

## **Phosphorus cycling from a coastal upwelling zone in the southeastern Arabian Sea**

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### **Abstract**

The present study examined the seasonal cycling of phosphorous (P) along the southwest coast of India (SWCI) based on two cruises during the southwest monsoon (SWM) and northeast monsoon (NEM) of 2018. During SWM, the entire SWCI experienced intense upwelling manifested by the incursion of cold, nutrient-rich, and hypoxic waters. During NEM, the region was transformed into a warm, well-oxygenated and nutrient-deplete environment. Dissolved inorganic phosphorus (DIP) was significantly high in the subsurface during SWM due to its release from sediments. The sediment P was high and showed an increasing trend towards the south, principally dependent on the sediment texture, organic carbon, and Fe concentrations. Bioavailable P, the sum of exchangeable (P<sub>Ex</sub>) and reducible (P<sub>Fe</sub>) fractions, was almost consistent (5-20%) over seasons, though P<sub>Fe</sub> showed a marked reduction during SWM. Authigenic fraction (P<sub>Aut</sub>) was the most dominant (46%), followed by detrital (P<sub>Det</sub> 41%) and residual (P<sub>Res</sub> 8%) fractions. Principal Component Analysis (PCA) of geochemical parameters for SWM was indicative of the high dissolution of Fe (oxy)hydroxides under hypoxia releasing P and its complexation with organic matter and Fe. PCA results for the NEM was different, as it indicated increased preservation of P associated organic matter and Fe, alternately favouring the formation of P<sub>Aut</sub> in sediments. The study's significance is the observation that the bottom water oxygen concentration can significantly influence sedimentary P cycling in tropical coastal upwelling zones.

**Keywords:** Phosphorous; Fractionation; Upwelling; Hypoxia; Bioavailability

## 1.Introduction

Phosphorous (P) is one of the essential nutrients that limit the primary productivity in marine ecosystems (Carpenter et al., 1998; Tyrrell, 1999). Sediments are commonly regarded as the source and sink of P, while its excess concentration in water can lead to eutrophication (Søndergaard et al., 1996; Jarvie et al., 2005; Huang et al., 2015). Most of the P derived anthropogenically or naturally, reaches the aquatic environment, where it is adsorbed onto sediments (Withers and Jarvie, 2008; März et al., 2014) to become the sink and source of P (Spivakov et al., 1999) causing eutrophication (Søndergaard et al., 2003; Schindler, 2006; Lewis et al., 2007). Therefore, quantification of P fractions in sediments is essential to understand its geochemical cycling. Geochemistry of P depends significantly on the sediment quality and depositional environment (Søndergaard et al., 1996). P released from sediments can substantially impact the aquatic ecosystems (Malecki et al., 2004; Reddy et al., 2007), though its availability depends on the relative proportion of its fractions in sediments. The dominant fractions (Fe or Al oxides, CaCO<sub>3</sub>) of P are either adsorbed or precipitated as apatite or Ca-phosphate (Khare et al., 2007; Filippelli, 2008). Calcareous sediments also concentrate apatite (Berg et al., 2004), whereas P adsorption to metal oxides predominates in non-calcareous sediments (Berg et al., 2004). The adsorption of P by metal oxide occurs at pH<6.5, while it is adsorbed onto calcium carbonate at higher pH (Wang et al., 2010; Yin et al., 2013). Factors such as redox condition, sedimentation rate, grain size and metal (oxy)hydroxides have a significant impact on the dynamics of P. Authigenic P called phosphorites (Cook, 1984) are found to be rich in sediments of upwelling areas like Oman margin (Schenau et al., 2000), the continent margin of Peru (Froelich et al., 1988) and shelf of Namibia.

The southwest coast of India is characterised by coastal upwelling during the SWM (May to September) and by downwelling during the NEM (November to February) (Shetye et al., 1989; Shetye et al., 1990; Shah et al., 2019). The biogeochemistry of SWCI is influenced by seasonal changes in the mixed layer dynamics caused by the southwest monsoon and northeast monsoon (Gupta et al., 2016). During SWM, the cold nutrient-rich and oxygen-depleted waters brought by upwelling make the SWCI one of the most productive regions, while well oxygenated and nutrient-depleted conditions prevail during the NEM (Qasim, 1982; Naqvi et al., 2006, 2009; Sudheesh et al., 2016). However, the upwelling also leads to the incursion of hypoxic waters through the bottom, which influences the P dynamics substantially (Jacob et al., 2010). There are only a few studies on the P fractions in sediments along the SWCI (Babu and Nath, 2005; Jacob et al., 2010; Sudheesh et al., 2017; Linsy et al., 2018), whereas all other studies focused on total sedimentary P (Murthy et al., 1966; Setty and Rao, 1972; Rao et al., 1978, 1987; Paropkari, 1990). Hence, a comprehensive study on P fractionation in sediment

was undertaken to explain the P dynamics in a productive coastal environment. The different P fractions were quantified in the sediments along the SWCI during two seasons of SWM and NEM.

## **2 Materials and Methods**

### **2.1 Study Area**

The present study mainly covered the inner shelf (10-50 m) of the southeastern Arabian Sea (SEAS) between  $\sim 9^\circ$  and  $13^\circ$  N (Fig. 1). The SWCI bordered on the east by the Western Ghats and the Arabian Sea on the west. More than 40 small west-flowing rivers (streams) originating from the western Ghats debouch into the Arabian Sea through several lagoons and backwaters in the coastal belt (Murthy, 1975; Mallik et al., 1987). Intense rainfall (approximately 250 cm) during the SWM induce freshwater plumes over the inner shelf of SWCI. The low saline waters protrude out of the estuarine mouth into the nearshore region floats over the high saline oceanic water. The outward extension of these freshwater patches depends on a number of factors including volume of outflow, inlet width, tidal actions, winds, and bathymetry (Nair et al., 1989; Seena et al., 2019). The monsoonal freshwater discharge brings a high amount of nutrients, heavy metals, organic matter, and sediments into the coastal environment. India's west coast is densely populated, and the coastal waters are likely to be altered by anthropogenic interventions such as heavy metal pollution, acidification, and eutrophication (Laluraj et al., 2005; Cheriyan et al., 2015; Sreekanth et al., 2015). The intense upwelling during SWM makes SEAS one of the world's highly productive regions (Prakash and Ramesh, 2007; Gupta et al., 2016). Consequently, the upwelling induced hypoxia increases the oxygen demand for organic matter mineralisation due to high surface production (Gupta et al., 2016; Sudheesh et al., 2016).

### **2.2 Sampling**

Water and sediment sampling was carried out across six transects of Alappuzha (A), Cochin south (C), Cochin North (N), Kozhikode(K), Payyannur (Y) and Mangalore (M) onboard the coastal research vessel Sagar Purvi during 11-18 September 2018 (late SWM) and 19-25 December 2018 (NEM) along the southwest coast of India (Fig. 1). Each transects covered three stations at a water depth 10m, 30m and 50m, respectively. Water samples collected from standard depths using a Niskin sampler were sub-sampled for nutrients and dissolved oxygen (DO) measurements. Water column temperature and salinity were recorded using a CTD profiler (SEABIRD 19 plus). Surface sediments were collected using a Van Veen grab and subsampled into acid cleaned high-density polyethylene bottles, capped, sealed and kept frozen till analysis.

## 2.3 Analytical methods

### 2.3.1 Dissolved oxygen (DO) and dissolved inorganic phosphorus (DIP)

Dissolved Oxygen was analysed following Winkler's method (Grasshoff et al., 1999) using an automatic titration system (Metrom 865 Dosimat plus; detection limit 2  $\mu\text{M}$ ). Samples for DIP were filtered through glass fibre filter paper (GF/F) and estimated following standard procedure (Grasshoff et al., 1999) using an auto-analyser (Skalar, SAN++). A UV lamp attached to the autoanalyser was used to oxidise the samples for total dissolved P (Grasshoff et al., 1999). Dissolved Organic P (DOP) was calculated by subtracting DIP from total dissolved P (detection limit 0.07  $\mu\text{M}$ ). The precision of these analyses is ensured by measuring standards and triplicates and was within  $\pm 3\%$ .

### 2.3.2 Sediment texture and other geochemical parameters

Sediment texture (sand, silt and clay) was estimated by pipette analysis of wet sediment after removing inorganic carbon by 1M HCl and organic matter by 30%  $\text{H}_2\text{O}_2$  (Folk 1974). The texture was analysed using a Laser Particle Size Analyser (Mastersizer 3000), and accuracy was  $\pm 0.7\%$  for polystyrene latex standards. Total Organic Carbon (OC) was analysed using a Vario EL III CHNS analyser after treating the freeze-dried homogenised samples with 1M HCl to remove inorganic carbon. Acetanilide was used as the standard which yielded a detection limit of 0.07 %, and accuracy was within  $\pm 2\%$ . Fe was quantified by digesting the sediment in a mixture of  $\text{HNO}_3$ : HCl: HF (7:2:1) acids in a microwave digester (Milestone Ethos Easy, USA) and analysing the extract using Inductively Coupled Plasma-Optical Emission Spectrophotometer (ICP-OES, Thermo Scientific-CAP 7000 Series).

### 2.3.3 Fractionation of phosphorus

Sediment samples were subjected to P speciation using the SEDEX sequential extraction procedure modified by Ruttenberg et al. (2009). The five P fractions sequentially extracted by this method are i) exchangeable or loosely adsorbed ( $\text{P}_{\text{Ex}}$ ) ii) Fe-(oxy) hydroxide ( $\text{P}_{\text{Fe}}$ ) iii) authigenic apatite ( $\text{P}_{\text{Aut}}$ ) iv) detrital apatite ( $\text{P}_{\text{Det}}$ ) and (v) residual organic ( $\text{P}_{\text{Res}}$ ).  $\text{P}_{\text{Ex}}$  was quantified using bicarbonate-dithionite (BD) reagent suggested by Jensen and Thamdrup (1993), because i) citrate ion may dissolve Ca bound P also to overestimate  $\text{P}_{\text{Ex}}$  and ii) BD can minimise the interference due to molybdate complex. All extracts were filtered (GF/F, 0.7  $\mu\text{m}$  pore size) and analysed following the standard procedure (Grasshoff et al., 1999) using an autoanalyser (Skalar SAN++). The extract from step ii (NaBD) was purged with purified air to remove dithionite. For estimation of organic phosphorous, samples were oxidised using sodium persulphate and irradiated by ultraviolet light. Each analysis was accompanied

by blanks and standards (in triplicates) to minimise contamination from chemicals and other laboratory practices, and the standard deviation was  $\pm 3\%$  ( $P_{Ex}$ ,  $P_{Fe}$  and  $P_{Res.}$ ) and  $\pm 5-6\%$  ( $P_{Aut}$  and  $P_{Det}$ ).

#### 2.3.4 Statistical analysis

One-way Analysis of variance (ANOVA), correlation analysis and factor analysis were done using 'Statistical Package for Social Sciences (SPSS), version-24'. Spatial and seasonal variations were assessed using ANOVA with season and space (stations) as the source of variation. The log (x+1) transformation was used to obtain a normal distribution of the data set, and normality was checked using Webster's criteria, 2001. Principal component analysis (PCA) was used to extract information from the most meaningful parameters which better described the overall data and afford data reduction with minimal loss of information (Katsaounos et al., 2007). Factor loading was considered significant if they were  $>0.50$ .

### 3 Results

#### 3.1 Temperature and salinity

The water column was warm ( $>28^{\circ}\text{C}$ ) and vertically mixed with a deep mixed layer (ML) during NEM, whereas the SWM season experienced a drastic change due to upwelling that leads to a shallow ML of  $< 5$  m (Fig. 2). It can be noted that the depth of  $26^{\circ}\text{C}$  isotherms ( $D_{26}$ ), considered as the progression of upwelling (Gupta et al., 2016) closely indicated the bottom of the ML. An upsloping of  $D_{26}$  was noticed along the southwest coast with varying intensities. In Alappuzha transect,  $D_{26}$  was at 6m in the coastal station (20m), which deepened to 10m in the offshore (40m). The upsloping of  $D_{26}$  was also evident in the south Cochin transect, though a layer of warm freshwater from the Cochin estuary restricted the upwelling to the subsurface. Further north, the intensity of upwelling gradually was found to increase between Calicut and Mangalore.  $D_{26}$  was as shallow as at 4-5 m along Calicut, while it almost reached the surface in Payyannur and Mangalore transects. From the vertical salinity profiles, the progression of upwelling over the entire study domain is evident (Fig. 3). The salinity was generally high during SWM due to Arabian Sea high saline waters and low during NEM due to the incursion of Bay of Bengal waters.

#### 3.2 Dissolved oxygen

The entire water column along the southwest coast of India remained well-oxygenated (6-8 mg/l) during NEM. An upwelling induced incursion of hypoxic waters was the dominant feature of the SWM (Fig. 4). In Alappuzha, the oxygen deficiency during SWM was not so acute at 10 m (1.79 mg/l), but it was hypoxic (0.8 mg/l) at 50m depth. The coastal waters of Cochin (south) were hypoxic

(0.4 mg/l) up to 30 m in the bottom waters, but remained less oxygen-deficient (2.1 mg/l) at 50 m. The bottom oxygen deficiency was a common feature of SWM from between Cochin and Mangalore. The hypoxia was less intense in Alappuzha and Cochin(S) but increased towards Mangalore, reaching suboxic in Payyannur and Mangalore transects.

### *3.3 Dissolved inorganic and organic P*

DIP and DOP were in general, low during NEM due to the lower terrestrial inputs, absence of upwelling and intrusion of BoB waters (Fig. 5). DIP and DOP ranged from 0.26 to 1.2 $\mu$ M and 0.10 to 0.50 $\mu$ M respectively in all the transects. During SWM, the upwelling was found to induce a four-fold enrichment of DIP (0.50 to 2.37 $\mu$ M) over the entire study domain (Fig. 5). The bottom DIP levels showed a steady increase towards Mangalore (M), in accordance with the intensity of hypoxia in the region. DOP also showed an increase (0.20 to 2.00  $\mu$ M) in the surface, especially at Calicut (K), Payyannur (Y) and Mangalore (M) (Fig. 6). Enrichment of DOP in the bottom was observed from Cochin north (N) till Payyannur (Y) during SWM. A northward increase in DIP enrichment, especially in the bottom, could be due to the release of P from sediments under hypoxic conditions.

### *3.4 Sediment characteristics*

With a change in the season from SWM to NEM, the sediment texture generally exhibited a clear transition from silt to clay. The nearshore (10m) stations were silty, except in Alappuzha, where the sediments were clayey. The sediments in the Cochin shallow region remained clayey silt during both seasons. In the mid-shelf (30m), silt was predominant in Cochin, Payyanur, and Mangalore, whereas Kozhikode and Cochin North were sandy. In the offshore region (50m), clay dominated in all transects. Although there was only a slight seasonal variation in the textural composition, significant spatial variation was evident. In the nearshore region(10m), there was a change from clayey sediment in Alappuzha to silty sediment in Mangalore. The offshore area (50m) was clayey silt in Alappuzha, whereas it was clayey in Mangalore.

Sediment organic carbon generally showed both spatial and seasonal variations and exhibited a positive correlation with clay and negative correlation with sand (Fig.7). In Alappuzha, OC was 1-2.2% during SWM and 2-7.91% during NEM. In Cochin south, OC varied from 3.23-7.04% during SWM and 2.2-6.22% during NEM. In Cochin north, the lower OC values (0.5-6%) were observed during SWM and the highest values (1.5-6%) during NEM. In Kozhikode transect, OC was 0.1-3.45% and 0.2-6.8% during SWM and NEM, respectively. In Payyanur, OC increased from 1.67-5.69% during SWM to 2.3-6.5% during NEM. Similarly, in Mangalore, OC increased from 1.9-5.25% during SWM to 1.43-6% during NEM.

Diagenesis of phosphorous in the marine environment can also be studied using changes in the Fe and Mn concentrations in sediments (Álvarez-Iglesias et al., 2003). The result of Pearson correlation analysis of seasonal geochemical data was presented in Table 1. Mn exhibited significant spatial variation ( $p < 0.05$ ), though there was no correlation with P fractions. Fe showed a significant positive correlation with TP ( $p < 0.01$ ) during both seasons, indicating Fe's influence in the enrichment of P in sediments. Bioavailable P fractions ( $P_{bio}$ ) which is the sum of  $P_{Ex}$  and  $P_{Fe}$  showed a significant positive correlation with exchangeable Fe fraction ( $Fe_{ex}$ ) ( $p < 0.05$ ) showing the strong relation of  $P_{bio}$  with  $Fe_{ex}$ . The negative correlation of  $P_{bio}$  with total Fe ( $p < 0.05$ ) indicated that there were no significant contributions by the persistent Fe fractions, even though stable Fe fractions were a significant factor in the enrichment of P in sediments.

Total Phosphorus (TP) in sediments did not vary seasonally (Fig 8a), though there was a marginal reduction in Mangalore. TP was in the range 260-1686 $\mu$ g/g (Alappuzha), 504-1439 $\mu$ g/g (Cochin south), 174-1707 $\mu$ g/g (Cochin north), 75-1170 $\mu$ g/g (Kozhikode), 585-873 $\mu$ g/g (Payyanur) and 389-957 $\mu$ g/g (Mangalore). TP was high in the nearshore regions (278-1707 $\mu$ g/g) and decreased towards mid-shelf (174-975 $\mu$ g/g) and offshore (331-799.24 $\mu$ g/g) and towards the north (Mangalore). The low TP in the mid-shelf region could be due to increased sand content, and its reduction towards Mangalore could be due to hypoxia. TP also showed a positive correlation with clay and negative correlation with sand.

### 1.5 Phosphorous fractions

The variations in the different P fractions are illustrated in Fig 8b. Exchangeable fraction ( $P_{Ex}$ ) ranged from 13.2 -58.73  $\mu$ g/g and comprised 2-12% of TP during SWM. During NEM,  $P_{Ex}$  ranged from 12.68-84.79  $\mu$ g/g and on an average comprised 5% of TP.  $P_{Ex}$  in the nearshore region increased from 1.5-7.67% of TP during NEM to 3-11.37% of TP during SWM.  $P_{Ex}$  was lowest in Mangalore during both seasons. In the mid-shelf region,  $P_{Ex}$  was high (3.12-18.6%) during SWM and low (1.63-7.84%) during NEM. High  $P_{Ex}$  in Cochin north and Kozhikode are associated with a sandy texture. In the offshore region,  $P_{Ex}$  varied from 2-5.42% of TP during the SWM to 2.49- 7.84% during NEM. Overall,  $P_{Ex}$  showed an evident spatial variation with a decreasing trend towards Mangalore and away from the coast during both seasons.

Fe bound fraction ( $P_{Fe}$ ) is bioavailable since it is bound to Fe (oxy)hydroxides and the sum of  $P_{Ex}$  and  $P_{Fe}$ , constitute the total bioavailable ( $P_{bio}$ ) fraction.  $P_{Fe}$  ranged from 2 -79  $\mu$ g/g and comprised 0.2-10% of TP during SWM. During NEM,  $P_{Fe}$  ranged from 0.9-79  $\mu$ g/g and on an average comprised 3% of TP. In the nearshore region (10m),  $P_{Fe}$  was low (0.31-4.63%) during SWM and high (1.6-7.15%)

during NEM. In the mid-shelf region (30m), it was low (0.19-3.48%) during SWM and high during NEM (0.5-1.35%). In the offshore region (50m), it was low (0.26-2.76%) during SWM and high (0.85-10%) during NEM. The high values in Cochin south, north and Mangalore during SWM may be due to increased fluvial supply that altered the texture. A decline in  $P_{Fe}$  observed during SWM was also following hypoxia.

Authigenic P ( $P_{Aut}$ ) was one of the dominant fractions in all transects, which on an average was  $339.8 \pm 281 \mu\text{g/g}$  and  $343 \pm 263 \mu\text{g/g}$  during SWM and NEM respectively. The nearshore region accounted for 21.3-53.4% of TP during SWM, 20-51.9% in the mid-shelf and 25-64.3% in the offshore. During NEM,  $P_{Aut}$  accounted for 29-74% in the nearshore, 38-59.8% in the mid-shelf and 20.4-43% in the offshore region. A decreasing trend of  $P_{Aut}$  from Alappuzha to Mangalore observed during SWM was absent during NEM.  $P_{Aut}$  exhibited a negative correlation with the detrital fraction during both the seasons ( $p < 0.01$ ). Detrital fraction ( $P_{Det}$ ) was the second most abundant after  $P_{Aut}$ , which on an average was  $386.6 \pm 267 \mu\text{g/g}$  and  $340 \pm 204 \mu\text{g/g}$  during SWM and NEM respectively. In regions of high  $P_{Aut}$ , the  $P_{Det}$  was low and vice versa. In the nearshore region,  $P_{Det}$  was 30-63% of TP during SWM and 12-60% during NEM. In the mid-shelf, it was in the range 33.07-49.82% of TP, whereas it was accounted for 34-73% in the offshore during both seasons. Both  $P_{Det}$  and  $P_{Aut}$  remained almost constant without any spatial and seasonal variations due to their high concentrations.

Residual organic fraction ( $P_{Res}$ ) on average was  $34 \pm 25 \mu\text{g/g}$  and  $52 \pm 35 \mu\text{g/g}$  during SWM and NEM, respectively.  $P_{Res}$  accounted for 0.8-14% of TP in the nearshore and mid-shelf regions with an increasing trend towards Mangalore, whereas the offshore area exhibited a decreasing trend (1.01-13.62%) towards Mangalore.  $P_{Res}$  were relatively low in the offshore region than the shallow area and did not show seasonal variations.

#### **4 Discussion**

The coastal upwelling is the main causative factor that significantly lowers the temperature, dissolved oxygen, and increases the nutrient concentration along India's southwest coast (Banse, 1959; Shah et al., 2019; Gupta et al., 2016). This region receives freshwater influx from more than 40 small rivers (stream) originating from the Western Ghats. The coastward impact of these rivers is minimal, probably in the nearshore region and depends on a number of factors including volume of outflow, inlet width, tidal actions, winds, and bathymetry (Nair et al., 1989; Seena et al., 2019). Previous literature has revealed that the impact of freshwater plumes along the southwest coast of India was observed in short spatial scales in the adjoining river mouths (Lallu et al., 2014; Vinita et al., 2015; Santhikrishnan et al., 2021). Therefore, the impact of land derived phosphorus content has a significant effect in the



nearshore region (maximum up to 5-10 m water depth), beyond which upwelling induced nutrient enrichment is the main contributing factor.

The variation observed in the P distribution is generally in accordance with the seasonal changes in the hydrography along the southwest coast of India. The nutrient-deplete (DIP  $\sim 0.50 \mu\text{M}$ ) water environment during NEM was drastically changed to the nutrient-replete environment (DIP range 1.5-4.4 $\mu\text{M}$ ) during SWM due to intense coastal upwelling and re-mineralisation (Schenau and De Lange, 2001). The nutrient enrichment during SWM subsequently enhanced the plankton productivity, which on decomposition intensified the oxygen deficiency in the water column (Gireeshkumar et al., 2017; Jyothibabu et al., 2018), facilitating the growth of anaerobic bacteria (Anas et al., 2018). Fe likely entrained from deeper anoxic sediment layers during the dissolution of Fe oxides may re-precipitate and enriched in the surface sediments (Krom and Berner, 1980; Jensen et al., 1995; Slomp et al., 1996). Such a condition may not arise in hypoxic waters, since all the excess P released are immediately used for enhanced biological production.

#### *4.1 Geochemical forms of Phosphorous*

Phosphorous geochemistry of coastal marine systems in India are well documented. The dominance of organic P, as well as the immobilisation of P in the form of authigenic, detrital and humic acid, bound P is the primary process behind P cycling in mangrove ecosystem in the southeastern and southwestern coast of India (Bala Krishna Prasad and Ramanathan, 2009; Ranjan et al., 2010; Joseph et al., 2010; Resmi et al., 2016). The estuarine dynamics of P in the southwest and southeast coast of India largely depends on the strong seasonal heterogeneity of Fe bound P concerning the prevailing salinity fluctuations and emphasised the internal loading of P in estuaries (Ashraf et al., 2006; Renjith et al., 2011; Gireeshkumar et al., 2012; Renjith et al., 2015; Barik et al., 2018). Therefore, this study describes the P dynamics with respect to the varying redox conditions in the sediment-water interface.

The variation in TP (174-1707  $\mu\text{g/g}$ ) observed in the present study is comparable with previous reports from the same region (Acharya et al., 2016; Sudheesh et al., 2017). Since the hydrography of the SWCI undergoes distinct changes from SWM (hypoxic) to NEM (oxic), the biogeochemical properties are expected to change substantially. Thus,  $P_{\text{Aut}}$  (41-92%) was the major fraction in sediments followed by  $P_{\text{Det}}$  (12-73%) and  $P_{\text{Res}}$  (0.8-14%), whereas the contributions of  $P_{\text{Ex}}$  (1.5-8%) and  $P_{\text{Fe}}$  (0.5-7%) were relatively minor.  $P_{\text{Ex}}$  is a bioavailable fraction usually released during early diagenesis (Andrienx and Aminot, 2001; Kaiserli et al., 2002; Yang et al., 2017). In the present study,  $P_{\text{Ex}}$  was relatively high in the nearshore than the offshore regions, especially in Alappuzha. The positive correlation of  $P_{\text{Fe}}$  with labile Fe (reactive Fe) indicates their common origin.  $P_{\text{Aut}}$  was low during

SWM and high during NEM in an earlier study (Edwin and Meenakumari, 2006), which was not observed during the present study. Moreover, the  $P_{Res}$  in this study is also lower than that of the east coast of India. Studies on the mangrove intertidal systems have identified  $P_{Fe}$  as a significant fraction and attributed this to the absence of hypoxia and low productivity along India's east coast (PrakashBabu and Ramaswamy, 2017; Prasad and Ramanathan, 2010; Mohanty et al., 2018).

#### 4.2 Influence of Fe on P fractions

Fe (oxy) hydroxides are major scavengers of P under oxic condition (Slomp et al., 1996), while dissolution of Fe (oxy) hydroxide during hypoxia can release of more P to water (Kraal et al., 2017; Sudheesh et al., 2017). Since the bioavailable fraction of P is immediately used for biological production,  $P_{Fe}$  is expected to be low in the study region during SWM. However, there were locations such as Cochin and Mangalore where  $P_{Fe}$  was high (Fig 9), indicating that there may be several factors influencing the dissolution and entrapment of  $P_{Fe}$ . P enrichment can also be observed using Fe/P ratios (Sondergaard et al., 2003; Coelho et al., 2004). High Fe/P ratio ( $\geq 20$ ) during oxic conditions points out a high removal of P by Fe oxides, while a low ratio indicates its release through dissolution under oxygen-deficient conditions (Caraco et al., 1993; Søndergaard et al., 2003). Accordingly, during SWM, Fe-P was very low over the entire study region (Fig 9), while the high ratios at Cochin ( $\leq 15$ ) and Mangalore ( $\geq 30$ ) were indicating high retention of P in sediment. Enrichment of DIP in the bottom during upwelling may also be due to its release from sediment.  $P_{Fe}$  concentrations showed a spike in sandy sediments of Cochin North during SWM and Kozhikode during NEM. There was a significant correlation for Fe with silt ( $p < 0.01$ ) throughout the study domain. Overall, a decrease in  $P_{Fe}$  was evident during SWM, except in regions of sandy substrates or hypoxic conditions. The significant positive correlation of  $P_{Fe}$  ( $p < 0.05$ ) with organic P (OP) indicates its biogenic origin.  $P_{Aut}$  was the major component in sediments followed by  $P_{Det}$  and did not show any spatial or seasonal variations. During both seasons, the average percentages of  $P_{Aut}$  (46, 41) and  $P_{Det}$  (45, 43) were almost comparable, while  $P_{Res}$  varied from 0.8 to 14 % and were independent of sediment texture.

#### 4.3 Influence of organic carbon on phosphorus fractions

The biogenic fluxes in the northern Arabian Sea are consistently high due to intense upwelling during SWM and convective mixing during NEM (Gauns et al., 2005). Consequently, most of this biogenic flux gets oxidised in the oxygen minimum zone, and only a fraction reaches the bottom. In the absence of productivity data and P flux in the present study, OC/OP ratio (Fig. 9) was used to quantify the residual organic ( $P_{Res}$ ) fraction (Babu and Nath, 2005). OC/OP higher than Redfield OC/OP values have been linked to the preferential regeneration of OP compared to OC during

decomposition (Filippelli and Cowie 2017; Ingall et al., 1993; Andrieux-Loyer and Aminot, 2001; Monbet et al., 2007; Jordan et al., 2008; Gikuma-Njuru et al., 2009; Reimer et al., 2010). In the present study,  $C/P_{Res}$  was  $> 106$  during SWM suggesting an active removal of P, whereas it was lower ( $159 \pm 88$ ) or close to Redfield OC (106) during NEM indicating an active degradation of OC. P released during degradation is either bound to oxides or transformed as  $P_{Aut}$  (Slomp et al., 1996; Ruttenger and Berner 1993).

#### 4.4 Principal Component Analysis

Principal component analysis (PCA) was carried out to delineate the important biogeochemical processes regulating the P cycling in the study region. The results showed a significant difference in the geochemistry P over the season. The prominent loading of parameters as Principal Components (PCs) and their clustering are used to explain their geochemical interactions in sediments (Table 2 a & b).

PCA for the SWM season resolved five PCs that explained 91% variance. PC1 could alone explain 24% variance (eigen value-4.81) and was mainly contributed by  $P_{bio}$  ( $P_{Ex} + P_{Fe}$ ) and environmental factors such as DO, salinity and temperature. Thus, PC1 indicates the redox sensitivity of  $P_{Fe}$  release during the dissolution of Fe (oxy) hydroxides. Similarly, PC2 (22% variance; eigen value-3.51) is contributed by OC, Fe and TP indicating the role of organic matter and Fe in the deposition of P. PC3 accounted 18% of the variance (eigen value-2.08) and composed of  $P_{De}$ , silt and clay indicate its lithogenic contribution. PCA results for the NEM season also yielded five PCs that could explain 82% variance. But there was a difference in the loading parameters indicating the seasonal influence on the biogeochemical cycling of P. PC1 accounting 24% variance (eigen value-4.69) was positively loaded with TP, silt, OC and Fe. PC2 accounting 19% variance (eigen value-2.47) had positive loading of  $P_{Aut}$ , TOP and OC. PC2, therefore, indicated the preference of P accumulation by organic matter and Fe, alternately favouring re-mineralisation to form  $P_{Aut}$  as a major pathway of P cycling in sediments.

## 5 Conclusion

The present study examined the changes in the P fractions in sediments along the SWCI over two seasons. The water column was hypoxic and nutrient-replete during the SWM, while NEM was characterised by an oxic and nutrient-depleted water column. The enrichment of DIP in the subsurface during the SWM was due to its release from sediments. P fractionation showed that texture, organic matter, and Fe are the major factors controlling the P cycling in sediments. The dissolution of  $P_{Fe}$  releasing P into the overlying water column was a significant process during the SWM. In contrast, an

increased re-mineralisation leading to the formation of  $P_{Aut}$  was the dominant pathway during the NEM.

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## Figure captions:

**Figure 1** Map of the study region showing locations of sampling stations along the southwest coast of India (Five coastal transects; Alappuzha, Cochin South, Cochin North, Kozhikode, Payyannur and Mangalore. Three stations were sampled at each transect at a water depth of 10m, 30m and 50 m and the red dots indicate these station locations).

**Figure 2** Seasonal distribution of temperature in the coastal transects along the southwest coast of India.

**Figure 3** Seasonal variability of salinity in the coastal transects along the southwest coast of India.

**Figure 4** Distribution of Dissolved Oxygen (DO) in the coastal transects along the southwest coast of India.

**Figure 5** Cross shelf variations of dissolved inorganic P (DIP) in the coastal transects.

**Figure 6** Cross shelf variations of dissolved organic phosphates (DOP) in the coastal transects

**Figure 7** Seasonal variation of total organic carbon (TOC) and sediment texture in the study region.

**Figure 8** (a) Seasonal variations of TP and (b) relative abundance of various geochemical forms of P during southwest monsoon (SWM) and northeast monsoon (NEM).

**Figure 9** (a) Seasonal variation in OC/OP and Fe/TP ratio during southwest monsoon (SWM) and northeast monsoon NEM.

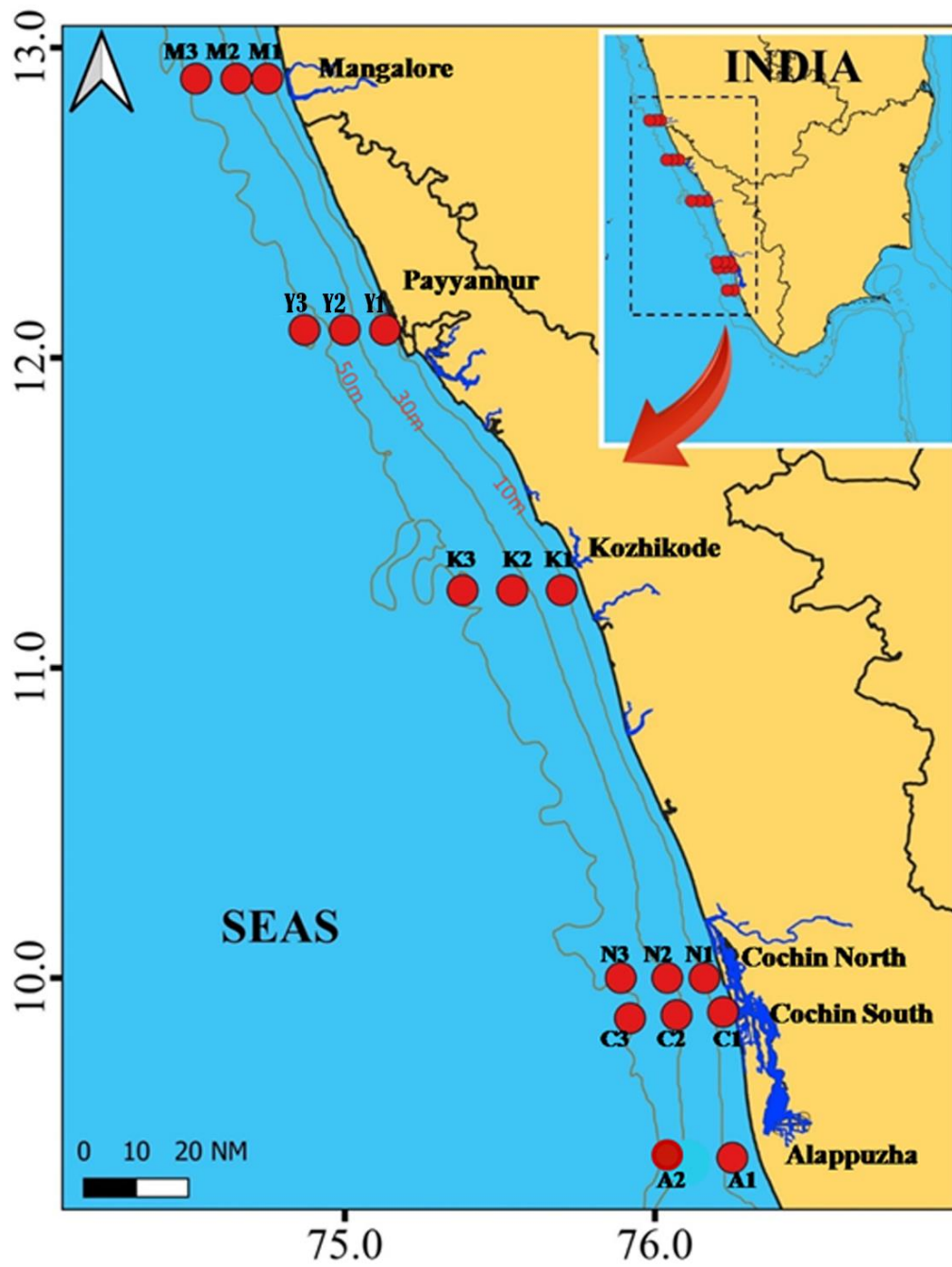


Figure 1

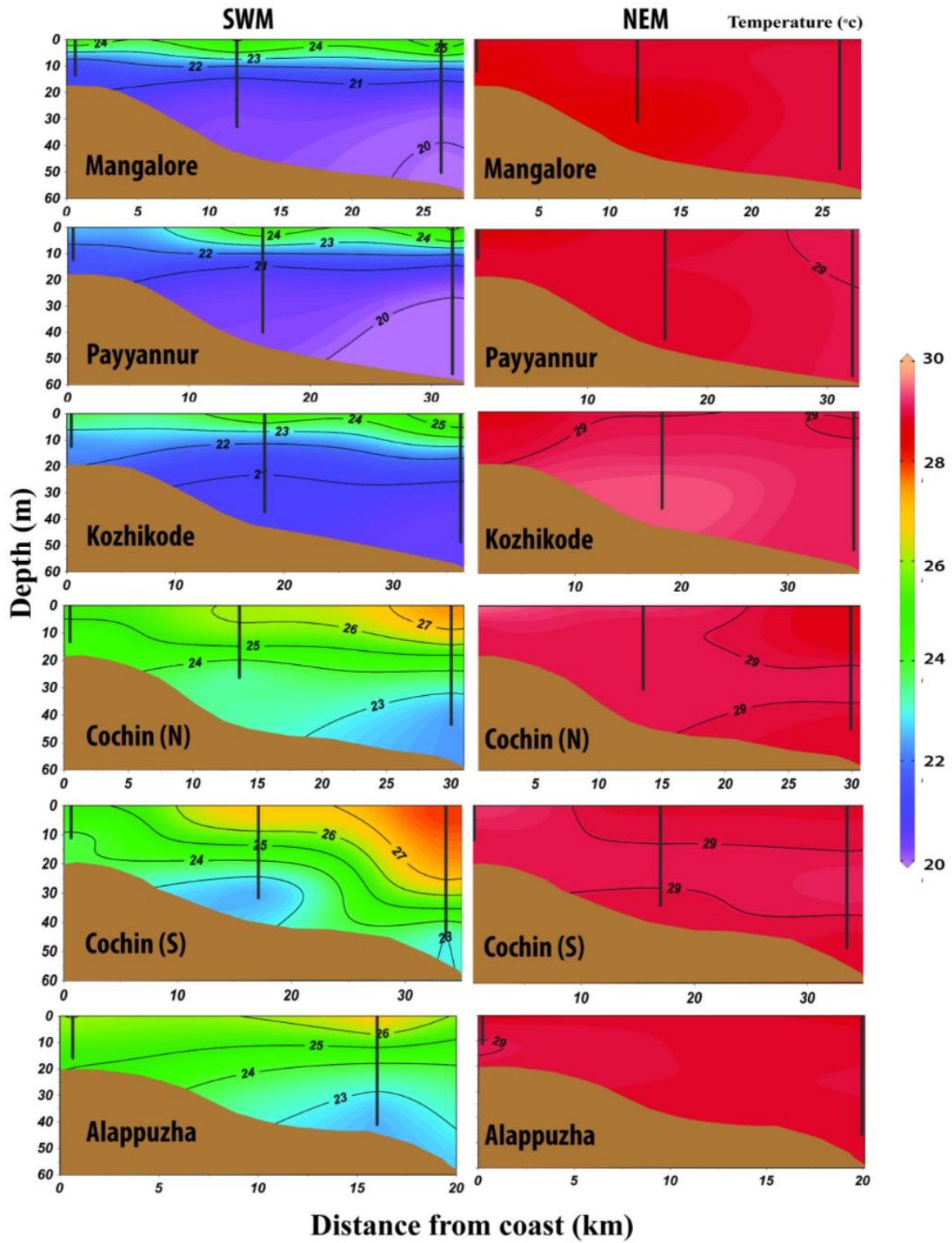


Figure 2

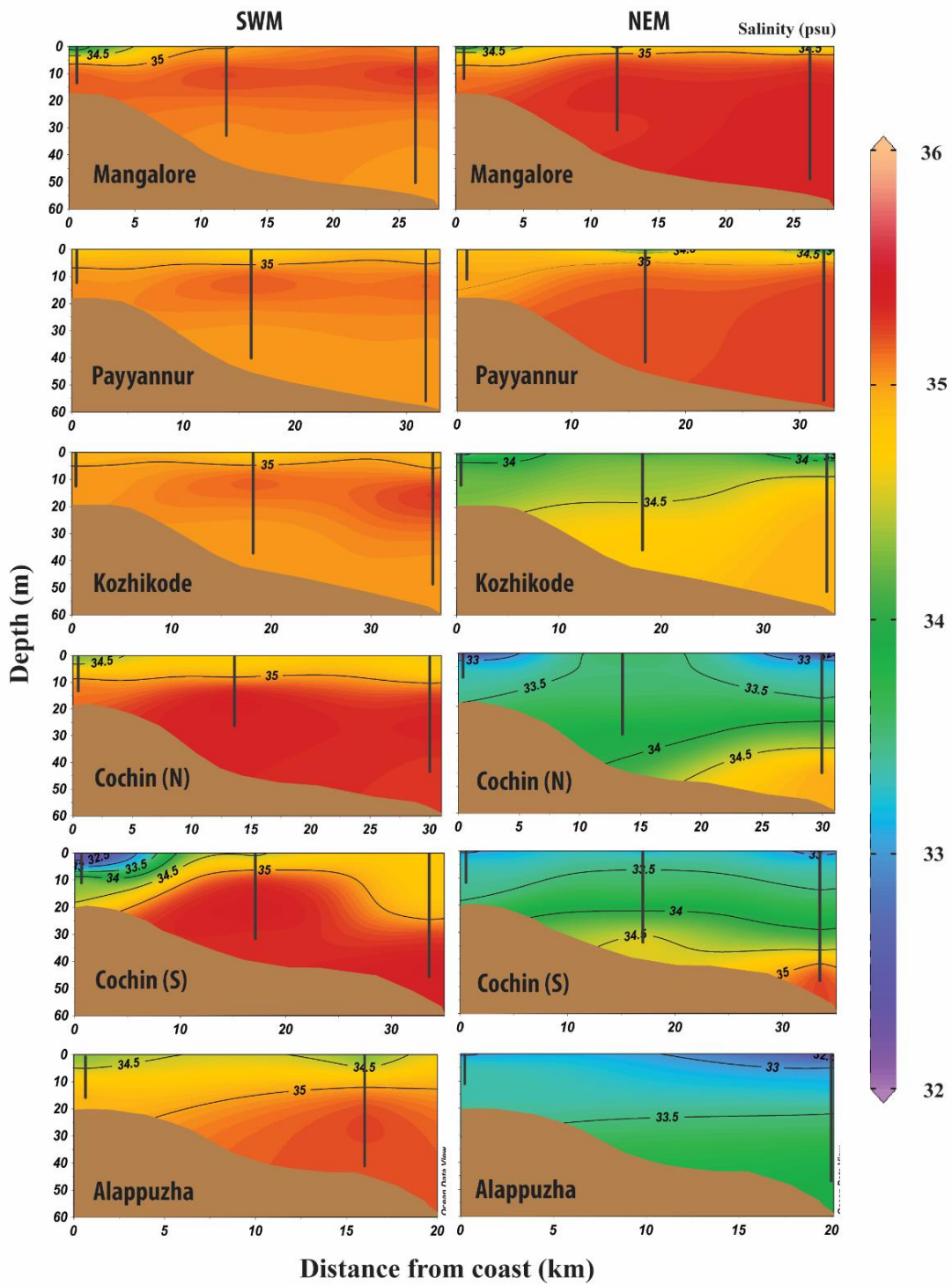


Figure 3



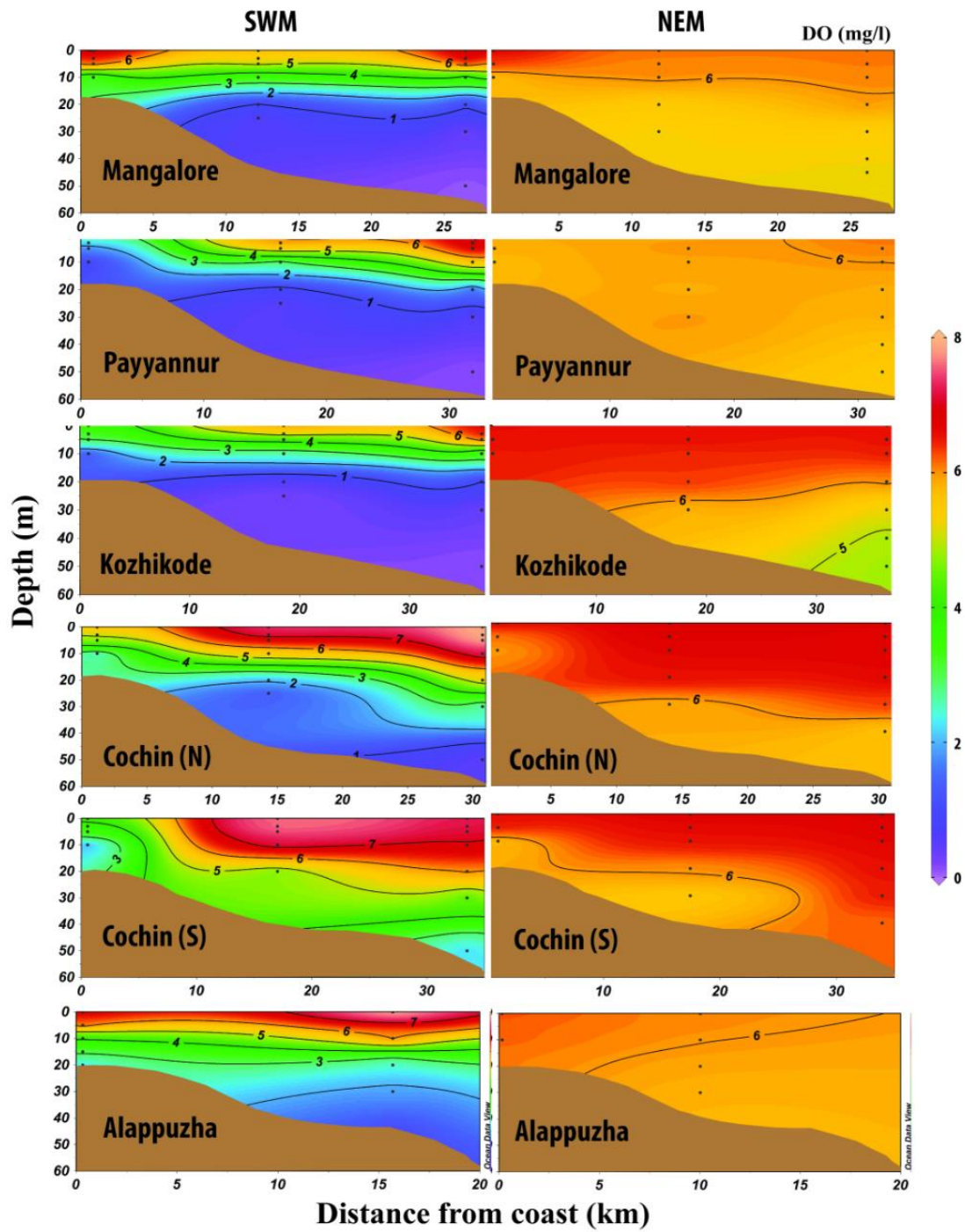


Figure 4



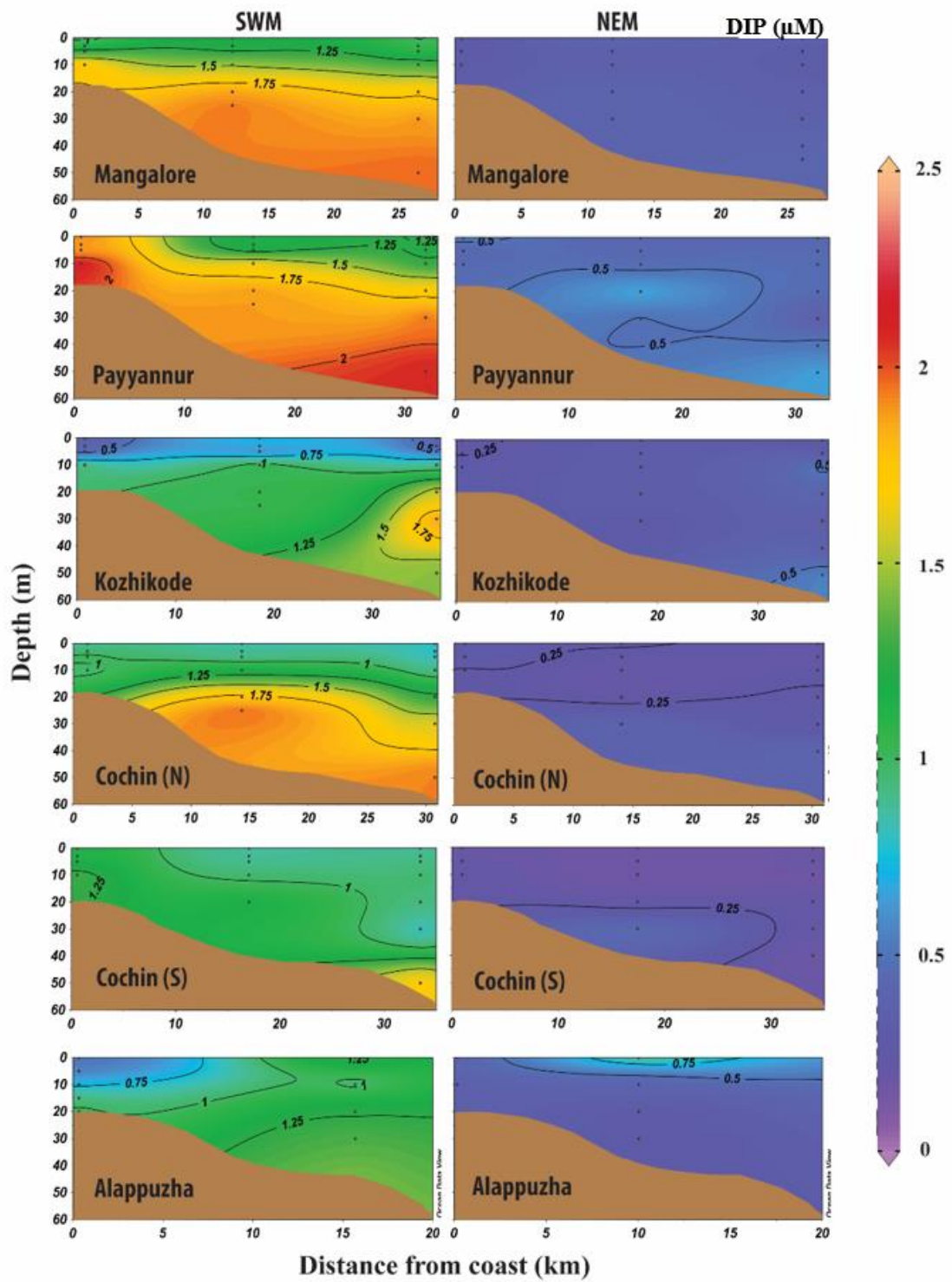


Figure 5

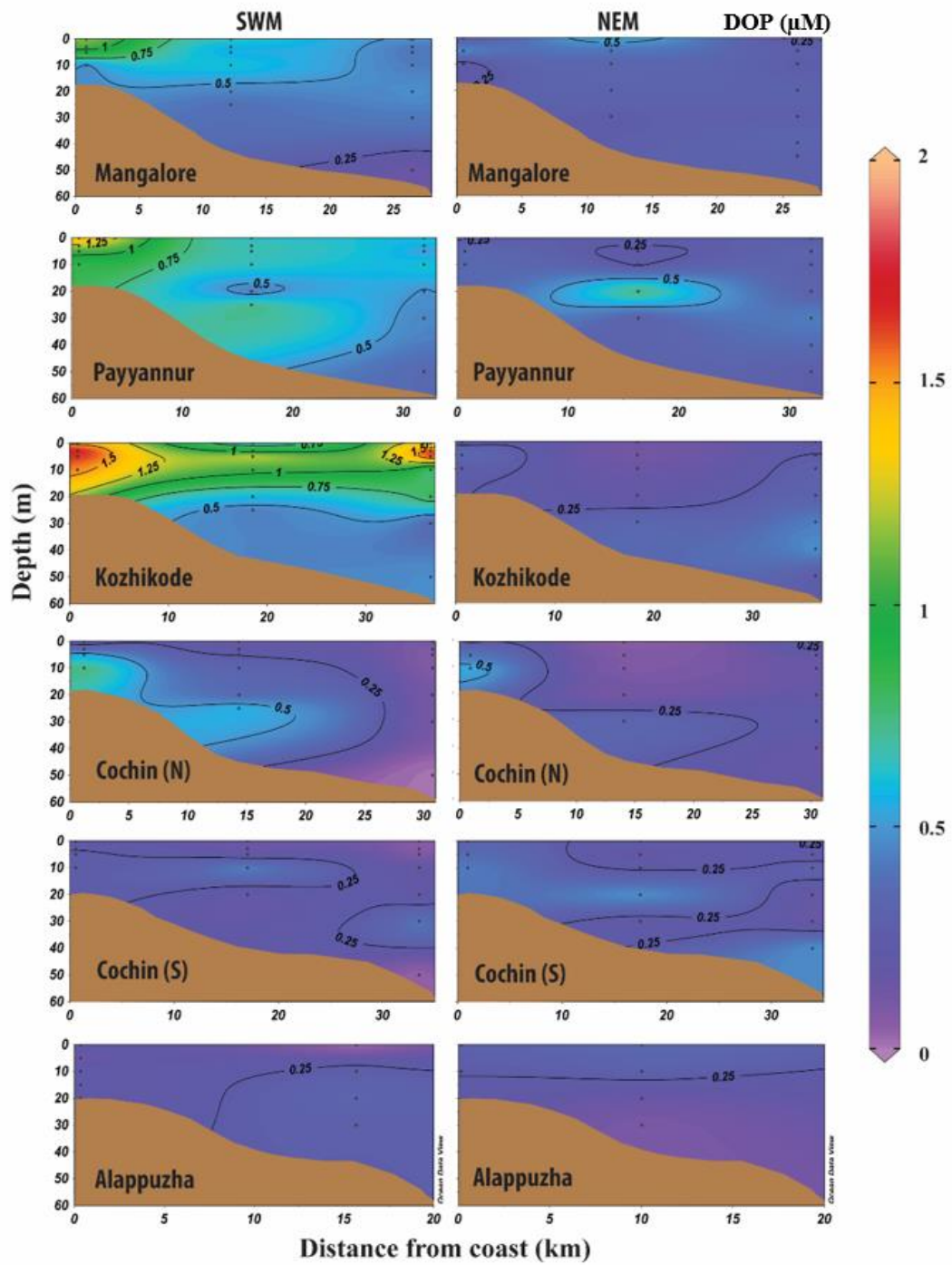


Figure 6

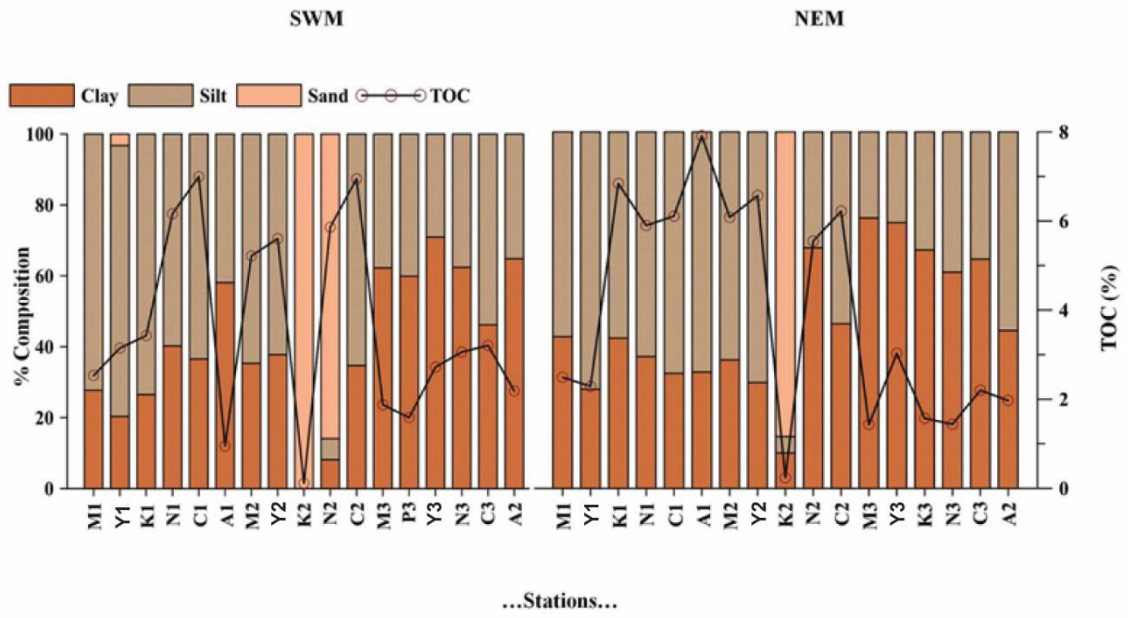


Figure 7

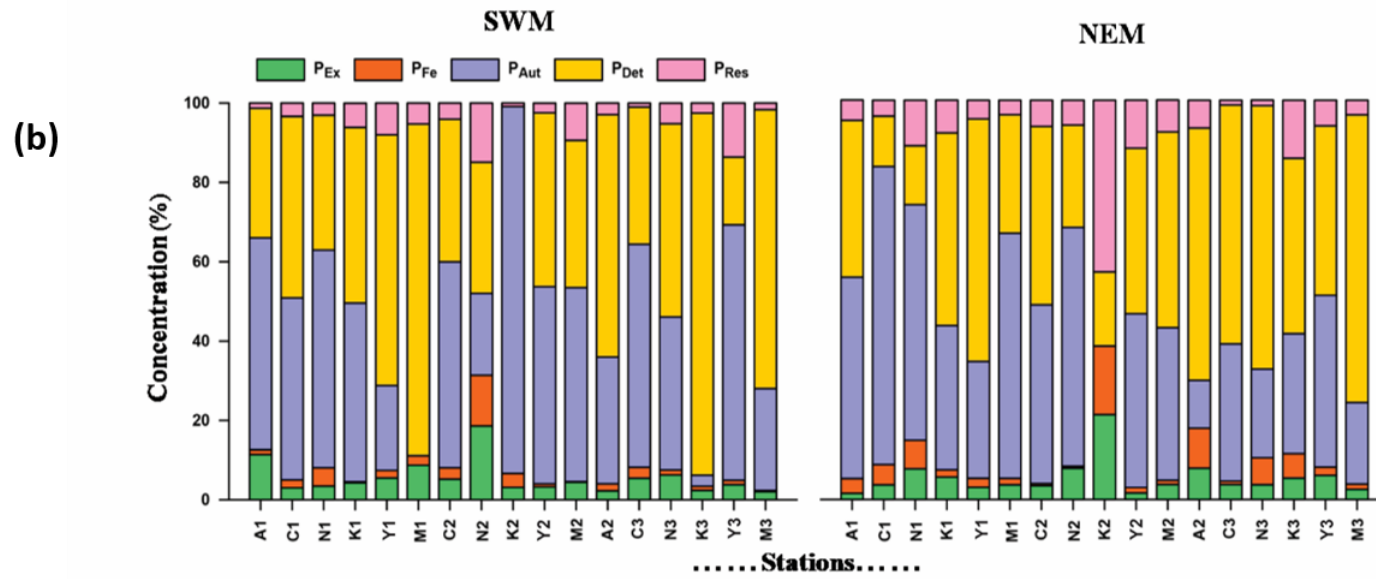
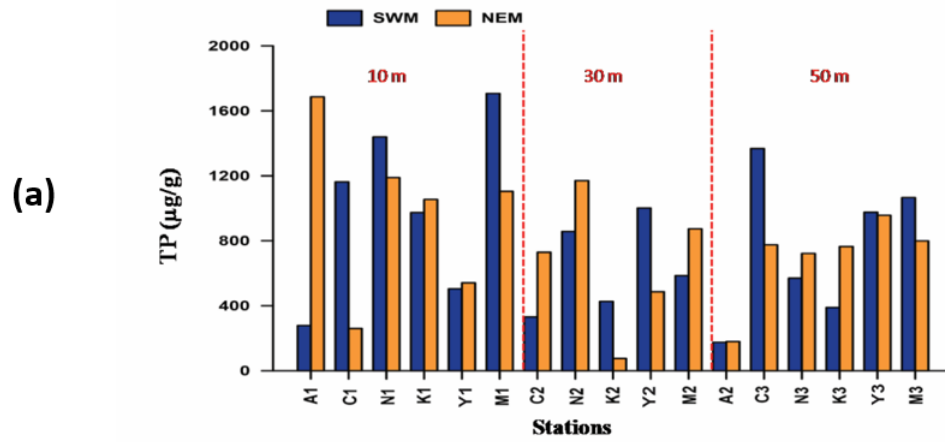


Figure 8

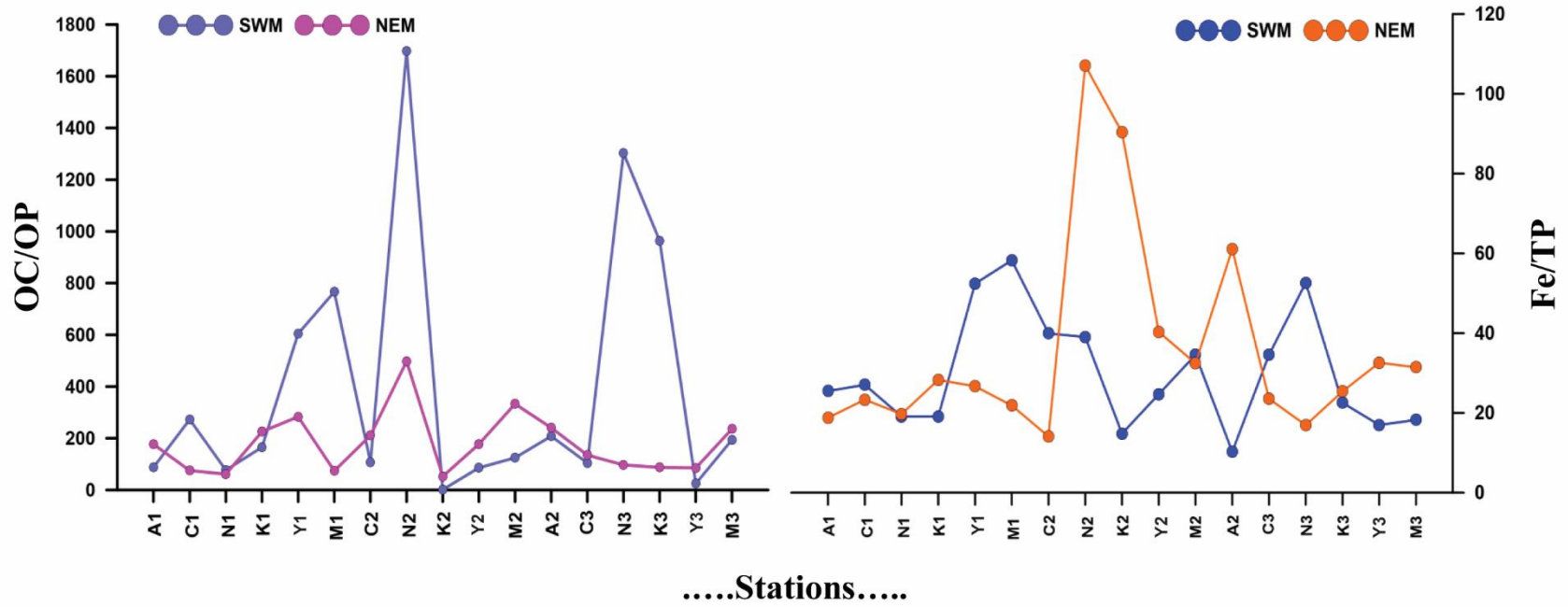


Figure 9

**Table 1.**

a. Result of Pearson correlation analysis of geochemical data for SWM

	<i>P<sub>Ex</sub></i>	<i>P<sub>Fe</sub></i>	<i>P<sub>Aut</sub></i>	<i>P<sub>Det</sub></i>	<i>P<sub>Res</sub></i>	<i>DO</i>	<i>SAL</i>	<i>TEMP</i>	<i>OP</i>	<i>Sand</i>	<i>Silt</i>	<i>clay</i>	<i>OC</i>	<i>DOP</i>	<i>DIN</i>	<i>pH</i>	<i>Eh</i>	<i>TP</i>	<i>Fe</i>	<i>Mn</i>	
<i>P<sub>Ex</sub></i>	1.00																				
<i>P<sub>Fe</sub></i>	<b>0.75</b>	1.00																			
<i>P<sub>Aut</sub></i>	-0.17	-0.10	1.00																		
<i>P<sub>Det</sub></i>	-0.24	-0.24	<b>-0.84</b>	1.00																	
<i>P<sub>Res</sub></i>	0.49	0.45	-0.18	-0.36	1.00																
<i>DO</i>	0.39	0.23	0.17	-0.29	-0.30	1.00															
<i>SAL</i>	<i>0.67</i>	<i>0.42</i>		-0.22		<i>0.77</i>	1.00														
<i>TEMP</i>	0.34	0.46	0.03	-0.30	-0.13	0.47	<i>0.60</i>	1.00													
<i>OP</i>	-0.16		<b>0.87</b>	<b>-0.76</b>	-0.04		-0.28	-0.19	1.00												
<i>Sand</i>	0.44	<i>0.69</i>	0.28	-0.20	0.21				0.53	1.00											
<i>Silt</i>	-0.27	-0.47					0.13		-0.38	<b>-0.75</b>	1.00										
<i>clay</i>	-0.36	<i>-0.52</i>	-0.35	0.20	-0.25	0.16	-0.11	-0.15	-0.38	<i>-0.68</i>	0.03	1.00									
<i>OC</i>	0.10	0.31	-0.17	-0.30	0.20		0.17	0.45	-0.28	-0.15	0.41	-0.22	1.00								
<i>OP</i>		0.12	-0.11	-0.11	0.21	-0.33	-0.34	0.13			0.20	-0.34	0.25	1.00							
<i>DIN</i>	0.33	0.17	-0.31	-0.12	-0.15	<i>0.58</i>	0.44	0.22	-0.31	-0.12	-0.25	0.46	0.11	-0.39	1.00						
<i>pH</i>		0.15	0.10	-0.10	-0.25	0.42	0.10	0.39	0.16	0.20	<i>-0.55</i>	0.30	-0.36	-0.12	0.34	1.00					
<i>Eh</i>		-0.15	-0.11	0.10	0.25	-0.43	-0.10	-0.39	-0.16	-0.20	<i>0.56</i>	-0.30	0.38	0.13	-0.36	-1.00	1.00				
<i>TP</i>	<i>-0.65</i>	-0.29			-0.33	-0.26	-0.41	0.17	-0.16	-0.42	0.38	0.22	0.52	0.32	-0.14	-0.14	0.15	1.00			
<i>Fe</i>	-0.39	-0.26	-0.13	0.10	-0.15	-0.28	-0.10	0.11	-0.27	-0.49	<b>0.71</b>		0.75	0.08	-0.14	<i>-0.50</i>	<i>0.52</i>	<i>0.67</i>	1.00		
<i>Mn</i>	-0.17	-0.24	-0.52	<b>0.75</b>	-0.08	-0.40	-0.23	-0.48	-0.40	-0.23	0.27				-0.34	-0.49	<i>0.50</i>	0.15	0.33	1.00	

**Bold**-Correlation is significant at the 0.01 level; *italics*-Correlation is significant at the 0.05 level

b. Result of Pearson correlation analysis of geochemical data for NEM

	<b>P<sub>Ex</sub></b>	<b>P<sub>Fe</sub></b>	<b>P<sub>Aut</sub></b>	<b>P<sub>Det</sub></b>	<b>P<sub>Res</sub></b>	<b>DO</b>	<b>SAL</b>	<b>TEMP</b>	<b>OP</b>	<b>Sand</b>	<b>Silt</b>	<b>clay</b>	<b>OC</b>	<b>DOP</b>	<b>DIN</b>	<b>pH</b>	<b>Eh</b>	<b>TP</b>	<b>Fe</b>	<b>Mn</b>	
<i>P<sub>Ex</sub></i>	1.00																				
<i>P<sub>Fe</sub></i>	<b>0.81</b>	1.00																			
<i>P<sub>Aut</sub></i>		-0.25	1.00																		
<i>P<sub>Det</sub></i>	-0.42	-0.28	-0.93	1.00																	
<i>P<sub>Res</sub></i>	<b>0.88</b>	<b>0.76</b>		-0.43	1.00																
<i>DO</i>		-0.08	0.10		-0.10	1.00															
<i>SAL</i>	-0.12	-0.27	-0.44	<i>0.53</i>		-0.36	1.00														
<i>TEMP</i>	<i>0.64</i>	<i>0.58</i>		-0.30	<i>0.66</i>		-0.36	1.00													
<i>OP</i>	0.35	0.46	0.54	<b>-0.72</b>	0.40		-0.34	0.21	1.00												
<i>Sand</i>	<b>0.90</b>	<b>0.77</b>		-0.35	<b>0.93</b>			<i>0.62</i>	0.29	1.00											
<i>Silt</i>	-0.62	-0.38	0.31		-0.48	0.23	-0.36	<i>-0.51</i>		-0.57	1.00										
<i>clay</i>	-0.34	-0.45	-0.31	0.44	-0.52	-0.23	0.35		-0.39	-0.50	-0.42	1.00									
<i>OC</i>	-0.40	-0.45	<i>0.59</i>	-0.36	-0.27	0.41	-0.52		0.11	-0.39	<i>0.66</i>	-0.26	1.00								
<i>OP</i>	<i>-0.61</i>	-0.41	0.36		-0.43	0.29	-0.35	-0.26		-0.45	<i>0.66</i>	-0.20	0.69	1.00							
<i>DIN</i>	0.31	0.18	0.38	-0.44	0.19	0.24	-0.32	0.36	0.44	0.22	-0.11	-0.13			1.00						
<i>pH</i>	-0.20	-0.27		0.19	-0.15	<i>-0.69</i>	<i>0.66</i>	-0.42			-0.28	0.44	-0.34	-0.08	-0.30	1.00					
<i>Eh</i>	0.50	0.52	-0.40		0.47			0.26		0.46	-0.49		-0.35	-0.20			1.00				
<i>TP</i>	-0.49	-0.53	0.41		-0.48			-0.26		-0.47	0.48		0.34	0.21			-1.00	1.00			
<i>Fe</i>	-0.53	-0.52	0.26		-0.36	0.28	-0.28	-0.25	-0.08	-0.46	<i>0.62</i>	-0.15	<b>0.74</b>	<i>0.69</i>		-0.25	-0.34	0.34	1.00		
<i>Mn</i>	-0.35	-0.33			-0.20	<i>-0.51</i>	0.23	-0.14		-0.30	0.10	0.22		0.20		0.42	-0.20	0.22	0.36	1.00	

**Bold**-Correlation is significant at the 0.01 level; *italics*-Correlation is significant at the 0.05 level

**Table 2**

a. Result of principal component analysis of geochemical parameters in the SWM

Parameters	PC1	PC2	PC3	PC4	PC5
P <sub>Ex</sub>	<b>0.631</b>	-0.468	-0.024	-0.065	0.551
P <sub>Fe</sub>	<b>0.654</b>	-0.101	<b>-0.640</b>	-0.043	0.185
P <sub>Aut</sub>	0.012	0.064	-0.018	<b>0.915</b>	-0.107
P <sub>De</sub>	0.153	0.336	<b>0.650</b>	<b>-0.613</b>	0.155
P <sub>Res</sub>	-0.098	0.036	0.037	-0.085	<b>0.944</b>
DO	<b>0.889</b>	-0.148	0.237	0.001	-0.205
Salinity	<b>0.912</b>	-0.191	0.166	-0.063	0.106
Temperature	<b>0.836</b>	0.253	-0.183	0.085	-0.075
TOP	0.020	-0.081	-0.234	<b>0.897</b>	0.023
TP	-0.335	<b>0.825</b>	0.140	0.076	-0.347
Silt	0.108	<b>0.530</b>	<b>0.779</b>	-0.149	0.177
Clay	0.072	0.264	<b>0.879</b>	-0.222	-0.056
OC	0.073	<b>0.904</b>	0.364	0.018	0.078
Fe	-0.075	<b>0.900</b>	0.221	-0.163	0.072
% of variance	24	22	18	15	11

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization.



b. Result of principal component analysis of geochemical parameters in the NEM

Parameters	PC1	PC2	PC3	PC4	PC5
P <sub>Ex</sub>	<b>-0.681</b>	0.230	0.352	0.227	0.111
P <sub>Fe</sub>	-0.013	-0.123	<b>0.937</b>	0.153	-0.023
P <sub>Aut</sub>	0.191	<b>0.911</b>	-0.257	-0.007	0.064
P <sub>De</sub>	-0.047	<b>-0.905</b>	-0.229	-0.192	-0.063
P <sub>Res</sub>	0.192	0.233	0.111	<b>0.732</b>	-0.4
DO	0.184	0.057	-0.074	-0.023	<b>0.902</b>
Salinity	-0.139	-0.366	-0.437	<b>-0.551</b>	<b>-0.501</b>
Temperature	-0.258	-0.051	0.060	<b>0.773</b>	0.131
TOP	0.210	<b>0.566</b>	<b>0.570</b>	-0.116	-0.199
TP	<b>0.756</b>	0.179	-0.012	-0.126	-0.014
Silt	<b>0.802</b>	0.219	0.319	-0.005	0.223
Clay	<b>-0.866</b>	-0.182	-0.238	-0.076	-0.172
OC	<b>0.505</b>	<b>0.592</b>	-0.224	0.375	0.32
Fe	<b>0.662</b>	0.150	-0.302	0.433	0.151
% of variance	24	19	14	14	11

Extraction Method: Principal Component Analysis; Rotation Method: Varimax with Kaiser Normalization.