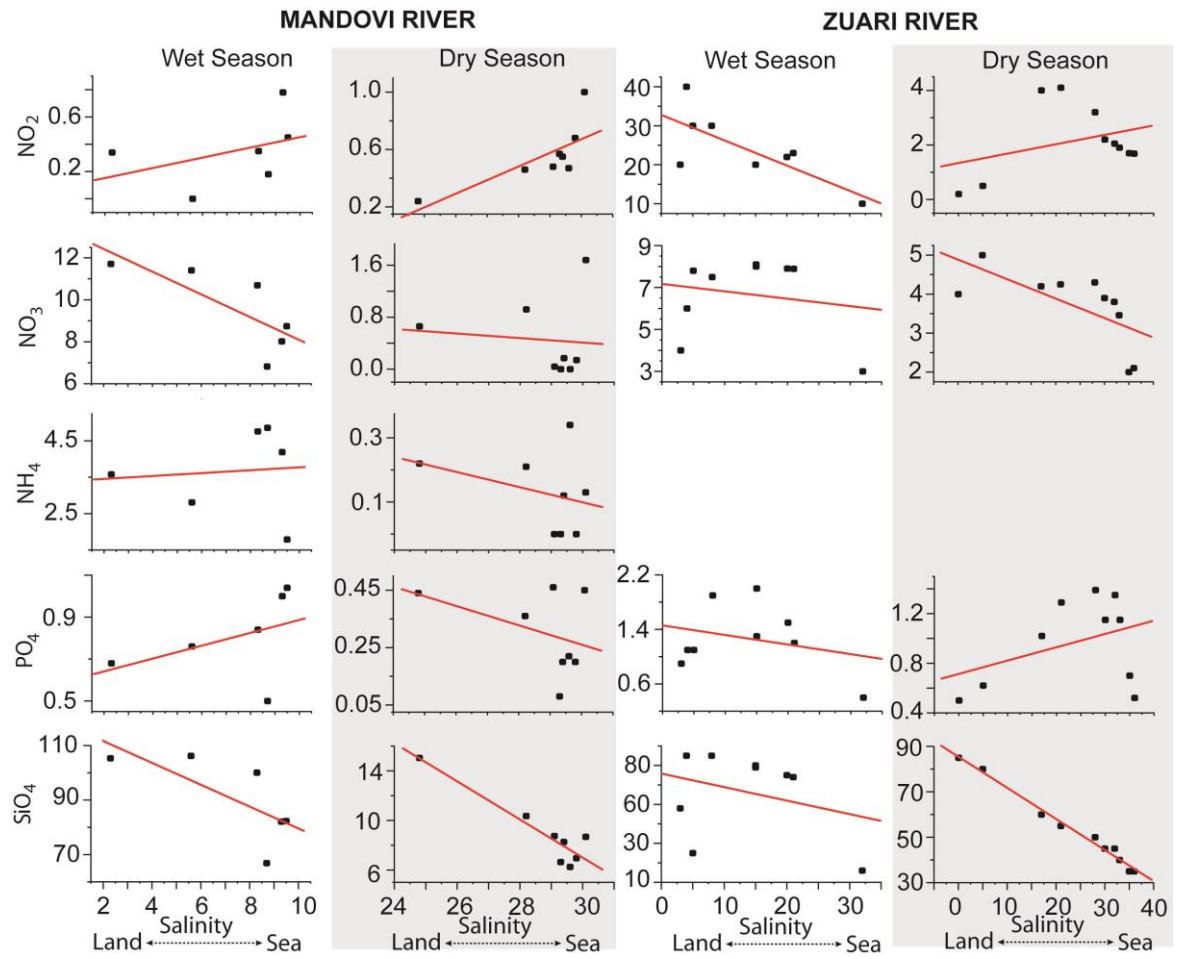


Fig. 5b

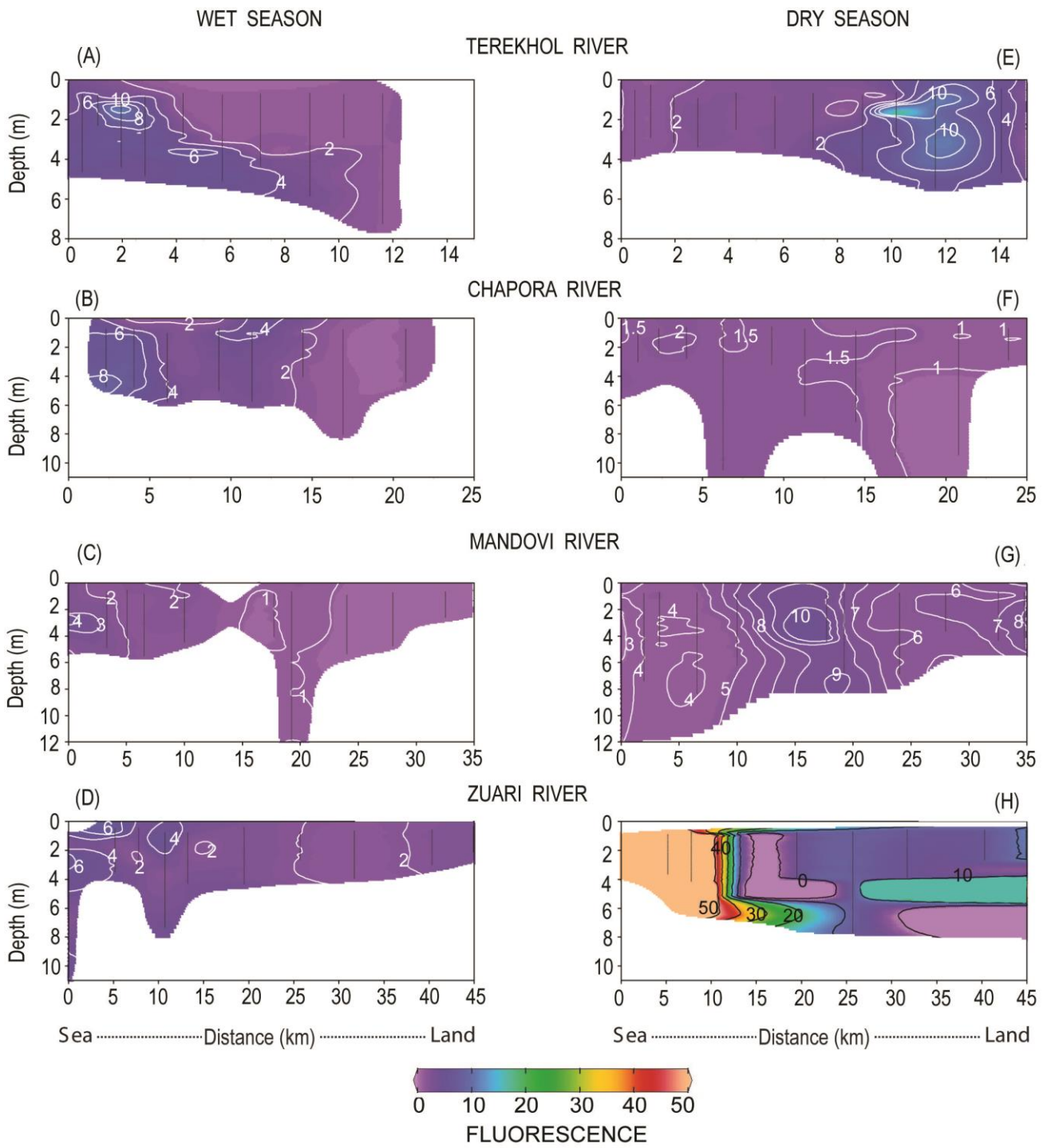


Fig. 6