

## Seasonal dynamics of mangrove outwelling and its impact on estuarine productivity: insights from multi-parameter analysis across tidal variations

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### Abstract

Tropical mangroves are subjected to extreme environmental conditions yet remain highly productive ecosystems. The Mandovi and Zuari estuaries of Goa on the western coast of India are lined by mangroves and are a rich source of fisheries that supports the coastal livelihood. Despite their ecological and economic significance, the nutrient and organic matter dynamics in tropical mangrove ecosystems remain poorly studied. The hydrographic conditions in the mangrove and adjacent estuarine waters are dictated by monsoonal precipitation, freshwater input, tides, and influx of seawater, resulting in subsequent changes in their physicochemical parameters and organic matter concentrations. The impact of these changes on the phytoplankton biomass and primary productivity in the estuarine waters was investigated during the pre-monsoon, monsoon and post-monsoon seasons. Dissolved inorganic nutrients such as nitrite, nitrate, ammonia, phosphate and silicate displayed wide seasonal variability and were higher during the low tide than those in high tide. Isotopic and elemental ratios of carbon and nitrogen revealed that primary productivity in the estuaries was enhanced by the outwelling of mangrove-derived organic matter. The highest chlorophyll *a* and primary productivity were observed during the pre-monsoon season, with Zuari exhibiting higher levels compared to Mandovi. Multivariate statistical analyses confirmed that primary productivity was influenced mainly by temperature, salinity, pH, dissolved oxygen and organic matter. Results from our study emphasizes the role of outwelling of organic matter from mangroves and their influence on primary productivity in adjacent estuarine waters.

**Keywords:** Primary productivity, Organic matter dynamics, Mangroves, Outwelling, Nutrients

## 1. Introduction

Mangroves are one of the most productive ecosystems in the world and support a great wealth of biodiversity (Meera et al. 2021). The biological productivity of coastal waters was attributed to the organic matter (OM) outwelled or exported from shallow water hotspots such as, mangroves by Odum (1968). Since then, there has been constant speculation regarding the contribution of mangroves to the productivity of adjacent ecosystems supporting fisheries, coral reefs, salt marshes, seagrass and seaweed beds. Several studies support this hypothesis (Dittmar et al. 2006; Jennerjahn and Ittekkot 2002; Granek et al. 2009; Abrantes et al. 2015) by highlighting mangroves as a vital source of carbon (C) and nitrogen (N) to the adjacent coastal waters. While certain studies propose that mangroves serve as biofilters, thus mitigating eutrophic conditions (Marchand et al. 2014); others suggest they directly contribute nutrients to coastal waters (Tanaka and Choo 2000; Dittmar et al. 2006). Recent studies indicate that mangrove vegetation stores ambient CO<sub>2</sub>, which is subsequently released into coastal waters through the porewater discharge of dissolved organic and inorganic C (Maher et al. 2018; Santos et al. 2019). Significant C inputs represented by the primary productivity (PP) of phytoplankton in mangrove dominated estuaries plays a pivotal role in ecosystem dynamics and global biogeochemical cycles (Sala and Austin 2000; Moore et al. 2013; Saifullah et al. 2015). Phytoplankton, as primary producers, are fundamental for sustaining the food web and providing energy for numerous organisms within mangrove estuarine ecosystems (Khatoon et al. 2010). Therefore, understanding the PP of mangrove dominated estuaries helps to assess the overall health and resilience of these fragile habitats (Sala and Austin 2000).

Unfortunately, there is a scarcity of studies focusing on PP of tropical mangrove-dominated estuaries compared to temperate estuaries worldwide (Navas-Perejo et al. 2020). Specifically, limited research from Indian tropical mangrove estuaries have been reported inspite of accounting for over 45% of South Asia's total mangrove cover (Forest Survey of India 2017; Singh et al. 2023). Moreover, the mangrove dynamics is shaped by a complex interplay of factors such as local geomorphology (Vaslet et al. 2012), tidal variations (Ayukai et al. 1998), areal extent of forests (Guest et al. 2004), freshwater input and precipitation (Adame and Lovelock 2011) and physico-chemical conditions (Ylla et al. 2012). Given the variability of these factors, the role of mangroves in the estuarine dynamics across various seasonal, tidal and spatial scales is still ambiguous and remains an ongoing challenge in coastal ecology.

As mangroves inhabit transitional zones between marine and freshwater ecosystems, OM comprises a heterogeneous mixture of various dissolved and particulate matter. This mixture can be from allochthonous (e.g., riverine or terrigenous inputs) or autochthonous (e.g., mangrove litter)

sources (Prasad et al. 2017). Large volumes of litter are produced by falling leaves, branches, and other debris in mangrove habitats. The process of decomposition recycles nutrients and produces OM in the mangroves and its adjacent ecosystems. The OM that is not exported by tides settle in the sediment and is subjected to microbial degradation, the byproducts of which supplement the food web (Kristensen et al. 2008). The outwelled OM and nutrients enriches the estuarine waters and, ultimately boost fishery resources (Saifullah et al. 2015). Thus, to validate the sources of OM, the signatures of  $\delta^{13}\text{C}_{\text{sed}}$  and  $\delta^{15}\text{N}_{\text{sed}}$  coupled with elemental C:N ratios in the mangrove and estuarine sediments were studied. The identification of the source(s) of OM has been carried out using dual isotopic tracers in different mangrove ecosystems (Hu et al., 2006; Zhang et al., 2007; Ranjan et al. 2011; Aschenbroich et al. 2015; Krishna et al. 2015; Chu et al. 2020). The Mandovi (M) and Zuari (Z) estuaries harbour 80% of the mangrove cover in Goa, India (Jagtap 1985) with an area of 700 ha and 900 ha, respectively (Wakle et al. 2018). Both these estuaries serve as a rich source of fisheries sustaining the coastal food and economy (Rodrigues et al. 2011). In the case of the M and Z estuaries, dual isotopic tracer analysis for the identification of OM origin has gained impetus only in the recent decade (Maya et al. 2011; Bardhan et al. 2015; Shynu et al. 2015). The use of stable isotopic studies to understand the outwelling of OM from mangroves and its implications on the M and Z estuarine productivity has not been addressed earlier.

The objective of this study was to test the outwelling hypothesis on the M and Z estuaries by identifying the sources of OM using isotopic ratios of carbon  $^{13}\text{C}/^{12}\text{C}$  ratio ( $\delta^{13}\text{C}$ ) and nitrogen  $^{15}\text{N}/^{14}\text{N}$  ratio ( $\delta^{15}\text{N}$ ) coupled with organic C and N elemental ratios. The impact of physico-chemical parameters, tidal patterns, and prevailing monsoon conditions on the variability of OM and PP in the M and Z estuaries was also investigated. By employing this comprehensive approach, our study seeks to elucidate the role of mangroves in enhancing estuarine productivity through the outwelling of OM and nutrients, thus contributing to a deeper understanding of tropical mangrove ecosystem dynamics.

## **2. Materials and methods**

### **2.1. Sampling locations**

Sampling was carried out at two different estuaries, Mandovi (M) and Zuari (Z). At each estuary, six sampling sites separated by a distance of ~ 400 m were chosen for sample collection. Locations  $M_m1$ ,  $M_m2$ ,  $M_m3$  (M mangroves) and  $Z_m1$ ,  $Z_m2$ ,  $Z_m3$  (Z mangroves) were selected within the mangrove swamps of M and Z, respectively. Similarly, locations  $M_w4$ ,  $M_w5$ ,  $M_w6$  (M estuarine waters) and  $Z_w4$ ,  $Z_w5$ ,  $Z_w6$  (Z estuarine waters) were stationed mid-river (~ 300-400 m away) opposite to locations of  $M_m$  and  $Z_m$ , respectively (**Fig.1**).

## 2.2. Sampling design

Water and sediment samples were obtained during the premonsoon (PM) (March-May), monsoon (Mo) (June-September) and postmonsoon (PoM) (October-November) seasons for two years (2018-19). Surface water samples (depth < 0.5) from the mangrove and adjacent water sites were collected manually and using a Niskin sampler, respectively at low tide (LT) and high tide (HT). Sediment samples were collected using polyvinyl chloride (PVC) pipe corer (length 30 cm and diameter 7 cm) for the mangrove sites and Van Veen grab (area 1m<sup>2</sup>) for adjacent water sites. The samples from M<sub>m</sub>1, M<sub>m</sub>2 and M<sub>m</sub>3 served as triplicates for the location M<sub>m</sub>. Similarly, the samples from M<sub>w</sub>4, M<sub>w</sub>5 and M<sub>w</sub>6; Z<sub>m</sub>1, Z<sub>m</sub>2, Z<sub>m</sub>3 and Z<sub>w</sub>4, Z<sub>w</sub>5 and Z<sub>w</sub>6 represented M<sub>w</sub>, Z<sub>m</sub> and Z<sub>w</sub>, respectively.

## 2.3. Determination of physico-chemical and biological parameters of water

A portable thermometer was used to measure the surface water temperature at each sampling site. Salinity was measured using a handheld refractometer (ATAGO PAL-06S Pocket refractometer). The pH was determined using a pH meter (Eutech pH 700). Dissolved oxygen (DO) concentrations were estimated by Winkler's iodometric method (Carpenter 1965; Trivedi and Goel 1986). Dissolved concentrations of nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonia (NH<sub>4</sub><sup>+</sup>) phosphate (PO<sub>4</sub><sup>3-</sup>) and silicate (SiO<sub>4</sub><sup>4-</sup>) were determined using an Autoanalyser (Skalar San Plus) following standard colorimetric methods (Grashoff et al. 1983). Total organic carbon (TOC) was estimated using a TOC analyzer (Shimadzu TOC LCPH) in which potassium hydrogen phthalate (KHP) was used as a quality control to check the performance of the TOC analyzer. The organic matter (OM) content was obtained by multiplying the TOC by a factor of 1.724 (Trask 1939).

## 2.4. Organic matter sources and characterization

Sediment samples were decalcified with 1N HCl, rinsed completely with deionized water, and dried to determine C and N content and isotopic ratios. The  $\delta^{13}\text{C}_{\text{sed}}$  and  $^{15}\text{N}/^{14}\text{N}$   $\delta^{15}\text{N}_{\text{sed}}$  ratios, along with C and N content, were determined in continuous-flow mode using an elemental analyzer (EURO3000 Eurovector) linked to an isotope ratio mass spectrometer (Thermo-Finnigan Delta V) (Owens and Rees, 1989). Regarding Pee Dee Belemnite (PDB) and ambient N, isotopic ratios are stated in standard delta notation ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ). As established by the working standard, -Amino-n-Caproic Acid or ACA ( $^{13}\text{C} = 25.3$  and  $^{15}\text{N} = 4.6$ ) and an in-house sediment standard COD ( $^{13}\text{C} = 21$  and  $^{15}\text{N} = 7.5$ ), the precision of C and N isotope readings was more than  $\pm 0.2\%$ . The C and N content of the sediment samples was determined using an ACA calibration curve with C and N standards ranging from 6 to 24  $\mu\text{M}$  and 1 to 4  $\mu\text{M}$ , respectively.

## 2.5. Phytoplankton biomass and Primary productivity

For Chlorophyll a (Chl a) analysis, a known volume of water sample was filtered through a 0.7 µm Whatman GF/F filter paper and pigments were extracted in 90% acetone (UNESCO 1994). The resultant fluorescence was then measured on a fluorometer (Turner 7200-000) which was calibrated using the Chl a standard (Sigma). PP was estimated in the adjacent water locations using the <sup>14</sup>C assimilation method (Strickland and Parsons 1972). Two light bottles and two dark bottles (300 ml capacity) containing water samples from each site were spiked with labelled NaH<sup>14</sup>CO<sub>3</sub> (activity: 5 µCi ml<sup>-1</sup>; Bhabha Atomic Research Centre, Mumbai, India) and incubated for 12 hours under natural light and in-situ temperature. After incubation, water samples were immediately filtered through a 0.45-µm filter (Millipore). The filter was then subjected to acid fumes for 1 min to remove radiolabeled dissolved inorganic carbon (DI<sup>14</sup>C) and placed in scintillation vials with 5 ml of scintillation cocktail in dioxane (Spectrochem, Mumbai, India). Radioactivity was measured in a liquid scintillation counter (Hidex Triathler 425-034).

## 2.6. Statistical analyses

The statistical softwares PAST 4.03 (Hammer and Harper 2001) and IBM<sup>®</sup> SPSS 23.0 (IBM Corp., Armonk, NY, USA) were used to determine the statistical significance and each result was stated in mean ± standard deviation (SD). The relationship between physicochemical parameters, Chl a and PP was understood using a two-tailed Pearson's correlation analysis (p<0.05). To minimize the number of inter-correlated variables, principal components analysis (PCA) was performed with physicochemical parameters, Chl a and PP. To improve the interpretation of factor loadings, the analysis used Varimax rotation with Kaiser Normalization. The factor coefficients obtained were then utilized to calculate factor scores. The components with eigen values >1 was used as predictors to avoid multicollinearity in multiple regression analysis. One way analysis of variance (ANOVA) was performed to understand the impact of seasonal variations on the observed physical, chemical and biological parameters during LT and HT.

## 3. Results

### 3.1. Spatio-temporal variation of physico-chemical parameters

#### 3.1.1. Temperature, salinity, pH, dissolved oxygen

During the sampling period, the average ambient water temperature ranged between 27 to 32°C at LT and 27 to 30°C at HT in both the M and Z estuaries (**Fig.2a, b**). Tidal variations in the surface water temperatures were not prominent. The highest temperatures were observed during the PM (average 30.59°C), followed by PoM (average 28.75°C) and Mo (average 28.11°C) (**Fig.2a, b**).

Irrespective of seasons, higher temperatures were observed in the estuarine waters (i.e.,  $M_w$  and  $Z_w$ ) compared to the mangrove waters (i.e.,  $M_m$  and  $Z_m$ ). Distinct changes in the salinity were recorded varying from 2 to 6 ppt in Mo, 17 to 23 ppt in PoM and 27 to 31 ppt in PM at LT (**Fig.2c**). During HT, salinities of 1 to 8 ppt in Mo, 21 to 29 ppt in PoM and 29 to 33 ppt in PM were observed (**Fig.2d**). A decrease in salinity was observed during Mo followed by a steady increase from PoM to PM. pH displayed variation over a very narrow range with the highest values during PM (7.50 to 7.69) and lowest during Mo in all our sampling sites (6.95 to 7.36). No variation was observed in the pH between LT (7.0 to 7.6) and HT (7.0 to 7.7) (**Fig.2e, f**). The average DO concentrations at LT were maximum during Mo (6.74 mg/L), followed by PoM (6.09 mg/L) and PM (4.92 mg/L) in both the estuaries (**Fig.2g**). During HT, the highest DO concentrations were observed during Mo (6.29 mg/L) > PoM (5.39 mg/L) > PM (4.63 mg/L) (**Fig.2h**).

### 3.1.2. Dissolved inorganic nutrients

During LT, concentrations of  $\text{NO}_2^-$  varied from 0.07 to 5.28  $\mu\text{mol/L}$ ;  $\text{NO}_3^-$  were between 2.17  $\mu\text{mol/L}$  to 24.23  $\mu\text{mol/L}$ ;  $\text{NH}_4^+$  fluctuated between 0.32 to 8.05  $\mu\text{mol/L}$ ;  $\text{PO}_4^{3-}$  ranged from 0.06 to 3.64  $\mu\text{mol/L}$  and  $\text{SiO}_4^{4-}$  ranged between 14.75 to 74.42  $\mu\text{mol/L}$  (**Table 1**). In case of HT,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{SiO}_4^{4-}$  concentrations varied between 0.03 to 4.25  $\mu\text{mol/L}$ ; 0.51 to 19.72  $\mu\text{mol/L}$ ; 0.11 to 37.39  $\mu\text{mol/L}$ , 0.06 to 6.06  $\mu\text{mol/L}$  and 6.04 to 125.66  $\mu\text{mol/L}$ , respectively (**Table 1**).

Notably, highest concentrations of  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$  and  $\text{SiO}_4^{4-}$  was observed during Mo, followed by PM and PoM in both the estuaries (**Table 1**). Lower nutrient concentrations observed during PoM and PM coincided with increased salinity and lesser freshwater inflow (**Table 1**). Also, nutrient concentrations were higher in  $M_m$  and  $Z_m$  in comparison to their corresponding adjacent sites i.e.,  $M_w$  and  $Z_w$  (**Table 1**).

### 3.1.3. Organic matter

At LT, organic matter in water ( $\text{OM}_w$ ) concentration varied from 8.48 to 69.87 mg/L in M and from 5.84 to 68.97 mg/L in Z (**Fig.3a**). During HT, values of  $\text{OM}_w$  varied between 7.60 to 75.89 mg/L and 4.28 to 70.49 mg/L in M and Z, respectively (**Fig.3b**). During LT, organic matter in sediment ( $\text{OM}_s$ ) in M ranged between 2.29 to 62.61 mg/g and in Z from 4.71 to 57.36 mg/g (**Fig.3c**). During HT,  $\text{OM}_s$  concentrations varied from 2.61 to 48.65 mg/g in M whereas in Z concentrations were recorded from 4.04 to 57.48 mg/g (**Fig.3d**). Higher concentrations were witnessed mostly during the LT in comparison to the HT. The seasonal variation of  $\text{OM}_w$  and  $\text{OM}_s$  were in the order: Mo>PoM>PM in both the estuaries during both tides. The OM in the mangrove waters and sediment were higher than in its adjacent waters and sediments for both the estuaries.

### 3.2. Spatiotemporal variability of isotopic and elemental ratios of carbon and nitrogen

The  $\delta^{13}\text{C}_{\text{sed}}$  values recorded in M varied between  $-26.14\text{‰}$  to  $-24.31\text{‰}$  while in Z it ranged between  $-25.67\text{‰}$  to  $-24.54\text{‰}$  (**Fig. 4**). The average  $\delta^{13}\text{C}_{\text{sed}}$  in  $M_m$  was  $-25.76\text{‰}$  and in  $M_w$  was  $-24.81\text{‰}$ . While in  $Z_m$  and  $Z_w$  the average  $\delta^{13}\text{C}_{\text{sed}}$  values were  $-24.76\text{‰}$  and  $-25.23\text{‰}$ , respectively. The  $\delta^{15}\text{N}_{\text{sed}}$  values ranged from  $2.20\text{‰}$  to  $7.96\text{‰}$  in M while it varied from  $2.73\text{‰}$  to  $6.04\text{‰}$  in Z (**Fig.4**).  $M_m$  (average  $4.90\text{‰}$ ) and  $Z_m$  (average  $5.92\text{‰}$ ) had depleted  $\delta^{15}\text{N}_{\text{sed}}$  values than their respective estuarine sites  $M_w$  ( $5.34\text{‰}$ ) and  $Z_w$  (average  $4.80\text{‰}$ ). The C:N<sub>sed</sub> ratio in M was recorded between 10.01 to 18.71 and in Z between 7.54 to 15.69 (**Table 2**). The average C:N<sub>sed</sub> ratios obtained from this study were 13.44, 12.69, 11.90 and 11.27 in  $M_m$ ,  $M_w$ ,  $Z_m$  and  $Z_w$ , respectively. It was observed that the ratios in  $M_m > M_w$  and  $Z_m > Z_w$ . C:N<sub>sed</sub> was highest during Mo (13.18 to 18.71) and least in PM (7.54 to 10.74).

### 3.2. Chlorophyll a

At LT, the average Chl a concentrations were found to be the highest during PM ( $6.73\text{ }\mu\text{g/L}$ ), followed by Mo ( $2.27\text{ }\mu\text{g/L}$ ) and PoM ( $1.21\text{ }\mu\text{g/L}$ ) in both the estuaries (**Fig.5a**). Comparatively, lower Chl a concentrations were observed at HT during PM ( $3.72\text{ }\mu\text{g/L}$ ), Mo ( $1.57\text{ }\mu\text{g/L}$ ) and PoM ( $0.83\text{ }\mu\text{g/L}$ ) (**Fig.5b**). The highest Chl a concentrations coincided with low rainfall intensity, high temperatures and high salinity. While the lower concentrations were prevalent during high water column turbidity and light inhibition due to cloud cover. Interestingly, the concentration of Chl a was inversely proportional to the salinity in the two estuaries as the latter changed with the flood and ebb tides.

### 3.3. Primary productivity

The PP in  $M_w$  ranged from 2.55 to  $15.86\text{ }\mu\text{gC/L/hr}$  and in  $Z_w$  from 2.56 to  $10.25\text{ }\mu\text{gC/L/hr}$  (**Fig.6**). In both  $M_w$  and  $Z_w$ , the maximum PP was observed during the PM ( $9.81$  to  $15.86\text{ }\mu\text{gC/L/hr}$ ), intermediate during Mo ( $5.12$  to  $8.42\text{ }\mu\text{gC/L/hr}$ ) and least during the PoM ( $2.55$  to  $4.04\text{ }\mu\text{gC/L/hr}$ ). This pattern of seasonal variation of PP was in conjunction with that of Chl a. Although the nutrient enrichment was highest during the Mo, it was interesting to note that the PP maxima did not occur during Mo in both the estuaries. Alternatively, the maximum PP levels was observed during PM with lesser nutrients availability than the Mo.

### 3.4. Relationship between physico-chemical parameters, chlorophyll a and primary productivity

Pearson's correlation analysis revealed that there is a strong positive relationship between the productivity parameters i.e., Chl a and PP with temperature, salinity, pH and DO irrespective of the tides (**Fig.7a, b**). With regards to nutrients, the correlation with Chl a and PP is nominal and negative

(Fig.7a, b). Distinct negative correlations were found between  $OM_w$  and  $OM_s$  with Chl a and PP (Fig.7a, b).

Using PCA analysis, a total of four components were obtained with eigenvalue  $>1$ . To reduce multicollinearity, three components were selected, representing 71.95% of the total variance (Fig.8). The first component contributed to 48.13% of the variance and consisted of temperature, salinity and pH. The second component showed a variance of 14.90% representing DO,  $NO_3^-$ ,  $OM_w$  and  $OM_s$ . The third component had a variance of 8.93%, constituting  $NO_2^-$ ,  $NH_4^+$ ,  $PO_4^{3-}$  and  $SiO_4^{4-}$ . The fourth component had a variance of 7.85% and was not considered for linear regression as they failed to represent any specific variable. For linear regression, factor scores of the first, second, and third components were considered as the independent variable. The dependent variables were Chl a and PP (Table 3). It is noteworthy to state that component 1 showed the highest significance for both Chl a and PP ( $p < 0.0001$ ) while component 2 was significant for PP only. One-way ANOVA aided us in further illustrating the impact of the seasonal variations on the observed parameters during LT and HT (Table 4, Table 5). The spatio-temporal variations of temperature, salinity, pH, DO,  $NO_2^-$ ,  $NO_3^-$ ,  $NH_4^+$ ,  $PO_4^{3-}$ ,  $SiO_4^{4-}$ ,  $OM_w$ ,  $OM_s$ , Chl a and PP were found to be significantly different ( $p < 0.001$ ).

## 4. Discussion

### 4.1. Ambient environmental conditions

It is interesting to note that the M and Z estuaries are highly susceptible, yet remain remarkably adaptive to the continuous and dynamic changes observed throughout the study period. The surface water temperatures recorded were higher in  $M_w$  and  $Z_w$  than  $M_m$  and  $Z_m$  as a result of the dense mangrove canopy over the latter thereby, restricting the entry of sunlight. The seasonal variation in rainfall is an important contributor of freshwater flux exerting a considerable influence over the salinity patterns. These estuaries receive the highest amount of rainfall (460 to 1160 mm) during Mo (July to September), lesser rainfall (6.44 to 210 mm) during PoM (October to December) and almost no rainfall during the driest PM months of January and February (0.2 mm) ([https://disc.gsfc.nasa.gov/datasets/GPM\\_3IMERGHH\\_06/](https://disc.gsfc.nasa.gov/datasets/GPM_3IMERGHH_06/) summary). Additionally, freshwater discharge from rivers upstream regulates the salinities in these estuaries. It has been estimated that the freshwater supply increases by  $\sim 64\%$  during Mo,  $\sim 35\%$  during PoM and  $\sim 7\%$  during PM (Ghosh et al. 2021). While it is known that both these estuaries originate from the Western ghats and share a common point of discharge, Z maintains more saline conditions in comparison to M almost throughout the year. This phenomenon is attributed to the wider mouth of Z connecting to the sea and lower number of tributaries resulting in higher salinities recorded at Z (Padmavati and Goswami 1997). In



contrast, M receives a considerable amount of runoff through a larger tributary system (Qasim and Sengupta 1981) attaining an almost freshwater salinity range during Mo. This pattern of increasing salinity from Mo, PoM to PM seasons has also been documented in the tropical estuaries of Pondicherry, Sundarbans and Tamil Nadu (Prabu et al. 2008; Satheeshkumar and Khan 2009; Basu et al. 2021). The observed alterations in pH were not significant, consistent with findings reported by Basu et al. (2021) in the mangrove estuary of Tamil Nadu. The slightly elevated pH recorded during PM is caused by seawater intrusion which goes as far as 65 km into the estuarine zone, while lower pH observed during Mo is due to limited seawater extending only upto 10 km upstream in M and 12 km upstream in Z (Qasim and Sengupta 1981). The DO concentrations suggested well aerated surface waters in all the sites during the sampling period. Relatively higher DO concentrations during the Mo and PoM were due to the higher solubility of oxygen in freshwater (Mitra et al. 2018).

The nutrient profiles in the mangrove and estuarine waters are shaped by dual forces of the monsoonal pattern and the tidal inundation. The elevated concentrations of nutrients during LT in the mangrove swamps and its adjacent estuarine waters suggest a complex interplay of ecological dynamics. Unlike HT, where dilution effects might occur due to greater water volumes, the reduced water levels during LT concentrate nutrients within a smaller volume, leading to higher observed concentrations. This phenomenon could signify localized nutrient accumulation, possibly from sediment resuspension or the retention of nutrients within the confined area of the mangrove swamps (Hasan et al. 2022). Moreover, it emphasizes the ecological importance of mangroves during tidal fluctuations, highlighting their role as nutrient reservoirs or hotspots within the larger estuarine ecosystem. It was consistently observed that the nutrient concentrations in the mangrove waters i.e.,  $M_m$  and  $Z_m$  were higher than those of the estuarine waters i.e.,  $M_w$  and  $Z_w$ , suggesting the outwelling of nutrients from the mangrove swamps. The nutrient outwelling arising from OM decomposition or root exudates within mangroves elucidates the role of mangroves as crucial sources of essential nutrients. The highest nutrient concentrations in the M and Z estuaries were observed during Mo when freshwater input was the maximum which has been recorded previously by Mochemadkar et al. (2013). This trend aligns with previous observations by Prabu et al. (2008) and Basu et al. (2021). Apart from the freshwater inputs, the surge in  $\text{NO}_2^-$  concentration during Mo arises due to heightened biological activity such as phytoplankton excretion, ammonia oxidation, nitrate reduction, N recycling and bacterial decomposition of planktonic detritus (Govindasamy et al. 2000). The increased concentrations of  $\text{NO}_3^-$  in  $Z_m$  and  $Z_w$  during Mo has been reported previously by Maya et al. (2011), despite receiving lower freshwater input compared to M. This could also be a result of the greater expanse of mangrove forests in Z. Mangroves act as significant contributors of nitrogen compounds

through biological processes like nitrogen fixation and decomposition of OM. The larger coverage of mangroves in Z likely enhances biological activities, such as microbial nitrogen transformations and nutrient recycling, resulting in elevated  $\text{NO}_3^-$  concentrations despite relatively lower freshwater input compared to M. Similarly, the higher  $\text{NH}_4^+$  concentrations in Z might be attributed to the greater expanse of mangroves, leading to an accelerated rate of bacterial decomposition, mineralization, and ammonification of dissolved organic nitrogen originating from plant debris (Kristensen et al. 1988). Our results indicated a decrease in  $\text{PO}_4^{3-}$  concentrations as salinity increased, attributed to the tendency of higher salinity to cause phosphorus precipitation. This process results in the removal of phosphorus from the water column through sedimentation or its binding with other particles (De Jonge and Villerius 1989; Fang 2000). Reduced rainfall during PM and PoM led to a considerable decrease in  $\text{SiO}_4^{4-}$  concentrations as the  $\text{SiO}_4^{4-}$  supply becomes limited from natural weathering of rocks and erosion (Hessen 1999). Overall, the hydrographical conditions of the estuaries in our study were dictated primarily by the monsoon conditions, the freshwater input, nutrient outwelling and the proximity to the sea that regulates the ebb and flow of water.

#### **4.2. Outwelling of organic matter**

Higher OM observed in M than in Z can be attributed to the higher river runoffs in the former (Qasim and Sengupta 1981). The Mo season is characterized by maximum freshwater inputs and land runoffs; consequently, maximum OM concentrations were recorded during this season. Gireeshkumar et al. (2013) reported a similar seasonal peak in organic matter concentrations during the monsoon (Mo) period in the Cochin estuary. Higher OM in  $M_m$  and  $Z_m$  than in  $M_w$  and  $Z_w$  may have resulted from the breakdown of mangrove leaf litter as reported by Kristensen et al. (2008), indicative of the outwelling of OM from the mangroves. This phenomenon of elevated organic matter in surface sediments was also documented in similar mangrove-dominated aquatic systems (Kristensen et al. 2008; Prasad and Ramanathan 2009).

In general, the  $\delta^{13}\text{C}$  signatures of mangroves is close to terrestrial C3 plants ( $-32\text{‰}$  to  $-22\text{‰}$ ) (Boutton 1996), indicating that mangroves follow the C3 photosynthetic pathway (Calvin-Benson cycle). The recorded  $\delta^{13}\text{C}_{\text{sed}}$  values of  $M_m$  and  $M_w$  ( $-26.14\text{‰}$  to  $-24.31\text{‰}$ ) coincided with the range typical for mangroves plants ( $-30\text{‰}$  to  $-25\text{‰}$ ; Muzuka and Shunula 2006) as well as that for marine phytoplankton ( $-18\text{‰}$  to  $-24\text{‰}$ ; Fry and Sherr 1989). In the case of  $Z_m$  and  $Z_w$  ( $-25.67\text{‰}$  to  $-24.54\text{‰}$ ), similar observations were noted. The observed  $\delta^{13}\text{C}_{\text{sed}}$  ranges has also been reported from other tropical mangrove dominated estuaries, like the Pichavaram estuarine-mangrove ecosystem of India (Prasad and Ramanathan 2009), and the Guayas River Estuary ecosystem of Ecuador (Cifuentes et al. 1996). The mixture of terrestrial derived material and marine derived material in the sedimentary

OM has also been reported from the Hunts Bay, Forth estuary, Yangtze estuary, Pearl River estuary and Cochin estuary (Andrews et al. 1998; Graham et al. 2001; Zhang et al. 2007; Gireeshkumar et al. 2013). The concurrence of the  $\delta^{13}\text{C}_{\text{sed}}$  values suggests a mixed carbon input derived from both mangrove-derived OM and marine phytoplankton, indicating outwelling of OM from mangroves into the estuarine waters.

$\delta^{15}\text{N}$  signatures of marine plankton typically have an average of 6 ‰ ranging from 4 to 10 ‰, and terrestrial OM ranges from -10 to 10 ‰ averaging 2 ‰ (Alonso-Hernandéz et al. 2020). The  $\delta^{15}\text{N}_{\text{sed}}$  in  $M_m$  (4.08‰ to 5.31‰) and  $Z_m$  (5.60‰ to 6.40‰) indicated a consistent and narrower variation, implying a steady OM source predominantly originating from mangroves in these areas. Contrastingly, the wider variability in  $\delta^{15}\text{N}_{\text{sed}}$  observed in  $M_w$  (2.20‰ to 7.96‰) and  $Z_w$  (2.73‰ to 5.97‰) suggests a more diverse and mixed origin for the sedimentary OM. This broader range indicates the potential contribution from multiple sources, leading to a varied nitrogen isotopic composition within the sediment, reflecting a more complex input of OM in these estuarine waters. The possible contribution of OM from both the terrestrial and marine sources has also been reported from the Bay of Bengal (Krishna et al. 2013) and the estuarine system of West Africa (Dan et al. 2019).

The  $\delta^{13}\text{C}_{\text{sed}}$  and  $\delta^{15}\text{N}_{\text{sed}}$  data are often insufficient for source identification of OM in dynamic systems like the M and Z estuaries, which experience major seasonal variations in hydrology and biogeochemistry. Hence, the C:N<sub>sed</sub> ratio is a useful indicator of OM origin. For terrestrial OM, higher ratios of 12 to 200 have been recorded (Hedges and Mann 1979), whereas marine OM is defined by an observed excess of C over N with ratios of 10 or less (Pocklington and Leonard 1979). In our study, the peak C:N<sub>sed</sub> ratios recorded during  $M_o$  suggested a substantial terrigenous OM input originating from runoff events during this period. Moreover, the elevated C:N<sub>sed</sub> ratios in M corroborated with its higher terrigenous influence, attributed to the greater number of freshwater tributaries flowing into this estuary. Conversely, the lower C:N<sub>sed</sub> ratios in Z indicated a potentially higher proportion of marine-derived OM. Overall, the observed C:N ratios indicated a mixture of marine and terrestrial sources of OM, similar to findings reported for the Yellow River estuary and the Beibu Gulf (Liu et al. 2015; Liao et al. 2018).

#### **4.3. Impact of organic matter outwelling on phytoplankton biomass and productivity**

The relationship between OM and phytoplankton PP in estuaries is complex and multifaceted. OM serves as a crucial nutrient source for phytoplankton growth, providing essential elements such as C and N (Gobler et al. 2001). As phytoplankton photosynthesize, they utilize these nutrients along with sunlight to produce organic compounds through PP. In particular reference to the present study, the

source of OM has been attributed to both terrestrial (predominantly mangroves) as well as marine sources. Mangrove-dominated estuaries are acknowledged for their ecological richness, and the role of phytoplankton is believed to be a significant factor in sustaining and enhancing this productivity (Rahaman et al. 2013). The fluctuations in the phytoplankton biomass i.e., Chl a concentration observed across tidal variations in our study influences the quantity of pigment as a result of varying phytoplankton stocks (Dehadrai 1970). Higher concentration of Chl a during LT in comparison to HT during PM was due to the prevalence of lower turbidity and higher penetration of sunlight (Perumal et al. 2009). Conversely, lower concentrations during Mo were likely a consequence of light inhibition caused by cloud cover and heightened water column turbidity (Perumal et al. 2009).

The peak PP observed during the PM period is linked to maximal nutrient utilization by phytoplankton (Wilkerson et al. 2015). However, during the Mo, the extensive water dilution and stratification create conditions of freshwater salinity, resulting in turbid waters with limited light penetration, constraining phytoplankton production (Perumal et al. 2009; Bardhan et al. 2015). Despite the high nutrient inputs characteristic of the Mo season, their effective utilization by phytoplankton is hindered (Devassy and Goes 1989). Conversely, the PoM period witnessed the lowest PP, potentially due to insufficient N proportions in adjacent waters, which is critical for optimal phytoplankton production (Mathew et al. 2021).

The negative correlations found between Chl a and PP with  $OM_w$  and  $OM_s$  indicate a notable increase in the rate at which phytoplankton utilize OM. Additionally, the positive correlations observed between temperature, salinity, pH, and DO with both Chl a and PP signify strong interdependencies among these environmental factors. Collectively, Pearson's correlations suggest that phytoplankton abundance and productivity are intricately linked to the availability and utilization of OM and is influenced by temperature, salinity, pH, and DO. The PCA clearly segregated the parameters into distinct components and further validated the correlational findings by the subsequent regression analysis which showed that Chl a and PP are significantly influenced by temperature, salinity, pH, DO and OM. This suggests a complex relationship where environmental conditions significantly influence the growth and activity of phytoplankton within the estuarine ecosystem. Moreover, the significance of the impact of monsoonal variations on all the observed parameters i.e., during LT as well as HT was established by one-way ANOVA, affirming that the monsoonal precipitation exerts a noteworthy influence on the estuarine hydrography and productivity.

In summary, our study revealed notable differences in the phytoplankton abundance and productivity owing to seasonal variation of hydrological parameters. The study also highlighted the substantial impact of tidal influences on the outwelling of OM and nutrients from mangroves. The

$\delta^{13}\text{C}_{\text{sed}}$  values offered insights into the carbon sources, indicating contributions from both mangrove-derived and marine sources. Concurrently,  $\delta^{15}\text{N}_{\text{sed}}$  variations hinted at the diversity of N origin, with narrower ranges suggesting more stable sources, notably from mangroves. The C:N<sub>sed</sub> ratios complemented these findings, showcasing fluctuations in terrigenous inputs and OM composition across M and Z. Although the present study does not directly quantify the outwelling of OM from the M and Z estuaries, the dual isotopic and elemental ratios established the significance of mangroves as a valuable source of OM to the adjacent estuaries. These comprehensive insights highlight the complex interconnections among environmental parameters, nutrient availability, organic matter sources, and the resulting impact on phytoplankton dynamics within these estuarine ecosystems, consequently influencing overall productivity.

## **5. Conclusion**

Despite being a valuable resource of fisheries, mangrove forests are often susceptible to anthropogenic pollution, land reclamation for construction and deforestation resulting in habitat loss. Thus, it is critical to establish the indispensable role of mangroves in enhancing the productivity of the estuaries and surrounding coastal waters. Our study depicted the significance of ambient environmental conditions, tidal fluctuations and irregularity in freshwater inputs on the concentrations of OM and nutrients in M and Z mangrove and estuarine waters. The dual isotopic tracers ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) and C:N<sub>sed</sub> ratios revealed that the source of OM was from a combination of terrestrial (including mangroves) and marine sources. This implied that the productivity in the M and Z estuaries is enhanced by mangrove-derived OM facilitated by the process of outwelling. Multivariate statistical analysis confirmed that temperature, salinity, pH, DO and OM are the primary environmental drivers of PP. Thus, the resultant productivity in mangrove dominated estuaries ecosystems is based on a complex network of physical, chemical and biological processes. These findings have implications for understanding the trophic dynamics in estuaries, as primary productivity directly impacts the availability of OM for organisms at higher trophic levels.

### **Statement of Conflict of interest**

The authors declare that they have no competing interests.

### **Statement of Availability of Data**

All data generated or analyzed during this study are included in this manuscript.

## Statements and Declarations

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Figure captions

**Fig.1** Location of sampling sites in the Mandovi ( $M_m$  - Mandovi mangroves;  $M_w$  - Mandovi adjacent water) and Zuari ( $Z_m$  - Zuari mangroves;  $Z_w$  - Zuari adjacent water) estuaries, Goa, India

**Fig.2** Variations in physico-chemical parameters during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) seasons in the Mandovi and Zuari estuaries where (a, c, e, g) represent values during low tide and (b, d, f, h) represent values for high tide. ( $M_m$  - Mandovi mangroves;  $M_w$  - Mandovi adjacent water;  $Z_m$  - Zuari mangroves;  $Z_w$  - Zuari adjacent water)

**Fig.3** Variation of organic matter in water ( $OM_w$ ) (a - low tide; b - high tide) and organic matter in sediment ( $OM_s$ ) (c - low tide; d - high tide) during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) in the Mandovi and Zuari estuaries. ( $M_m$  - Mandovi mangroves;  $M_w$  - Mandovi adjacent water;  $Z_m$  - Zuari mangroves;  $Z_w$  - Zuari adjacent water)

**Fig.4** Variations in  $\delta^{13}C_{sed}$  and  $\delta^{15}N_{sed}$  during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) in the Mandovi and Zuari estuaries. ( $M_m$  - Mandovi mangroves;  $M_w$  - Mandovi adjacent water;  $Z_m$  - Zuari mangroves;  $Z_w$  - Zuari adjacent water)

**Fig.5** Variation of chlorophyll *a* (Chl *a*) (a - low tide; b - high tide) during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) in the Mandovi and Zuari estuaries. ( $M_m$  - Mandovi mangroves;  $M_w$  - Mandovi adjacent water;  $Z_m$  - Zuari mangroves;  $Z_w$  - Zuari adjacent water)

**Fig.6** Variation of primary productivity (PP) during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) in the Mandovi and Zuari estuaries. ( $M_w$  - Mandovi adjacent water;  $Z_w$  - Zuari adjacent water)

**Fig.7** Pearson's correlation coefficients between temperature, salinity, pH, dissolved oxygen (DO), nitrite ( $NO_2^-$ ), nitrate ( $NO_3^-$ ), ammonia ( $NH_4^+$ ), phosphate ( $PO_4^{3-}$ ), silicate ( $SiO_4^{4-}$ ), organic matter in water ( $OM_w$ ), organic matter in sediment ( $OM_s$ ), chlorophyll *a* (Chl *a*) and primary productivity (PP) in the Mandovi and Zuari estuaries

**Fig.8** Component plot generated by principal component analysis (PCA): Component 1 includes temperature, salinity and pH, Component 2 represents dissolved oxygen (DO), nitrate ( $NO_3^-$ ), organic matter in water ( $OM_w$ ) and organic matter in sediment ( $TOC_s$ ), component 3 includes nitrite ( $NO_2^-$ ), ammonia ( $NH_4^+$ ), phosphate ( $PO_4^{3-}$ ) and silicate ( $SiO_4^{4-}$ )

Table 1. Variations (mean±SD; n=3) of nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), ammonia (NH<sub>4</sub><sup>+</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), silicate (SiO<sub>4</sub><sup>4-</sup>) in µmol/L during pre-monsoon (PM), monsoon (Mo) and post-monsoon (PoM) at low tide (LT) and high tide (HT) in the Mandovi and Zuari estuaries during 2018 and 2019.

2018							
Nutrients	Location	PM		Mo		PoM	
		LT	HT	LT	HT	LT	HT
NO <sub>2</sub> <sup>-</sup>	M <sub>m</sub>	1.32±0.04	1.16±0.05	3.28±0.03	2.17±0.01	0.07±0.02	1.03±0.02
	M <sub>w</sub>	1.4±0.05	1.25±0.05	3.69±0.04	3.6±0.02	0.10±0.02	1.04±0.02
	Z <sub>m</sub>	1.06±0.01	1.02±0.01	4.7±0.03	2.38±0.06	0.19±0.04	0.14±0.10
	Z <sub>w</sub>	1.19±0.04	0.93±0.12	4.87±0.01	2.36±0.06	0.29±0.01	0.16±0.04
NO <sub>3</sub> <sup>-</sup>	M <sub>m</sub>	3.35±0.1	0.51±0.12	14.79±0.06	5.13±0.07	2.57±0.08	2.46±0.10
	M <sub>w</sub>	4.12±0.02	0.94±0.02	15.36±0.16	4.91±0.2	3.18±0.08	2.26±0.10
	Z <sub>m</sub>	3.05±0.04	2.61±0.05	22.49±0.02	12.24±0.02	2.64±0.05	3.00±0.06
	Z <sub>w</sub>	3.46±0.05	2.96±0.06	24.23±0.25	14.62±0.31	3.22±0.02	2.23±0.02
NH <sub>4</sub> <sup>+</sup>	M <sub>m</sub>	0.75±0.04	2.72±0.05	1.84±0.19	1.08±0.2	0.68±0.02	1.66±0.37
	M <sub>w</sub>	0.78±0.02	1.69±0.07	3.07±0.03	2.08±0.23	0.71±0.01	1.4±0.28
	Z <sub>m</sub>	4.65±0.15	0.4±0.02	6.17±0.06	6.66±0.04	0.80±0.01	1.13±0.15
	Z <sub>w</sub>	5.03±0.03	1.15±0.02	7.38±0.32	10.36±0.1	0.98±0.02	0.92±0.09
PO <sub>4</sub> <sup>3-</sup>	M <sub>m</sub>	0.54±0.04	0.18±0.05	1.89±0.01	0.55±0.04	0.06±0.02	0.05±0.02
	M <sub>w</sub>	0.81±0.04	0.06±0.04	1.62±0.02	1.77±0.05	0.12±0.05	0.11±0.02
	Z <sub>m</sub>	1.15±0.01	3.62±0.01	3.55±0.05	5.11±0.04	0.29±0.05	0.27±0.05
	Z <sub>w</sub>	1.49±0.1	3.34±0.05	3.64±0.05	6.06±0.01	0.36±0.03	0.19±0.01
SiO <sub>4</sub> <sup>3-</sup>	M <sub>m</sub>	16.6±0.04	20.75±0.05	67.60±0.16	122.62±0.23	14.7±0.30	23.29±0.02
	M <sub>w</sub>	18.52±0.06	16.22±0.02	72.61±0.19	120.35±0.04	17.98±0.23	20.35±0.01
	Z <sub>m</sub>	32.74±0.02	51.25±0.18	55.19±0.02	111.18±0.07	26.87±0.12	31.71±0.01
	Z <sub>w</sub>	37.64±0.02	56.49±0.04	57.04±0.08	125.66±0.39	25.79±0.07	33.42±0.02

2019							
NO <sub>2</sub> <sup>-</sup>	M <sub>m</sub>	1.30±0.02	0.13±0.06	4.07±0.02	3.81±0.07	0.09±0.04	0.09±0.02
	M <sub>w</sub>	1.54±0.03	0.07±0.06	5.04±0.03	4.25±0.02	0.12±0.03	0.1±0.04
	Z <sub>m</sub>	1.01±0.01	0.03±0.01	4.28±0.09	3.58±0.43	0.06±0	0.14±0.02
	Z <sub>w</sub>	2.09±0.01	0.08±0.01	5.28±0.09	4.09±0.02	0.09±0.02	0.15±0.02
NO <sub>3</sub> <sup>-</sup>	M <sub>m</sub>	6.25±0.02	4.67±0.26	15.56±0.31	15.8±0.38	2.44±0.14	6.95±0.17
	M <sub>w</sub>	8.90±0.08	4.88±0.1	16.35±0.03	18.83±0.04	2.59±0.18	8.23±0.22
	Z <sub>m</sub>	7.96±0.02	5.68±0.02	22.19±0.04	18.26±0.05	2.17±0.04	8.51±0.05
	Z <sub>w</sub>	8.85±0.06	6.83±0.07	23.34±0.04	19.72±0.05	2.92±0.04	9.94±0.05
NH <sub>4</sub> <sup>+</sup>	M <sub>m</sub>	1.26±0.02	5.57±0.31	2.23±0.02	0.42±0.24	0.41±0.07	3.94±0.04
	M <sub>w</sub>	1.46±0.03	4.5±0.06	2.50±0.23	0.27±0.1	0.32±0.04	5.93±0.2
	Z <sub>m</sub>	4.49±0.06	28.13±0.21	7.74±0.05	0.13±0.02	0.91±0.12	31.74±0.07
	Z <sub>w</sub>	5.04±0.05	37.39±0.07	8.05±0.11	0.11±0.02	0.72±0.12	32.34±0.18
PO <sub>4</sub> <sup>3-</sup>	M <sub>m</sub>	0.12±0.02	0.45±0.02	1.19±0.06	0.87±0.02	0.16±0.12	0.43±0.05
	M <sub>w</sub>	0.36±0.08	0.06±0.04	1.15±0.02	0.83±0.04	0.26±0.03	0.63±0.04
	Z <sub>m</sub>	1.38±0.09	1.24±0.01	3.41±0.35	0.61±0.11	0.12±0.02	3.08±0.01
	Z <sub>w</sub>	1.56±0.02	1.41±0.01	3.72±0.02	0.77±0.11	0.62±0.02	0.49±0.02
SiO <sub>4</sub> <sup>4-</sup>	M <sub>m</sub>	18.73±0.25	7.94±0.04	69.29±0.2	61.27±0.02	15.89±0.03	29.93±0.09
	M <sub>w</sub>	21.38±0.05	6.04±0.04	74.42±0.08	60.16±0.28	16.30±0.16	31.79±0.05
	Z <sub>m</sub>	28.44±0.17	6.91±0.07	43.12±0.02	17.99±0.06	20.91±0.06	23.29±0.15
	Z <sub>w</sub>	30.59±0.06	6.43±0.06	55.97±0.02	18.31±0.13	18.55±0.15	23.26±0.15

(Mm - Mandovi mangroves; Mw - Mandovi estuarine water; Zm - Zuari mangroves; Zw – Zuari estuarine water)

Table 2. Spatio-temporal variation of C:N<sub>sed</sub> ratios in the Mandovi and Zuari estuaries during 2018 and 2019.

	2018			2019		
	PM	Mo	PoM	PM	Mo	PoM
M <sub>m</sub>	10.74	18.71	13.58	10.38	15.73	11.51
M <sub>w</sub>	10.05	16.31	13.52	10.01	15.14	11.10
Z <sub>m</sub>	8.49	15.69	12.32	8.99	13.79	12.12
Z <sub>w</sub>	7.54	15.42	11.19	8.52	13.18	11.77

(M<sub>m</sub> - Mandovi mangroves; M<sub>w</sub> - Mandovi estuarine water; Z<sub>m</sub> - Zuari mangroves; Z<sub>w</sub> - Zuari estuarine water)



Table 3. Multiple regression model for predicting primary productivity (PP) and chlorophyll *a* (Chl *a*) using factor scores obtained from principal components analysis ( $p < 0.05$ ).

Dependent variable	Predictors	Standardized Coefficients ( $\beta$ )	t-value	Significance ( $p$ )	R <sup>2</sup>	Adjusted R <sup>2</sup>
PP	Component 1	0.828	17.531	<0.0001	0.688	0.681
	Component 2	-0.014	-0.297	<0.0001		
	Component 3	-0.037	0.784	0.767		
Chl <i>a</i>	Component 1	0.857	20.255	<0.0001	0.749	0.744
	Component 2	-0.104	-2.446	0.016		
	Component 3	0.056	1.324	0.188		

Table 4. Spatio-temporal variations of physico-chemical and biological parameters analyzed through one-way ANOVA in the Mandovi and Zuari estuaries during low tide and their significance (p<0.001)

		Sum of				
		Squares	df	Mean Square	F	Sig.
Temperature	Between Groups	204.196	23	8.878	143.914	.000
	Within Groups	2.961	48	.062		
	Total	207.158	71			
pH	Between Groups	8373.284	23	364.056	3960.596	.000
	Within Groups	4.412	48	.092		
	Total	8377.696	71			
Salinity	Between Groups	3.080	23	.134	9.099	.000
	Within Groups	.707	48	.015		
	Total	3.787	71			
Dissolved oxygen	Between Groups	65.613	23	2.853	110.464	.000
	Within Groups	1.240	48	.026		
	Total	66.852	71			
NO <sub>2</sub> <sup>-</sup>	Between Groups	244.973	23	10.651	8004.939	.000
	Within Groups	.064	48	.001		
	Total	245.037	71			
NO <sub>3</sub> <sup>-</sup>	Between Groups	20727.415	23	901.192	1.042	.438
	Within Groups	41520.778	48	865.016		
	Total	62248.193	71			
NH <sub>4</sub> <sup>+</sup>	Between Groups	17792.996	23	773.609	66475.491	.000
	Within Groups	.559	48	.012		
	Total	17793.555	71			
PO <sub>4</sub> <sup>3-</sup>	Between Groups	101.133	23	4.397	395.590	.000
	Within Groups	.534	48	.011		
	Total	101.667	71			

SiO <sub>4</sub> <sup>4-</sup>	Between Groups	29293.24	23	1273.619	69840.515	.000
		6				
	Within Groups	.875	48	.018		
OM <sub>w</sub>	Total	29294.12	71			
		1				
	Between Groups	11986.20	23	521.140	100568.334	.000
OM <sub>s</sub>		9				
	Within Groups	.249	48	.005		
	Total	11986.45	71			
OM <sub>s</sub>		8				
	Between Groups	11117.16	23	483.355	962.425	.000
		6				
Chl <i>a</i>	Within Groups	24.107	48	.052		
	Total	11141.27	71			
		3				
Primary productivity	Between Groups	516.287	23	22.447	1713.351	.000
	Within Groups	.629	48	.013		
	Total	516.916	71			
Primary productivity	Between Groups	1567.369	23	68.146	8.545	.000
	Within Groups	382.782	48	7.975		
	Total	1950.151	71			

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Table 5. Spatio-temporal variations of physico-chemical and biological parameters analyzed through one-way ANOVA in the Mandovi and Zuari estuaries during high tide and their significance ( $p < 0.001$ ).

		Sum of				
		Squares	df	Mean Square	F	Sig.
Temperature	Between Groups	65.839	23	2.863	22.216	.000
	Within Groups	6.185	48	.129		
	Total	72.024	71			
pH	Between Groups	10351.953	23	450.085	1383.103	.000
	Within Groups	15.620	48	.325		
	Total	10367.573	71			
Salinity	Between Groups	3.776	23	.164	10.563	.000
	Within Groups	.746	48	.016		
	Total	4.522	71			
DO	Between Groups	47.723	23	2.075	3.671	.000
	Within Groups	27.129	48	.565		
	Total	74.852	71			
NO <sub>2</sub> <sup>-</sup>	Between Groups	151.812	23	6.601	659.413	.000
	Within Groups	.480	48	.010		
	Total	152.293	71			
NO <sub>3</sub> <sup>-</sup>	Between Groups	2434.579	23	105.851	5075.785	.000
	Within Groups	1.001	48	.021		
	Total	2435.580	71			
NH <sub>4</sub> <sup>+</sup>	Between Groups	9433.715	23	410.162	15101.830	.000
	Within Groups	1.304	48	.027		
	Total	9435.018	71			
PO <sub>4</sub> <sup>3-</sup>	Between Groups	192.115	23	8.353	3956.612	.000
	Within Groups	.101	48	.002		
	Total	192.217	71			
SiO <sub>4</sub> <sup>4-</sup>	Between Groups	103675.060	23	4507.611	256154.707	.000
	Within Groups	.845	48	.018		
	Total	103675.905	71			
OM <sub>w</sub>	Between Groups	10310.631	23	448.288	54660.047	.000

	Within Groups	.394	48	.008		
	Total	10311.025	71			
OM <sub>s</sub>	Between Groups	7636.516	23	332.022	11167.717	.000
	Within Groups	1.427	48	.030		
	Total	7637.943	71			
Chl <i>a</i>	Between Groups	135.571	23	5.894	296.842	.000
	Within Groups	.953	48	.020		
	Total	136.524	71			
Primary productivity	Between Groups	1567.369	23	68.146	8.545	.000
	Within Groups	382.782	48	7.975		
	Total	1950.151	71			

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Fig.1

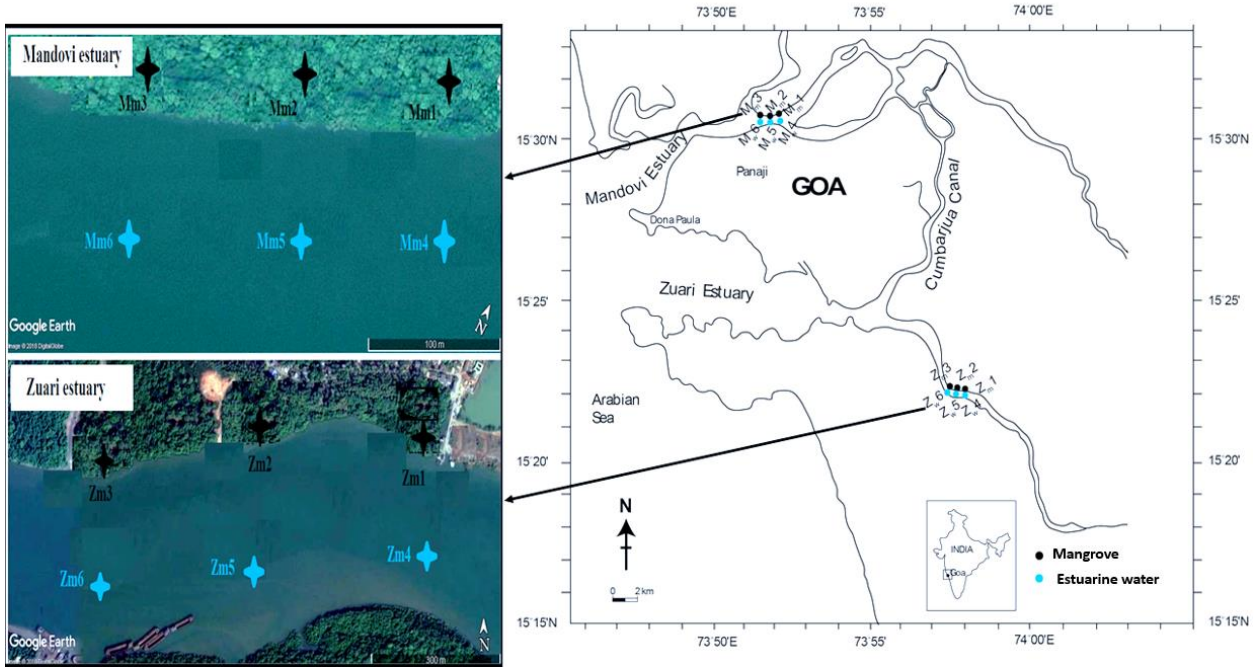


Fig. 2

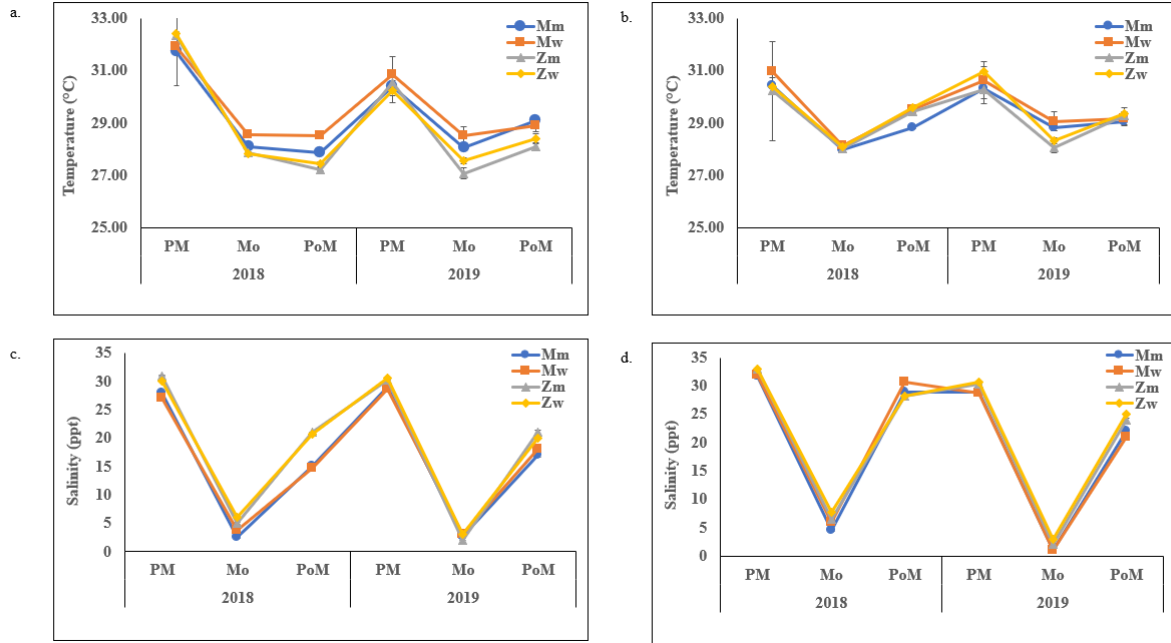


Fig. 2

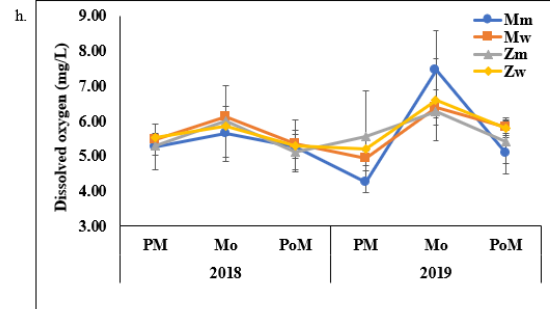
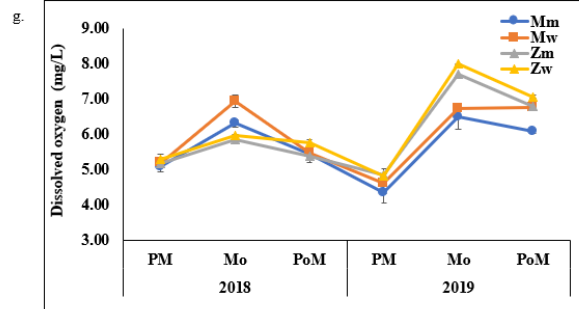
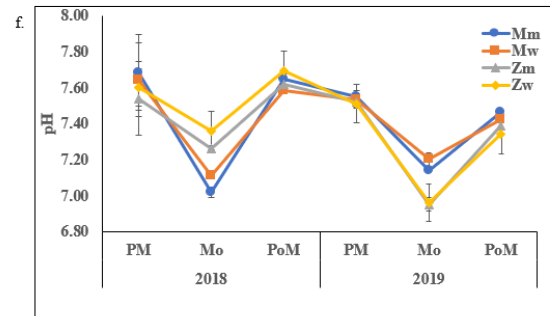
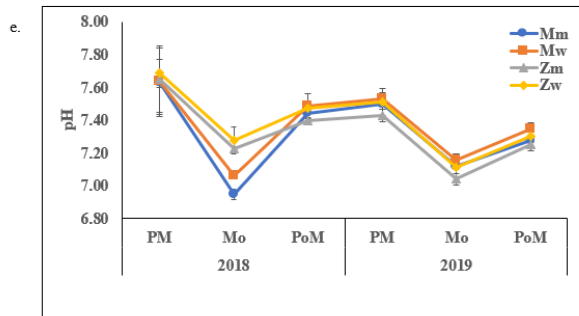




Fig. 3

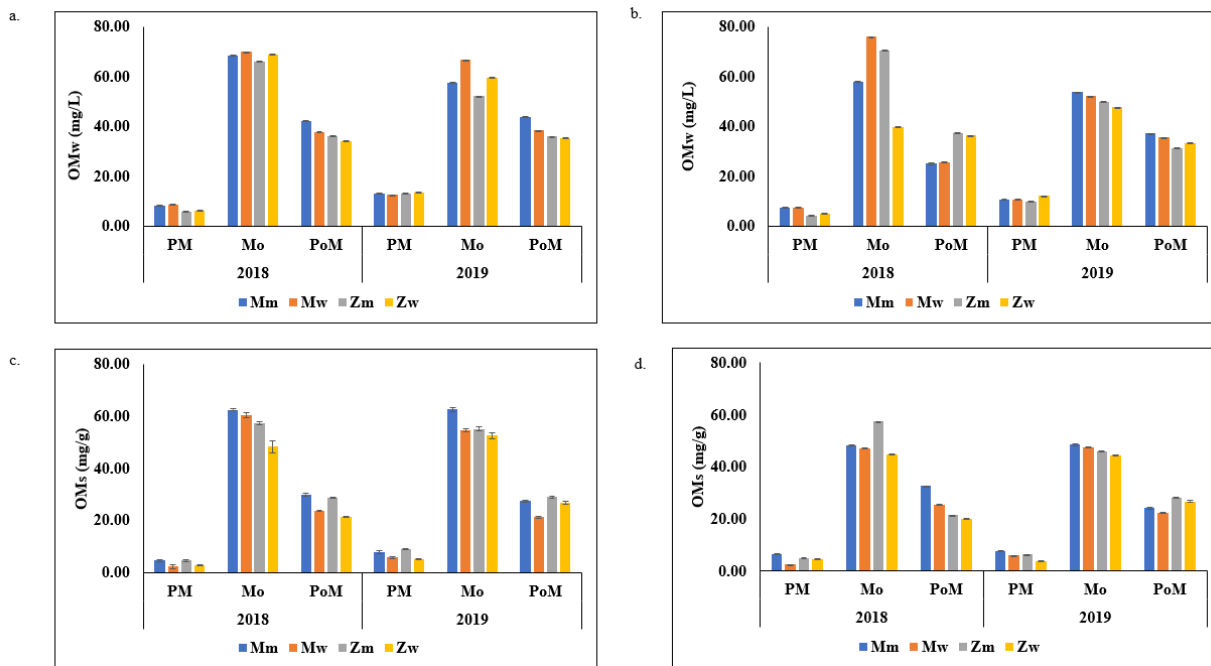


Fig. 4

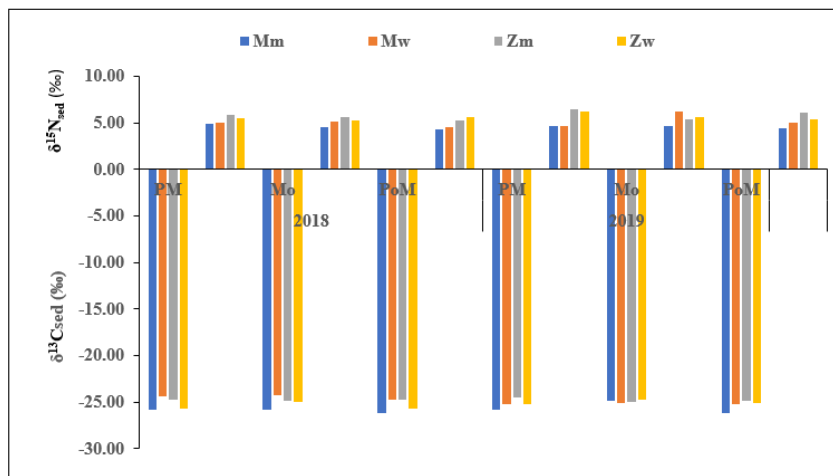


Fig. 5

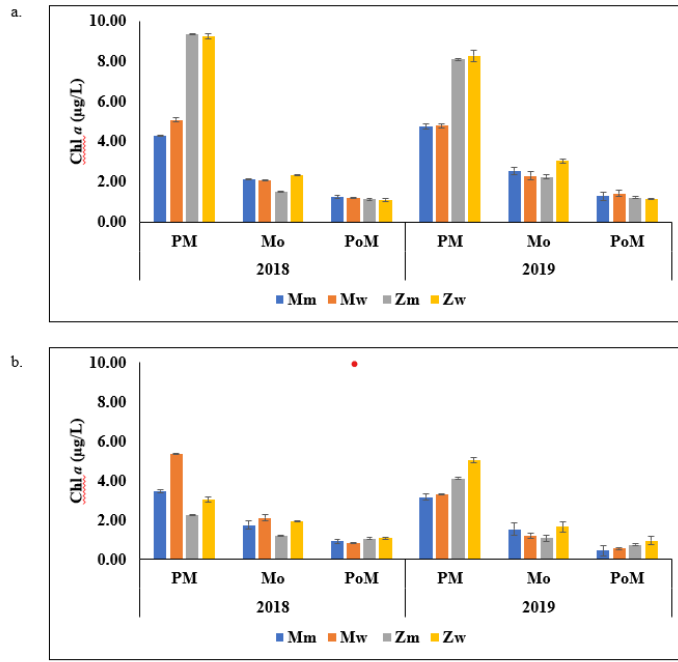


Fig. 6

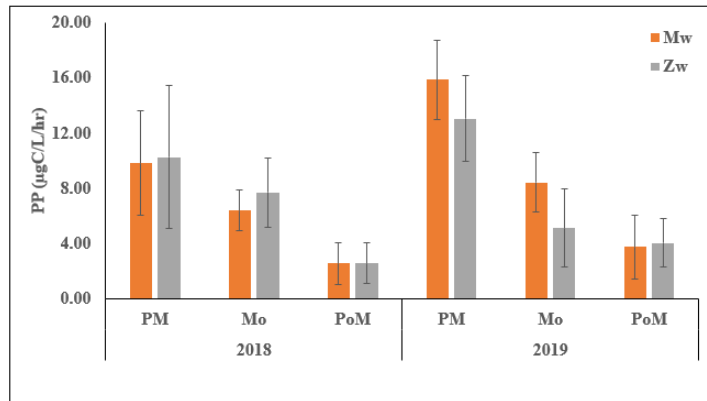


Fig. 7

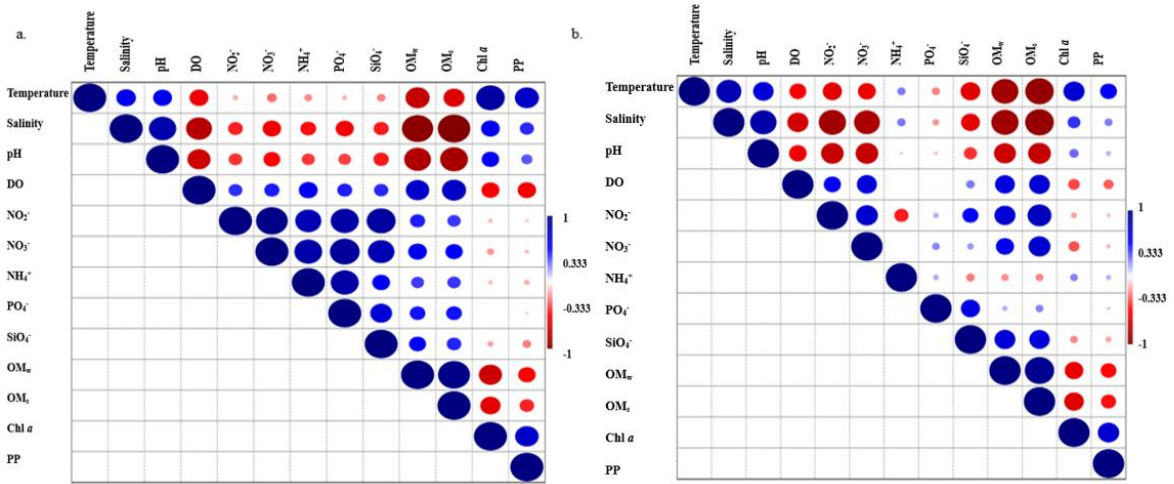
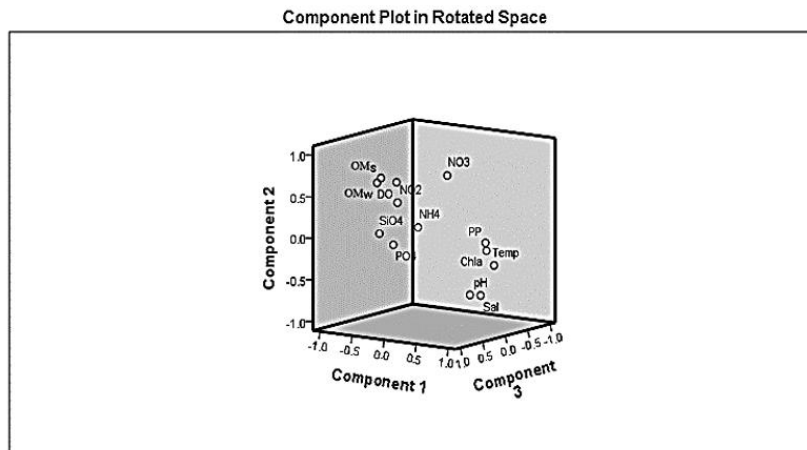


Fig. 8



Component	Eigen value	% of variance	Cumulative % of variance
1	6.25	48.13	48.13
2	1.93	14.89	63.02
3	1.16	8.92	71.95