# Influence of hypoxia on phosphorus cycling in Alappuzha mud banks, southwest coast of India

DayanaMathew<sup>a</sup>., Gireeshkumar, T.R<sup>\*a</sup>., Balachandran, K.K<sup>a</sup>., Udayakrishnan, P.B<sup>b</sup>., Shameem, K<sup>c</sup>., Deepulal, P.M<sup>a</sup>., Nair, M<sup>a</sup>., Madhu, N.V<sup>a</sup>., Muraleedharan, K.R<sup>a</sup>.,

 <sup>a</sup>CSIR - National Institute of Oceanography, Regional Centre, Kochi - 682 018, India Phone: +914842390814, Fax: +914842390618
 <sup>b</sup>CSIR - National Institute of Oceanography, Regional Centre, Mumbai - 400 053, India Phone: +912226359605, Fax: +912226364627
 <sup>c</sup>Inter University Centre for Development of Marine Biotechnology
 School of Marine Sciences, Cochin University of Science and Technology. Kochi-682016

\*Corresponding author's E-mail address:gkumar@nio.org

# Abstract

The southwest coast of India is known to experience two concurrent processes during the southwest monsoon, namely, coastal upwelling and mud banks at selected stretches such as that in off Alappuzha. Since the mud bank sediments contain very high concentrations of phosphorus (ave.  $2255\pm278 \ \mu g/g$ ), changes in the elements such as carbon, phosphorus, iron, and manganese were measured in the Alappuzha mud banks to understand the influence of upwelling on the cycling of these elements. The results showed that the upwelling brought hypoxic waters into the mud bank region during the peak southwest monsoon to induce significant changes in the phosphorus fractions in the sediment. There was an enrichment of easily reducible iron (Fe extracted by dithionite), caused by the efflux of reactive Fe from the subsurface sediment layers and depletion of manganese due to its release as a result of the reductive dissolution of Mn oxides. The low molar ratios of total organic carbon to total nitrogen  $(9\pm1)$  and total organic carbon to organic phosphorus  $(118\pm57)$ generally indicated that the organic matter was relatively fresh and derived from marine plankton. Sedimentary phosphorus also exhibited wide fluctuations in its geochemical forms during hypoxia. Five geochemical forms of P such as exchangeable P (Ex-P), Fe and Mn bound P (Fe-P), P from Al oxides, non-reducible Fe bound P and organic P (Non Red-P), calcium bound P (Ca-P) and refractory P (ROP) were extracted adopting sequential extraction procedure. The ranges of various P forms were Ex-P(2-11%), Fe-P(4-25%), Non Red-P (4-10%) and ROP (4-12%), respectively. The fractionation study revealed that precipitation of vivianite and apatite are the major pathways of phosphorus enrichment in mud bank sediments. The significance of the study is that the enrichment of the labile fractions could be influencing an enhanced biological production in the Alappuzha mud banks during the southwest monsoon.

Key Words: Upwelling;Hypoxia; Phosphorus; Fractionation; Labile fractions

#### 1. Introduction

Phosphorus plays an important role in the growth of planktonic and other organisms as a structural component, an essential part of the energy source (ATP), and macro-nutrient (Lomas et al., 2010). The major source of P is rock weathering (Ruttenberg and Berner, 1993; Yang et al., 2017) and its fate in the coastal environment depends on various processes including physical (upwelling), chemical (adsorption/desorption, precipitation/dissolution) and biological (bioturbation, uptake and release by bacteria, excretion by microfauna) interactions or a combination of the above(Slomp et al., 1996; García and de Iorio 2003; Gireeshkumar et al., 2013). The oxygen deficiency in aquatic systems may favor diagenetic processes in sediments to increase phosphorus content of pore waters (Gireeshkumar et al., 2013)that is then precipitated as apatite under oxic conditions (Kraal et al., 2010; Jilbert et al., 2011; Kraal et al., 2015).

The southwest coast of India draws special attention due to the occurrence of mud banks in the littoral waters during the southwest monsoon (CMFRI 1984). These mud banks are of exceptional biological productivity and remain unique in their formation and functions (Nair, 1978). Mud banks are usually found in a semi-circular shape extending up to about 8 km from shore at a water depth of about 7-15 m and about 4 km alongshore (Balachnadran, 2004). The mud banks exhibit remarkable wave attenuation to enable safe fishing grounds towards the shore during southwest monsoon, while the high waves make fishing almost impossible outside of the mud banks (Jyothibabu et al., 2018). Another process occurring along the entire southwest coast during monsoon is the upwelling (Gupta et al., 2016; Hareeshkumar and Anand, 2016), which brings hypoxic waters inducing substantial changes in the water column and benthic environment (Gireeshkumar et al., 2017). Since mud bank sediments are highly enriched in phosphorus, the changes brought by hypoxia on the cycling of such elements are very important (Sheshappa et al., 1953; Nair et al., 1990; Dinesh and Jayaprakash, 2008). In view of the above, the present study examines the influence of hypoxia on phosphorus cycling in the Alappuzha mud banks.

#### 2. Materials and methods

# 2.1 Time series sampling

Fortnightly observations were carried out at three locations (M1, M2, M3) in and around the Alappuzha mud banks covering the monsoon and non-monsoon periods of 2016 (Fig. 1). Station M2 (7 m water depth) was in the mud banks, while stations M1 and M3 were the two non-mud bank stations located 7 km north (7 m water depth) and at an offshore area (13 m) to the west of M2. The salinity (accuracy $\pm 0.001$ ) and temperature (accuracy $\pm 0.0001$ ) were recorded using a CTD profiler

(Seabird 19 plus). Water samples were collected from different water depths using a 5 L Niskin sampler and subsamples were taken to measure dissolved oxygen (DO), dissolved inorganic P (DIP) and dissolved organic P (DOP). Sediments were collected using a Van Veen grab (0.04 m<sup>2</sup> surface area), the surface layers (0-3 cm) was transferred to an acid cleaned HDPE bottles in an inert atmosphere and kept frozen till analysis.

#### 2.2Analytical methods

#### 2.2.1 Water chemistry

DO was analyzed following Winkler's method (Winkler, 1888) using an automatic titration system (detection limit 2  $\mu$ M). Samples for inorganic phosphorus were filtered through glass fiber filter paper (GF/F) and analyzed using an auto-analyzer (Skalar, SAN++). A UV attached digester was used for the estimation of total dissolved P (Grasshoff et al., 1983) and the dissolved organic phosphorus (DOP) was calculated from the difference (detection limit 0.07  $\mu$ M). Aliquots (500 ml) of seawater was filtered through GF/F filter paper (0.7  $\mu$ m) and extracted for chlorophyll *a* using 90% acetone in the dark at 4°C. Chlorophyll a was estimated (detection limit 0.02 mg/m<sup>3</sup>)using a Trilogy Turner Fluorometer following the standard protocol (JGOFS 1994).

#### 2.2.2 Geochemistry

Textural characteristics of sediments were determined using pipette analysis (Folk 1980). Sediments were freeze-dried, homogenized and powdered using an agate mortar and pestle and analyzed for total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS). Prior to TOC analysis, the powdered samples were treated with 1 M HCl to remove carbonates, washed with Milli-Q water to remove salts and were finally freeze-dried. The TOC, TN and TS were estimated using a Vario EL III CHNS Analyzer. Samples were always run with empty tin/silver cups to correct the carbon and nitrogen in the cups. Acetanilide standards were used to calibrate the instrument. The detection limits for TOC, TN and TS were 0.07%, 0.01% and 0.01% respectively. Sediments were acid digested with a mixture of HCl-HNO<sub>3</sub>-HF in a microwave digester (Milestone Ethos Easy) and analyzed for Fe (detection limit 12.50  $\mu$ g/g) and Mn (detection limit 3.50  $\mu$ g/g) using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Thermo Scientific i-CAP 7000 Series).

# 2.2.3 Fractionation of phosphorus

Sediments were subjected to P fractionation following Jensen and Thamdrup (1993) modified by Lukkari et al. (2007) (Fig. 3). Freeze-dried and powdered sediments were treated with 0.46 M sodium chloride (NaCl) solution in an orbital shaker to extract exchangeable P. The residue was treated with 0.11 M sodium dithionite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) in the presence of sodium bicarbonate buffer (NaHCO<sub>3</sub>) at pH 7 to extract the redox-sensitive P (oxides and hydroxides of Fe and Mn). The residue from the above was treated with 0.10 M sodium hydroxide (NaOH) to extract the P bound to the non-reducible fraction (oxides of Al, Fe, alkali-soluble organics). The fourth fraction (apatite bound P) was extracted using 0.5 M Hydrochloric acid (HCl), while the fifth fraction (residual P) was extracted by heating with 1 M hydrochloric at 550°C in a muffle furnace. All extracts were filtered through GF/F filters (0.45  $\mu$ m) and analysed following the standard procedure (Grasshoff et al., 1983) using an auto-analyser (Skalar SAN++). Extracts from Step 2 (NaBD extraction) were bubbled with purified air to remove dithionite. For estimation of organic phosphorous, the samples were oxidized using sodium peroxodisulphate and irradiated by UV light. Each analysis was accompanied by blank and standards (in triplicates) to minimize the contamination from chemicals and laboratory practices.

# 3. Results

#### 3.1 General hydrography

The study region generally remained warm and vertically mixed during April -May (30-32°C), though it started cooling (23-26°C) from June to September due to the coastal upwelling (Fig. 3a). Salinity did not exhibit wide fluctuations (Fig. 3b), except for a few low saline patches, which are erroneous values of CTD in contact with the fluid mud (Muraleedharan et al., 2017). There was a sharp decrease in the dissolved oxygen levels at M3 for a long period (2<sup>nd</sup>week of June to end of September) due to upwelling as compared to intermittent decrease atM1 and M2(2<sup>nd</sup>week of June to 1<sup>st</sup>week of August and in September, Fig.3c). The Chlorophyll *a* (ave.21±6 mg/m<sup>3</sup>) was markedly high at M2 (Fig.4) compared to the chlorophyll  $a(>5 \text{ mg/m}^3)$  levels atM1 and M3.

#### 3.2 Dissolved phosphate

The dissolved inorganic phosphorus (DIP)concentrations were comparatively low during April and May (0.10 to 0.50  $\mu$ M) which gradually increased in June to reach a maximum in September (1-3  $\mu$ M), which decreased thereafter. Similarly, DOP also showed a sudden increase in July ( $\approx$ 3  $\mu$ M)but decreased from July onwards (Fig.5).

#### 3.3 Sediment characteristics

The surface sediments in the Alappuzha mud banks were predominantly clayeyorsilty clay with moderateTOC ( $2.42\pm2.85\%$ ), TN ( $0.27\pm0.41\%$ ) and TS ( $1.04\pm1.30\%$ , Table 1). Fe concentration were relatively steady (ave. $61.37\pm2.68$  mg/g at M1,  $63.50\pm6.11$  mg/g at M2 and  $59.50\pm3.98$  mg/g at M3) with a slight decline during hypoxia. However, Mn concentration showed a

sharp decline (149.51 to 70.4 $\mu$ g/g) during the same period. Molar ratios(Fe/TP)ranged from 12.97 to 37.53 whereas TS/Fe ratio showed a sharp decrease from 23 to <1 from 14<sup>th</sup> June onwards(Table 1b).

# 3.4 Geochemistry of phosphorus

The total phosphorus(TP) in sediments varied from 1790 to 2436  $\mu$ g/g, 1641 to 3008  $\mu$ g/g and 2097 to 2779  $\mu$ g/g at M1, M2, and M3 respectively (Fig.6). Ex-P accounted for 2-11% (ave.86.66±26  $\mu$ g/g) of TP at M1, 2-6% (ave.71±19  $\mu$ g/g) at M2 and 2-5% (ave.62±21  $\mu$ g/g) at M3. Fe-P fraction accounted for 4-16% at M1 (ave.207±113  $\mu$ g/g), 4-18% at M2 (ave.265±96  $\mu$ g/g) and 4-25% at M3 (ave.260±167  $\mu$ g/g) (Fig. 6). Fe-P was very high during the upwelling period, especially at M3. The third fraction (Non Red-P) accounted for 4-10% at M1 (ave.15±35  $\mu$ g/g), 7-10% at M2 (ave.174±38  $\mu$ g/g) and 6-9% at M3 (ave.169±24  $\mu$ g/g). Ca-P was the major fraction contributing 62-75% of TP at M1 (ave.1489±160  $\mu$ g/g), 64-78% at M2 (ave.1519±311  $\mu$ g/g) and 65-77% at M3 (ave.1583±130  $\mu$ g/g). The contribution of ROP(ave. 184±39  $\mu$ g/g)was very less(4-12%) at all stations (Fig. 6).

In the Ex-P fraction, inorganic P (Ex-IP) was consistent (40 to 60  $\mu$ g/g) throughout the study area compared to organic P (Ex-OP) that ranged from 1-110  $\mu$ g/g with a peak during upwelling. Fe-IP and Fe-OP also followed a similar trend with values ranging from 85 to 250  $\mu$ g/g and 12 to 200  $\mu$ g/g respectively with marked enrichment during monsoon. The Non-redP was rich in organic form (16 to 182  $\mu$ g/g) followed by inorganic form (22-82  $\mu$ g/g, Fig. 7). Ca-P (1230-1900  $\mu$ g/g) form (apatite) was very high (61-76%) with a maximum(2396  $\mu$ g/g)at M2 in July, probably due to the formation of apatite (Ca-P). ROP was also relatively consistent throughout the study(Fig. 7).

#### 4. Discussion

The results show that upwelling was mainly responsible for the development of coastal hypoxia in the study region. Dissolved P (~1.5  $\mu$ M) present in moderate levels increased up to 4  $\mu$ M during peak southwest monsoon due to intense upwelling and re-mineralization (Schenau and De Lange, 2001). There was an enrichment of nutrients (N, P,and Si), leading to high organic production during the monsoon, which on decomposition intensified the hypoxic conditions (Gireeshkumar et al., 2017; Jyothibabu et al., 2018) favoring the growth of facultative an aerobicbacteria (Anas et al., 2018). The high TOC/TS ratio (2.1 to 3.5) during hypoxia was also suggested an organic enrichment(Raiswell et al., 1987). Fe(II) entraining from the deeper layers through the dissolution of Fe oxides, may re-precipitated as vivianite (Krom and Berner, 1980; Jensen et al., 1995; Slomp et al., 1996) to enrich the Fe levels in the surface sediments. In the case of Mn, under oxic water condition the oxidation of organic matter removes electrons (oxygen) in the sediment surface, whereas

reduction of  $Mn^{4+}$  to  $Mn^{2+}$  takes place in the deeper layers to release electrons that diffuse and reoxidize  $Mn^{2+}$  to  $Mn^{4+}$  in the surface (Froelich et al., 1979, Schulz and Zabel, 2006). However, during the periods of upwelling, the bottom water hypoxia in the study region was favorable for the reduction of  $Mn^{4+}$  to  $Mn^{2+}$ , which was released to the water column leading to a sharp decline in the Mn concentrations in the sediment surface.

#### 4.1 Geochemistry of phosphorus

TP in mud bank sediments is far higher( $1641-3008 \ \mu g/g$ ) than those reported from other locations (209 to 1081  $\mu g/g$ ) along the west coast of India(Acharya et al., 2016; Sudheesh et al., 2017; Table 2). The incursion of coastal upwelling into themud banks makes Alappuzha coastal environment, a unique region to study the biogeochemical cyclingof phosphorus. The most preferred form of phosphorus by phytoplankton is found to be the exchangeable fraction produced during early diagenesis (Andrienx-Loyer and Aminot, 2001; Kaiserli et al., 2002; Yang et al., 2017). Therefore, the enrichment of Ex-P in the mud banks during monsoon period was due to the increased diagenetic activity under hypoxic conditions (Schenau and De Lange, 2001). The increase in the labile organic fractions (Ex-OP, Fe-OP, and Non Red-OP) during monsoon indicates their algae origin (Uhlman et al., 1990; Hupfer et al., 1995). It is well accepted that algae and bacteria can utilize dissolved organic P (Nausch and Nausch 2004, Li and Brett 2013) and regenerate orthophosphate (Tarapchak and Moll 1990) which is substantiated by the enrichment of OP in sediment and a subsequent increase in DIP in the water column. However, P associated with the Non Red (IP) and mineral lattice fractions did not exhibit any significant variation.

It is widely known that Fe oxides are the major scavenger of P (Slomp et al., 1996; Yang et al., 2016;Linsy et al., 2018), but is released during the dissolution of Fe(oxy) hydroxides under hypoxia (Kraal et al., 2017; Sudheesh et al., 2017).In the present study, a rapid increase in the Fe-P fraction obtained during hypoxia was not associated with a corresponding increase in the organic production (Fe-P *vs*.OC,p< 0.05; Fe-P *vs*.OP,p< 0.05). Although reducing condition can cause dissolution of Fe(oxy) hydroxides releasing Fe(II)to the water column (Ruttenberg, 2003), the high concentration of Fe-P during the present observation is probably due to the formation of the mineral vivianite (Jilbert and Slomp, 2011; Slomp et al., 2013;Egger et al., 2015). Vivianite precipitation is substantiated by a very low TS/Fe<sub>T</sub> ratio <1.1 (Rothe et al., 2015) indicating Fe enrichment due to reduced sulphate reduction. Anaerobic oxidation of methane (AOM) could be another mechanism to support the above (Egger et al., 2015; Gireeshkumar et al., 2017), though it requires further corroboration.

P enrichment in sediments can also be studied from Fe/TP ratios (Sondergaard et al., 2003; Coelho et al., 2004). In general, high Fe/TP ratio during oxic condition is indicative of high removal/scavenging of P by Fe oxides, which is released (both Fe and P) during the dissolution (Caraco et al., 1993; Søndergaard et al., 2003). Thus, the Fe/TP(>24), in the present study is much higher than the threshold value (15) and shows high P retention capacity. However, the values fall behind (>12) indicates reductive dissolution of Fe-P during hypoxia. The increasing DIP during peak upwelling also reveals the subsequent release of P into the water column. In addition, a negative correlation of Fe-P fraction with OP indicates its labile character.

The high fish availability in the mud banks (Rao et al., 1984, Jyothibabu et al., 2018)could be one reason for the accumulation of fish debris that yields an immobile pool (sum of Ca-P andROP) of P in sediment (Schenauand De Langue,2001). It is, therefore, possible that hypoxic region scan undergo phosphorus enrichment in sediments through the formation of authigenic mineral sand refractory materials (Michalopoulos and Aller, 2004).

#### 4.2 Sources of organic P in sediments

The TOC/TN ratio (8-12; ave.  $9\pm1$ )in the mud bank sediments indicate the dominance of marine-derived organic matter. TOC/OP ratio can explain the transformation of organic matter in an environment (Kraal et al., 2012; Sekula-Wood et al., 2012; Yang et al., 2017), which is 106 for marine phytoplankton (Redfield, 1963) and 800-2050 for terrestrial plants (Likens et al., 1981; Simpson, 1996). In the present study, the TOC/OP ratio (ave.118±57) was very close to the Redfield ratio, confirming that the organic P is purely derived from marine plankton. It also suggests that despite being a coastal area, the contribution of terrestrial input in this region is quite insignificant. Moreover, the TOC/OP ratio also infers that the organic matter in the mud banks is relatively fresh due to increased microbial activity (Vadstein et al., 1988; Ruttenburg and Goni, 1997).

## 5. Conclusion

This study elaborates the P cycling in the Alappuzha mud banks experiencing seasonal hypoxia due to the monsoon induced upwelling. The mud bank sediments are highly enriched in phosphorus due to the increased precipitation of phosphorus as authigenic/detrital apatite (Ca-P). The enrichment of Fe-P fraction is also high in sediments due to the formation of vivianite under hypoxia. The low TOC/OP values indicate that the labile organic P derived from marine plankton are relatively fresh due to very high microbial activity in sediments. Future studies should, therefore, focus more on how the dynamics of phosphorus such as its uptake and release influence the biological productivity of the mud banks.

#### Acknowledgments

The authors thank the Director, CSIR-National Institute of Oceanography, Goa and the Scientist in Charge, Regional Centre-Kochi, for the encouragement and support. We are thankful forthe service rendered by colleagues in carrying out the filed sampling successfully. The critical comments given by reviewers have considerably helped to improve the clarity of the manuscript. This is NIO contribution No. .....

# References

- Acharya, S.S., Panigrahi, M.K., Kurian, J., Gupta, A.K., Tripathy, S., 2016. Speciation of phosphorus in the continental shelf sediments in the Eastern Arabian Sea. Cont. Shelf Res. 115, 65–75.
- Anas, A., Sheeba V. K., Jasmin. C, Gireeshkumar. T. R., Mathew. D., Krishna, K., Nair, S., Muraleedharan, K.R., Jayalakshmy, K. V, 2018. Upwelling induced changes in the abundance and community structure of archaea and bacteria in a recurring mud bank along the southwest coast of India. Reg. Stud. Mar. Sci. 18, 113-121.
- Andrieux-Loyer, F., Aminot, A., 2001. Phosphorous forms related to sediment grain size and geochemical characteristics in French coastal areas. Estuar. Coast. Shelf Sci. 52, 617-629.
- Balachandran, K.K., 2004. Does subterranean flow initiate mud banks off the southwest coast of India? Estuar. Coast. Shelf Sci. 59, 589–598.
- Berbel, G.B.B., Braga, E.S., 2014. Phosphorus in Antarctic surface marine sediments- chemical speciation in Admiralty Bay. Antarct. Sci. 26, 281–289.
- Balzer, W., 1986. Forms of phosphorus and its accumulation in coastal sediments of Kieler Bucht. Ophelia 26, 19-35.
- Bourguet, N., Goutx, M., Ghiglione, J.F., Pujo-Pay, M., Mével, G., Momzikoff, A., Mousseau, L., Guigue, C., Garcia, N., Raimbault, P., Pete, R., Oriol, L., Lefèvre, D., 2009. Lipid biomarkers and bacterial lipase activities as indicators of organic matter and bacterial dynamics in contrasted regimes at the DYFAMED site, NW Mediterranean. Deep. Res. Part II Top. Stud. Oceanogr. 56, 1454–1469.
- Caraco, N. F., Cole, J. J., Likens, G.E., 1993. Sulfate control of phosphorus availability in lakes- A test and re-evaluation of Hasler and Einsele's model. Hydrobiologia, 253 (13), 275-280.
- CMFRI Bulletin, 1984. Mudbanks of Kerala Coast. Central Marine Fisheries Research Institute Bulletin No. 31, Kochi-18.
- Coelho, J.P., Flindt, M.R., Jensen, h.S., Lillebo, A.I., Pardal, M.A., 2004. Phosphorous speciation and availability in intertidal sediments of a temperate estuary: relation to eutrophication and annual P-fluxes. Estuar. Coast. Shelf Sci. 61, 583-590.

Dinesh and Jayaprakash, 2008. Zaherite the key mineral. Curr. Sci. 95, 962–967.

Egger, M., Jilbert, T., Behrends, T., Rivard, C., Slomp, C.P., 2015. Vivianite is a major sink for

phosphorus in methanogenic coastal surface sediments. Geochim. Cosmochim. Acta. 169, 217-235.

- (FAO) Food and Agriculture Organization of the United Nations. 1981. Atlas of the living resources of the sea. FAO Fisheries Series.
- Folk, R.L., 1980. Petrology of sedimentary rocks. Hemphil publishing company, Austin, Texas 78703.
- Froelich, P.N, Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R, Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica et Cosmochimica Acta, 43, 1075-1090.
- Garcia, A.R., A. F. de Iorio., 2003. Phosphorous distribution in sediments of Morales stream tributary of Matanza-Riachuelo River, Argentina. The influence of organic point source contamination. Hydrobiologia, 492, 129-138.
- Giordani, P., Astorri, M., 1986. Phosphate analysis of marine sediments. Chem. Ecol. 2, 103-112.
- Gireeshkumar, T.R., Deepulal, P.M., Chandramohanakumar, N., 2013. Phosphorous speciation in surface sediments of the Cochin estuary. Environ. Monit. Assess. 185, 2535–2552.
- Gireeshkumar, T.R., Mathew, D., Pratihary, A.K., Naik, H., Narvekar, K.U., Araujo, J., Balachandran, K.K., Muraleedharan, K.R., Thorat, B., Nair, M., Naqvi, S.W.A., 2017. Influence of upwelling induced nearshore hypoxia on the Alappuzha mud banks, South West Coast of India. Cont. Shelf Res. 139, 1–8.
- Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. Methods of sea water analysis, 2<sup>nd</sup> edition. VerlagChemie, Weinheim.
- Gunduz, B., Aydin, I., Hamamci, C., 2011. Study of phosphorus distribution in coastal surface sediment by sequential extraction procedure (NE Mediterranean Sea, Antalya-Turkey). Micromchem. J. 98, 72-76.
- Gupta, G.V.M., Sudheesh, V., Sudharma, K. V, Saravanane, N., Dhanya, V., Dhanya, K.R., Lakshmi, G., Sudhakar, M., Naqvi, S.W.A., 2016. Evolution to decay of upwelling and associated biogeochemistry over the southeastern Arabian Sea shelf. 121, 159-175.
- Hareeshkumar, P.V., Anand, P., 2016. Coastal upwelling off the southwest coast of India: observations and simulations. Int.J. Digital earth.
- Hou, L.J., Liu, M., Yang, Y., Ou, D.N., Lin, X., Chen, H., XU, S.Y., 2009. Phosphorous speciation and availability in intertidal sediments of the Yangtze estuary, China. Appl. Geochem. 24, 120-128.
- Hupfer, M., Gachter, R., Ruegger, H., 1995. Polyphosphate in lake sediments: 31P NMR spectroscopy as a tool for its identification. Limnol. Ckeanogr. 40 (3), 610-617.
- Jensen, H.S., Mortensen, P.B., Anderson, F.O., Rasmussen, E., Jensen, A., 1995. Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. Limnol. Oceanogr. 40, 908-917.

- Jensen, H.S., Thamdrup, B., 1993. Iron-bound phosphorous in marine sediments as measured by bicarbonate-dithionite extraction. Hydrobiologia. 253, 47-59.
- JGOFS, Protocols for the Joint Global Ocean Flux Study., 1994. Intergovermental oceanographic commission, Scientific committee on ocean research.
- Jilbert, T., Slomp, C.P., Gustafsson, B.G., Boer, W., 2011. Beyond the Fe-P-redox connection: Preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles. Biogeosciences 8, 1699–1720.
- Jyothibabu, R., Balachandran, K.K., Jagadeesan, L., Karnan, C., Arunpandi, N., Naqvi, S.W.A., Pandiyarajan, R.S., 2018. Mud Banks along the southwest coast of India are not too muddy for plankton. Sci. Rep. 8, 1–13.
- Kaiserli, A., Voutsa, D., Samara, C., 2002. Phosphorus fractionation in lake sediments- Lakes Volvi and -Koronia, N. Greece. Chemosphere. 46, 1147-1155.
- Kotilainen, K.L.Æ.M.L.Æ.A., 2009. The chemical character and behaviour of phosphorus in poorly oxygenated sediments from open sea to organic-rich inner bay in the Baltic Sea 25–48.
- Kraal, P., Bostick, B.C., Behrends, T., Reichart, G.J., Slomp, C.P., 2015. Characterization of phosphorus species in sediments from the Arabian Sea oxygen minimum zone: Combining sequential extractions and X-ray spectroscopy. Mar. Chem. 168, 1–8.
- Kraal, P., Dijkstra, N., Behrends, T., Slomp, C.P., 2017. Phosphorus burial in sediments of the sulfidic deep Black Sea: Key roles for adsorption by calcium carbonate and apatite authigenesis. Geochim. Cosmochim. Acta 204, 140–158.
- Kraal, P., Slomp, C. P., de Lange, G. J., 2010. Sedimentary organic carbon to phosphorus ratios as a redox proxy in Quaternary records from the Mediterranean. Chem. Geol. 277, 167-117.
- Kraal, P., Slomp, C.P., Reed, D.C., Reichart, G.J., Poulton, S.W., 2012. Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea. Biogeosciences 9, 2603–2624.
- Krom, M.D., Berner, R.A., 1980. Adsorption of phosphate in anoxic marine sediments. Limnol. Oceanogr. 25, 797-806.
- Levin, L.A., Ekau, W., Gooday, A. J., Jorissen, F., Middelburg, J.J., Naqvi, S.W.A., Neira, C., Rabalais, N.N., Zhang, J., 2009. Effects of natural and human-induced hypoxia on coastal benthos. Biogeosciences. 6, 2063-2098.
- Li, B., Brett, M.K., 2013. The influence of dissolved phosphorus molecular form on recalcitrance and bioavailability. Environmental pollution. 182, 37-44.
- Likens, G.E., Bormann, F.H., Johnson, N.M., 1981. Interaction between major biogeochemical cycles in terrestrial ecosystems. Some Perspectives of the Major Biogeochemical Cycles. SCOPE 17. Wiley, New York. 93-112.
- Linsy, P., Nagender Nath, B., Mascarenhas-Pereira, M.B.L., Vinitha, P. V., Ray, D., Prakash Babu, C., Ramalingeswara Rao, B., Kazip, A., Sebastian, T., Kocherla, M., Miriyala, P., 2018. Benthic cycling of phosphorus in the Eastern Arabian Sea: Evidence of present dayphosphogenesis.

Mar. Chem. 199, 53-66.

- Liu, S.M., Zhang, J., Li, D.J., 2004. Phosphorus cycling in sediments of the Bohai and Yellow Seas. Estuar. Coast. Shelf Sci. 59, 209-218.
- Lomas, M.W., Burke, A.L., Lomas, D.A., Bell, D.W., Shen, C., Dyhrman, S.T., Ammerman, J.W., 2010. Sargasso Sea phosphorus biogeochemistry: an important role for dissolved organic phosphorus (DOP). Biogeosciences 7, 695–710.
- Lukawska-Matuszewska, K., Bolalek, J., 2008. Spatial distribution of phosphorus forms in sediments in the Gulf of Gdańsk (southern Baltic Sea). Cont. Shelf Res. 28, 977–990
- Lukkari, K., Leivuori, M., 2007. Fractionation of sediment phosphorus.Limnology and Oceanography-Methods. 433–444.
- Michalopoulos, P., Aller, R.C., 2004. Early diagenesis of biogenic silica in the Amazone delta: alteration, authigenic clay formation and storage. Geochimica et Cosmochimica Acta. 68, 1061-1085.
- Monbet, P., Brunskill, G.J., Zagorskis, I., Pfitzner, J., 2007. Phosphorus speciation in the sediment and mass balance for the central region of the Great Barrier Reef continental shelf (Australia). Geochim. Cosmochim. Acta 71, 2762–2779.
- Muraleedharan, K.R., Dinesh Kumar, P.K., Prasanna Kumar, S., Srijith, B., John, S., Naveen Kumar, K.R., 2017. Observed salinity changes in the Alappuzha mud bank, southwest coast of India and its implication to hypothesis of mudbank formation. Cont. Shelf Res. 137, 39–45.
- Nair, S.M., 1990. Studies on the nutrient chemistry of mud bank. Ph.D. thesis. Cochin University of Science and Technology.
- Nair, S.M., Balchand, A.N., Nambisan, P.N.K., 1993. Phosphate fractionation in mud bank sediments from the southwest coast of India.Hydrobiologia 252, 61–69.
- Nausch, M., Nauch, G., 2004. Bacterial utilization of phosphorus pools after nitrogen and carbon amendment and its relation to alkaline phosphatase activity. Aquatic Microbial Ecology. 37(3), 237-245.
- Raiswell, R., Buckley, F., Anderson, T.F., 1987. Degree of pyritization of iron as a palaeo environmental indicator of bottom-water oxygenation. J Sediment Petrol. 58, 812-819.
- Rao, D.S., Mathew, K.J., Gopinathan, C.P., Regunathan, A., Murthy, A.V.S., 1984. Ecology of mud banks- Hydrography. CMFRI. Bulletin-31, 25-27.
- Redfield, A.C., Ketchum, B., Richard, F., 1963. The influence of organisms on the composition of seawater. In: M.Hill (ed). The Sea. 2, 26-77.
- Rothe, M., Kleeberg, A., Gruneberg, B., Friese, K., Mayo, m, P., Hupfer, M., 2015. Sedimentary Sulphur: Iron ratio indicates vivianite occurrence: A study from two contrasting freshwater systems. PLOS One, 1-18.
- Ruttenberg, K.C., Berner, R.A., 1993. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. Geochim. Cosmochim. Acta 57, 991–1007.

- Ruttenberg, K.C., Goni, M., 1997. Phosphorus distribution, C:N:P ratios and 13C (OC) in arctic, temperate and tropical coastal sediments: Tools for characterizing bulk sedimentary organic matter. Marine Geology. 139, 123-145.
- Ruttenberg, K.C., 2003. The global phosphorus cycle. In Treatise in Geochemistry (ed. H. D. Holland, K. Turekian). Elsevier. 585-643.
- Schenau, S.J., De Lange, G.J., 2001. Phosphorous regeneration vs. burial in sediments of the Arabian sea. Marine Chemistry. 75, 201-217.
- Schulz, D.H., Zabel. M., 2006. Marine Geochemistry. Springer, Berlin, Heidelberg.
- Sekula-Wood, E., Benitez Nelson, C.R., Bennett, M.A., Thunell, R., 2012. Magnitude and composition of sinking particulate phosphorus fluxes in Santa Barbara Basin, California. Glob. Biogeochem. Cycles. 26, 1-15.
- Sheshappa, G., 1953. Phosphate Content of Mudbanks along the Malabar Coast. Nature 171, 526–527.
- Simpson, C.D., Mosi, A.A., Cullen, W.R., Reimer, K.J., 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in surficial marine sediments from Kitimat Harbor, Canada. The science of the Total Environment. 181, 265-278.
- Slomp, C.P., Mort, H.P., Jilbert, T., Reed, D.C., Gustafsson, B.G., Wolthers, M., 2013. Coupled dynamics of iron and phosphorus in sediments of an oligotrophic coastal basin and the impact of anaerobic oxidation of methane. PLoS One 8, e62386.
- Slomp, C.P., Van der Gaast, S.J., Van Raaphorst, W., 1996. Phosphorus binding by poorly crystalline iron oxides in North Sea sediments. Mar. Chem. 52, 55–73.
- Søndergaard, M., Jensen, J.P., Jeppesen, E., 2003. Role of sediment and internal loading of phosphorus in shallow lakes. Hydrobiologia 506–509, 135–145.
- Sudheesh, V., Movitha, M., Hatha, A.A.M., Renjith, K.R., Resmi, P., Rahiman, M., Nair, S.M., 2017. Effects of seasonal anoxia on the distribution of phosphorus fractions in the surface sediments of southeastern Arabian Sea shelf. Cont. Shelf Res. 150, 57–64.
- Sunby, B., Gobeli, C., Silverberg, N., 1992. The phosphorus cycle in coastal marine sediments. Limnol. Oceanogr. 37, 1129-1145.
- Tarapchak, S. J., Moll, R. A., 1990. Phosphorus sources for phytoplankton and bacteria in lake Michigan. Journal of Plankton Research. 12 (4), 743-758.
- Uhlmann, D., Roske, I., Hupfer, M., Ohms,G., 1990. A simple method to distinguish between polyphosphate and other fractions of activated sludge. Water res. 24, 1355-1360.
- Vadstein, O., Jensen, A., Olsen, Y., Reinertsen, H., 1988. Growth and phosphorus status of limnetic phytoplankton and bacteria. Limnol. Oceanogr. 33, 489-503.
- Vink, S., Chambers, R.M., Smith, S.V., 1997. Distribution of phosphorus in sediments from Tomales Bay, California. Mar. Geo. 139, 157-179.

- Winkler, L. W., 1888. The determination of dissolved oxygen in the water. Ber Dtsch Chem Ges Berlin. 21, 2843-2854.
- Yang, B., Cao, L., Liu, S.M., Zhang, G.S., 2015. Biogeochemistry of bulk organic matter and biogenic elements in surface sediments of the Yangtze River Estuary and adjacent sea. Mar. Pollut. Bull. 96, 471-484.
- Yang, B., Liu, S.-M., Wu, Y., Zhang, J., 2016. Phosphorus speciation and availability in sediments off the eastern coast of Hainan Island, South China Sea. Cont. Shelf Res. 118, 111–127.
- Yang, B., Liu, S.M., Zhang, G.L., 2017. Geochemical characteristics of phosphorus in surface sediments from the continental shelf region of the northern South China Sea. Mar. Chem. 198, 44–55.

# **Figure Captions**

- **Figure1** Time Series locations off Alappuzha (mud bank region), southwest coast of India.The white discourteous line indicates mud bank area. M1, M2,and M3 (dotes in red) denote the time series locations and stations.
- Figure2 Schematic representation of the sequential extraction procedure adopted for the study
- Figure3 Seasonal variations in temperature, salinity and dissolved oxygen in the Alappuzha mud banks.
- Figure4 Distribution of Chlorophyll *a* in the Alappuzha mud banks.
- **Figure5** Seasonal variations in Dissolved Inorganic Phosphorous (DIP) and Dissolved Organic Phosphorous (DOP) in the Alappuzha mud banks.
- **Figure6** Different P fractions in surface sediments of the mud banks. (I denote Ex-P; IIdenote Fe-P; IIIdenote Non Red-P; IV denotes Ca-P and V denote ROP).
- **Figure7** Seasonal variability in exchangeable P (Ex-IP& Ex-OP; a&b), Fe bound P(Fe-IP & Fe-OP; c &d), non-reducible P bound to Al and Fe (Non Red-IP and Non Red-OP; e and f), Ca bound P (Ca-IP and Ca-OP; g &h) and residual organic P (i) in the surface sediments.



Figure 1



Figure 2



Figure 3



Figure 4



Figure 5



Figure 6



Figure 7

Sampling																		
date	Clay (%)			Sand (%)		Silt (%)		TOC (%)			TN (%)			TS (%)				
	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3
20-Apr-16	40.92	76.48	70.19	1.07	0.73	1.60	58.01	22.79	28.21	2.42	2.82	2.48	-	0.41	0.33	-	0.81	0.95
11-May-16	36.25	39.15	60.17	8.85	7.58	0.44	54.89	53.27	39.39	2.54	2.85	2.85	0.31	0.38	0.34	1.06	0.81	0.93
08-Jun-16	67.28	61.64	70.27	0.78	1.89	0.15	31.94	36.47	29.58	2.63	2.57	2.76	0.27	0.34	0.36	1.21	0.86	0.88
14-Jun-16	73.50	61.78	68.64	1.36	0.29	0.04	25.15	37.93	31.33	2.88	2.88	2.85	0.32	0.41	0.38	1.17	0.84	0.83
24-Jun-16	67.08	62.02	84.90	0.01	0.29	0.50	32.91	37.68	14.60	3.16	2.83	2.57	0.36	0.37	0.36	1.25	0.83	0.95
10-Jul-16	87.07	82.96	78.22	0.52	0.35	1.52	12.41	16.69	20.26	3.13	3.19	2.71	0.34	0.34	0.36	1.27	1.31	0.95
27-Jul-16	87.72	80.63	86.10	3.34	1.05	2.61	8.94	18.32	11.29	3.19	2.74	2.77	0.34	0.37	0.33	1.3	0.84	0.95
10-Aug-16	85.43	87.23	92.37	0.34	3.44	0.64	14.23	9.33	6.99	3.01	2.38	2.59	-	-	-	-	-	-
26-Aug-16	92.41	35.67	30.44	0.60	0.36	0.76	6.99	63.98	68.80	3.1	2.86	2.59	0.33	0.37	0.36	1.04	0.9	0.93

Table 1a : Distribution of texture (clay/sand/silt), total organic carbon (TOC), total nitrogen (TN) and total sulphur (TS) in surface sediment

Sampling date	Fe (mgg <sup>-1</sup> )			]	Mn (µgg <sup>-1</sup>	)		Fe/TP		TS/Fe			
	M1	M2	M3	M1	M2	M3	M1	M2	M3	M1	M2	M3	
20-Apr-16	62.85	67.41	62.85	-	128	148	34.97	36.06	28.24	8.32	8.16	23.22	
11-May-16	61.14	74.34	59.13	142	136	135	28.07	27.77	24.59	0.82	8.91	9.11	
08-Jun-16	59.85	65.28	66.6	150	119	113	48.53	37.53	24.61	0.72	0.55	11.09	
14-Jun-16	66.99	69.93	53.34	122	93	92	28.53	35.67	-	0.87	0.56	0.56	
24-Jun-16	58.9	58.94	59.3	89	94	91	26.03	12.97	14.25	1.00	0.56	0.66	
10-Jul-16	59.45	56.06	62.2	95	91	77	24.12	13.99	16.19	1.15	1.18	0.89	
27-Jul-16	58.34	58.3	59.11	85	83	91	13.50	28.17	22.10	1.00	0.72	0.85	
10-Aug-16	62.27	59.85	57.45	-	-	-	26.23	24.61	20.44	-	-	-	
26-Aug-16	62.56	61.36	55.56	70	72	74	-	-	-	-	0.91	0.92	

 Table 1b: Distribution of Fe,Mn, Fe/TP and TS/Fe ratio in surface sediment

Location	TP ( $\mu g/g$ )	Reference
GBR continental shelf, Australia	167.25-464.56	Monbet et al., 2007
Continental shelf of NS China sea	157.96- 581.98	Yang et al ., 2018
East China sea shelf	324-810.4	Zhou et al ., 2016
Bohai and Yellow sea	232.61- 554.42	Liu et al., 2004
Adriatic sea	88- 271	Giordani and Astorri., 1986
NE Mediterranean sea	268.56-275.12	Gunduz et al., 2011
KielerBucht	157.96- 771.23	Balzer., 1986
Gulf of Gdansk	54.20- 1424.758	LukawskaMatuszewska and Bolalek, 2008
Admiralty Bay	713.62-1323.48	Berbel and Braga, 2014
Gulf of Saint Lawrence	1300.87- 1982.27	Sundby et al., 1992
Gulf of Mexico	474±41 - 1035±63	Adhikari et al., 2015
Continental shelf of eastern Arabian sea	743.35- 2570.75	Acharya et al., 2016
Eastern Arabian sea	1300.86- 2942.43	Linsy et al., 2018
South west coast of India	969-2496	Babu et al., 2005
Continental shelf of SE Arabian sea	209-1081	Sudheesh et al., 2017
Mud banks, south west coast of India	1641- 3008	Present study

**Table 2** : Comparison of TP data in the present study with those reported in other coastal systems.