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Impact of seasonal oxygen deficiency on the phosphorous geochemistry of surface sediments along the Western Continental Shelf of India

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Abstract

The intensification of the natural coastal hypoxic zone over the western Indian shelf in the recent years and its impact on the biogeochemistry and marine life is a matter of concern. This study examines the influence of the seasonal oxygen deficiency on the phosphorus geochemistry of the surface sediments along the western continental shelf of India (WCSI). Speciation of phosphorus along with the geochemical characteristics (total organic carbon – TOC, total nitrogen – TN, and total phosphorus – TP) of the surface sediments and the hydrography of the western continental shelf of India (WCSI) were studied, during late summer monsoon (LSM) and spring intermonsoon (SIM). The hydrography of the WCSI revealed upwelling and associated seasonal oxygen deficiency with denitrifying suboxic conditions along the inner shelf and hypoxic conditions along the outer shelf. High concentrations of dissolved phosphate (PO_4) and dissolved Iron (Fe) were also observed in the subsurface water of the inner shelf during LSM. The shelf water of the WCSI was oligotrophic and oxygen rich during SIM. A latitudinal enrichment of TOC, TN and TP in the surface sediments was observed at 13–17° N, along the WCSI during LSM, where seasonal suboxia was intense. Authigenic apatite bound phosphorus (P_{aut}) was the major phosphorus species along the WCSI during LSM whereas detrital flourapatite bound phosphorus (P_{det}) was the major species during SIM. Substantial depletion of reactive iron(III)-bound phosphorus (ΔP_{Fe}) was observed in the surface sediments of the WCSI during LSM which showed significant correlation with the enrichment of PO_4 (ΔPO_4) in the overlying water during LSM compared to SIM. PO_4 diffusing into the water column from the sediments by reductive dissolution of P_{Fe} probably leads to high dissolved PO_4 along the inner shelf water during LSM which agrees with the existing hypothesis. Hence, phosphorus geochemistry of the surface sediments plays a major role in the biogeochemical cycling of phosphorus during periods of seasonal oxygen deficiency along the WCSI. Similar studies carried out along the eastern continental shelf of India (ECSI), where any kind of seasonal oxygen deficiency has not been reported yet, showed an abundance of

P_{det} (~50% of TP) and P_{org} (~32% of TP) in the surface sediments. The characteristic hydrographical features of the region such as high terrigeneous input, low production in the surface euphotic layers and greater preservation of labile organic matter in the sediments is also reflected in the phosphorus geochemistry of the surface sediments along ECSI.

1 Introduction

Hypoxic zones (O_2<62.5 µM) in the marine environment naturally occur along the upwelling zones where nutrient-rich oxygen deficient water from offshore are transported to the surface layers of the continental margins, and also along the regions with restricted circulation such as silled basins and fjords (Helly and Levin, 2004). However, the intensity, duration, and frequency of hypoxic events are increasing in many coastal regions around the world (Diaz and Rosenberg, 1995, 2008; Middelburg and Levin, 2009). The reasons attributed for intensification of the hypoxia are human interventions and changes in oceanographic conditions due to global warming and climate change. Hypoxia causes physiological stress on the biota. Intensification of hypoxia also has significant impacts on the biogeochemical cycling of elements in the marine environment (Ekau et al., 2009; Levin et al., 2009). It causes intense redox conditions in the sediments which promote denitrification and phosphorus desorption from metal oxide-hydroxide complexes (Kemp et al., 1990; Slomp and van Capellan, 2007; Middelburg and Levin, 2009).

Along the western continental shelf of India (WCSI), the largest natural hypoxic zone, hypoxia is induced by upwelling and vertical stratification (Banse et al., 1959; Naqvi et al., 2000, 2006a) during summer monsoon. The hypoxic condition persists until November or early December along the Central West coast of India (Banse, 1959, 1968; Reddy and Shakaranarayanan, 1968; Sharma, 1968; Wyrki, 1973). Naqvi et al., (2000, 2006a) studied the seasonal oxygen deficiency along the Western Continental Shelf of India (WCSI), especially off the coast of Goa (15° N), and observed intensification of subsurface oxygen deficiency over the region after 1970s as a result of increasing loading of nitrogen through coastal inputs. Intense reducing conditions prevailed along WCSI (mainly north of 12° N) with its progressive intensification closer towards the inner shelf (<50 m) from outer shelf (200–100 m). Intense reducing conditions were observed during September-October which dissipate by December. The phenomenon described here occurs seasonally along the WCSI, distinct from the permanent oxygen minimum zone in the Arabian Sea (Naqvi et al., 2000, 2006a).

Intensification of the oxygen deficiency has geochemical impacts on the water column and the underlying sediments. Naqvi et al., (2006a) analyzed N/P ratio in the suboxic water from the WCSI and observed the ratio to be -79.1 (Richard's stochiometry) along the shelf. They found high dissolved phosphate (PO_4) in the water from inner shelf environment compared to outer shelf regions. Based on the observation they proposed that PO_4 is leached out from the sediments when redox conditions prevail during summer monsoon (Naqvi, 2006a). The mechanism of leaching involves reductive dissolution of iron(III)-bound phosphorus (P_{Fe}) from the sediments to the overlying water column.

Compared to WCSI, the hydrography of the eastern continental shelf of India (ECSI) is influenced by the discharges from six major rivers. The process introduces $\sim 1.4 \times 10^9$ tonnes of suspended sediments and 0.67 Sv of freshwater discharges into the ECSI (Subramaniam, 1995). Presence of thick surface layer of low saline water suppresses the upwelling process along the ECSI (Naidu et al., 1999). Since upwelling is much weaker and the nutrient loading into the region by the river discharges is not substantial, the coastal water is free from suboxia (Naqvi et al., 2006a).

The present study aims to examine the speciation of phosphorus in the surface sediments of the WCSI during and before the development of seasonal oxygen deficiency along the region. The study is supported by the data on the total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) contents of the surface sediments and the hydrographical characteristics of the shelf water. This study verifies the hypothesis proposed for the presence of high PO_4 in subsurface water along the WCSI during intense oxygen deficiency by Naqvi et al. (2006a). The results are compared with similar studies carried out in the ECSI where seasonal changes in redox conditions are insignificant. The present study on speciation of phosphorus in the surface sediments along the ECSI is the first of its kind in the region.

2 Materials and methods

2.1 Sampling

Surface sediment samples were collected onboard FORV Sagar Sampada from 15 locations along the WCSI during late summer monsoon (LSM) of 2003 (September–October) and during spring intermonsoon (SIM) of 2004 (April–May) (shown in Fig. 1). The September–October sampling period coincides with the terminal end of summer monsoon (June–September) and fall intermonsoon (October). But as the region was found to retain the characteristics of summer monsoon, the sampling period was designated as LSM. Sampling was done at 7 latitudes – one sample each from the inner shelf (∼50 m water depth) and the outer shelf (∼150 m water depth) except 8° N during LSM and 22° N during SIM, respectively. Along the ECSI, sampling was done during November–December, 2002, at 9 locations (Fig. 1). The near shore (<50 m water depth) is usually considered as the inner shelf but in our study, sediment samples from ∼50 m water depth are considered to represent the inner shelf.

The sediment samples were collected using Smith McIntyre grab (0.1 m^2) sampler supplemented with external lead weights. Sampling was repeated until the grab was completely filled to retrieve intact surface sediment layers. The surface sediment layers (0–1 cm) were immediately transferred and stored at –20 °C. Before analyses, these sediment samples were freeze dried and ground to a fine powder. Water samples were also collected from standard depths (0, 10, 20, 30, 50, 75, 100 and 150 m) using a Seabird Conductivity-Temperature-Depth Profiler (USA, model: SBE-911 plus; accuracy for conductivity ±0.0003 S/m, temperature ±0.001 °C and pressure ±0.015%)

fitted with 1.7 L Niskin sampler. For the analysis of dissolved iron (Fe), water samples were collected separately using pre-cleaned 5 L Teflon-coated Go-Flo bottles (General Oceanics) attached to polyvinyl chloride-coated stainless steel CTD-rosette sampler. On recovery, the water samples were filtered through 0.45 µm membrane (Millipore) filters to separate them into dissolved and particulate fractions. The filtered water samples were stored after acidifying with concentrated HCl. However, Fe was not measured from all the standard depths as mentioned above for the analyses of DO and dissolved inorganic nutrients. The sampling depths for Fe are shown in the distribution plot of Fe.

2.2 Analysis

2.2.1 Water

Dissolved Oxygen (DO) was estimated following Winkler's method and the dissolved inorganic nutrients were analysed using SKALAR 4-channel auto analyser onboard following standard procedures described in Grasshoff et al. (1983). The analyses of Fe in the filtered water samples were done using ammonium pyrrolidine dithiocarbamate-methyl isobutyl ketone extraction (Brooks et al., 1967) and subsequent measurement using Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, ZL-4110).

2.2.2 Sediment

The total organic carbon (TOC) and total nitrogen (TN) content of the powdered dry sediment samples were measured using a CHN elemental analyzer (VarioEL III EA) after treatment with 1M HCl to remove inorganic carbon (Hedges and Stern 1984). TN is assumed to represent organic nitrogen (Van der Zee et al., 2002). The sequential leaching experiment was carried out using the updated SEDEX procedure (Anderson and Delaney, 2000) modified by Schenau and De Lange (2000), by including NH_4Cl leaching step. The technique chemically isolates phosphorus from five different sedimentary components. 250 mg of the sediment was leached with 2 M NH_4Cl

(adjusted to pH 7 with ammonia) to isolate exchangeable or loosely sorbed, biogenic or fish borne apatite bound phosphorus (hydroxyapatites) (P_{bio}). The residual solid was treated with citrate-dithionite-buffer (CDB) (0.22 M Na-citrate, 0.33 M sodium dithionite, 1 M $NaHCO_3$, pH 7.6) to separate P_{Fe}. Authigenic apatite associated with authigenic phosphorus rich minerals (P_{aut}) was isolated from the residue using 1 M sodium acetate (buffered with acetic acid to pH 4) and $MgCl_2$. Detrital apatite phosphorus (detrital fluorapatite) (P_{det}) was separated using 1 M HCl. Organic phosphorus associated with organic matter (P_{org}) was extracted from the residue by ashing at 550 °C for 2 h, after drying in oven at 80 °C with 80% (w/v) of $Mg(NO_3)_2$, and finally treated with 1 N HCl for 24 h. All the leached solutions (except CDB solutions) were measured for phosphorus by standard ascorbic acid molybdate blue colorimetric technique (Grasshoff et al., 1983). For CDB leach, organic extraction technique developed by Watanabe and Olsen (1962) was used. Reproducibility based on the analysis of replicates of the individual phosphorus extractions was better than 5% except for CDB (16%) and P_{org} (10.5%) extraction. Total phosphorus (TP) was determined as the sum of the five individual phosphorus species analysed in a sample.

2.2.3 Statistical analysis

Spatial and temporal changes in TOC, TN, TP and the five different phosphorus species analyzed along the WCSI was tested by two-way analysis of variants (ANOVA) (Pusceddu et al., 1999) with latitude and seasons as factors, respectively.

3 Results

3.1 Hydrography

3.1.1 WCSI during LSM and SIM

The distribution of the physico-chemical parameters such as temperature, DO and dissolved inorganic nutrients along the WCSI during LSM and SIM is shown in Figs. 2 and 3, respectively. Our observations show cold, nutrient rich and oxygen deficient shelf water during LSM. Notable features are surfacing of the 27 °C isotherm and the simultaneous shift of the PO_4 and NO_3 isolines (Fig. 2d and e). The 0.8 µM isolines for PO_4 and the 2 µM isolines for NO_3 were found to be surfacing at both the inner shelf (Fig. 2i) and the outer shelf (Fig. 2ii). This indicated the prevalence of upwelling along the WCSI even during the end phase of summer monsoon. Oxygen deficient hypoxic (<20 µM) water (beyond 100 m) were observed in the outer shelf of the WCSI during LSM. In the inner shelf, particularly along 13–17° N, severe oxygen deficiency was observed leading to suboxia as indicated by the very low DO (<10 µM) and high NO_2 (>4 µM) in the intermediate water (30–40 m). During the LSM, inner shelf was characterized by high PO_4 (>2.2 µM) in the intermediate water during LSM and high PO_4 (2 µM) and NO_2 (>4 µM) near the bottom water at 12–16° N. Sediment denitrification during the upwelling period has been identified as a factor responsible for the annual nitrogen loss of 0.21–1.15 Tg from the WCSI (Naqvi et al., 2006b). The hydrography of the WCSI displayed in Fig. 3 reveals a general tendency of oxygen saturated (DO>200 µM) and oligotrophic conditions (NO_3<2 µM and PO_4<0.8 µM) during SIM. However, in the outer shelf ~15° N, the near bottom water showed anomalously low DO (<30 µM).

Distribution of Fe along the WCSI during LSM and SIM is shown in Fig. 4. Higher Fe concentrations in the surface water of 14–17° N during LSM may be due to higher land runoff and river discharges during the season. In the inner shelf, between 11–17° N, intermediate water (35–45 m) was found high in Fe concentration (>3.5 ppb) coinciding with the region with high phosphate concentration described earlier. Compared to the inner shelf, the outer shelf was found to be low in Fe during LSM.

3.1.2 ECSI

The ECSI was nutrient deficient and oxygen saturated during the sampling period. The inner shelf water was well mixed with negligible gradients in the physico-chemical parameters like DO, nitrate, nitrite and phosphate cancentrations. Along the outer shelf, the surface water was oxygen saturated and nutrient deficient whereas the bottom water (beyond 100 m) of the outer shelf was oxygen deficient (DO<50 m) (Fig. 5).

3.2 Geochemical characteristics of the surface sediments

During LSM, we observed higher concentration of TOC, TN and TP between 13–17° N along both the outer and the inner shelf of the WCSI (Fig. 6a), whereas statistical analysis using two-way ANOVA showed significant latitudinal variations for TOC ($F=5.65$, $P>0.01$) and TN ($F=5.84$, $P>0.01$). TOC, TN and TP were found higher along the outer shelf of 15° N during SIM coinciding with our earlier observation on low DO (<30 µM) in the near bottom water (Fig. 6b). The statistical analyses show insignificant variations of TOC, TN and TP between LSM and SIM. The sediments of the ECSI had low TOC and TP concentrations, but comparable with the WCSI in TN content (Fig. 6c).

3.3 Phosphorus speciation in the surface sediments

The distribution of the five different species of phosphorus (P_{bio}, P_{Fe}, P_{aut}, P_{org}, P_{det}) analysed in the surface sediments of the WCSI and the ECSI during the sampling periods are given in Fig. 7. Mean concentrations of the individual sedimentary phosphorus species are also represented (Fig. 8) as the fraction of TP in percent $\left(P_{\text{species}}=\frac{P_{\text{species}}}{\text{TP}}\times 100\right)$ (Filipelli and Delaney, 1996). P_{aut} (5.20–3784.0 ppm) was the major species of phosphorus along the WCSI during LSM. P_{org} was also higher along the WCSI during LSM than SIM. But P_{det} (1.59–2686.13 ppm) was the major phosphorus species along the shelf during SIM (Fig. 7). During LSM, TP along the inner shelf mainly constituted P_{aut} (0.81 to 74.5% of TP) and P_{org} (15.12 to 55.00% of TP) whereas TP along the outer shelf was mainly dominated by P_{det} (Fig. 8). P_{Fe} showed significant seasonality ($F=17.13$, $P>0.001$) with higher concentrations during SIM (0.33 to 11.14% of TP) compared to LSM (0.02 to 2.09% of TP) when P_{Fe} was very low along the shelf. P_{bio} was low along the WCSI during both the seasons. P_{bio} ranged from 0.81 to 12.71% of TP during LSM. During SIM, P_{bio} varied from 1.66 to 10.86% of TP with anomalously high concentrations observed in the outer shelf ~21° N (29.40% of TP).

TP along the ECSI (both the inner and outer shelf) was dominated by P_{det} (44.2 to 63.6% of TP) followed by P_{org} (20.2 to 45.9% of TP). Distribution of phosphorus species in the sediments were similar in the inner shelf and the outer shelf of the ECSI. P_{aut} (1.41 to 195.0 ppm) was less along ECSI compared to the WCSI. P_{Fe} (3.0 to 7.0% of TP) and P_{bio} (2.8 to 8.5% of TP) were the least abundant species as shown in Fig. 8c.

4 Discussion

4.1 Influence of the seasonal oxygen deficiency on the geochemistry of surface sediments along WCSI

Hydrography of the WCSI during LSM is distinguished by cold, nutrient rich upwelled water over the shelf. The high organic production in the surface eutrophic layers induced by the nutrient rich upwelled water causes oxygen deficiency in the subsurface water along the WCSI during LSM. High biological production associated with upwelling in the mixed layer is observed in the region till October (Banzon et al., 2004; Vijay, 2005). Intense oxygen deficiency leading to suboxia ($DO<10\,\mu M$; $NO_2>4\,\mu M$) with observed high PO_4 (>2 µM) and Fe was observed in the subsurface water (30–40 m) of the inner shelf between 13–17° N during LSM. We also observed high concentrations of TOC, TN and TP along 13–17° N in the surface sediments coinciding with the region experiencing suboxia during the same period. High concentration of TOC and labile organic carbon (total hydrolysable carbohydrates and proteins) in the surface sediments of WCSI along 13–17° N during LSM were earlier reported by Jacob et al. (2009). Sediments deposited under low-oxygen bottom water are expected to contain higher amounts of organic matter with high labile fraction (Moodley et al., 2005; Middelburg and Levin, 2009). An upcore increase in TOC is observed in the sediment cores from hypoxic zones (Gooday et al., 2009). Kurian et al. (2009) has reported a steady increase in the TOC (>3%) and the biomarkers dinosterol, phytol and stigmasterol in the upper core sediments (after ca. AD 1950) from off Goa (15° N) along the WCSI. This has been attributed to the high upwelling induced productivity in the recent decades due to increased solar irradiance and intensifying anoxia over the western Indian shelf. Sediment cores from Chesapeake Bay also exhibited upcore increase in TN and TOC due to the enhanced eutrophication by the intensification of hypoxia in the past 200 years (Cooper and Brush, 1991; Bratton et al., 2003). The C/N ratio showed values ranging between 6–14 (Table 1) suggesting that the source of sedimentary organic matter was mostly marine in origin (Tyson, 1995).

4.2 Speciation of phosphorus in the surface sediments of the WCSI during and before the seasonal oxygen deficiency

Sedimentation of organic matter is the most important process responsible for the transfer of reactive phosphorus from the water to the sediment (Froelich et al., 1982; Delaney, 1998). In this study, we observed P_{org} as one of the major phosphorus species in the surface sediments of the WCSI during LSM. This period coincides with the shelf experiencing higher production and seasonal oxygen deficiency. P_{aut} was another major phosphorus species along the inner shelf of the WCSI during LSM. Accumulation of high P_{aut} in the sediments (defined as phosphorites when containing more than 5 wt% P_2O_5) is a characteristic feature of the upwelling zones (Jahnke et al., 1983; Froelich et al., 1988; Fillippeli et al., 1994). Phosphorite deposites from the geological past (Holocene and pleistocene) have been reported from the western margin of India (Rao et al., 2000). Babu and Nath (2005) have reported ~50% P_{aut} in the surface sediments of Eastern Arabian Sea overlain by the permanent OMZ. Our observations on P_{det} (non-reactive form of P species) along WCSI show high concentration in the outer shelf compared to the inner shelf during LSM. P_{det} originates from the weathering of terrestrial igneous or metamorphic rocks (Ruttenberg, 1992) that is deposited along with other sediment fractions. High P_{det} in the continental slope sediment of Karwar (15° N) and in the inner shelf off Kochi (10° N) along the study region was reported earlier by Babu and Nath (2005). Schenau and De Lange (2001) showed high concentration of P_{bio} in the sediments from Arabian Sea (Oman and Pakistan margin) overlain by oxygen minimum zone. The dissolution of fish debris plays a major role in the formation of phosphorite (phosphogenesis) in the sediments along the Pakistan margin (Schenau and De Lange, 2000). But Babu and Nath (2005) observed relatively low P_{bio} (25–33%) along the slope regions of WCSI overlain by oxygen minimum zone. The present observations suggest that P_{bio} was low in the sediment samples collected during both LSM and SIM along the WCSI. During SIM, P_{det} was found to be the dominant phosphorus species while P_{aut} was low along the WCSI due to less productivity. The speciation of phosphorus in the surface sediments of the WCSI was found to be different during and before the seasonal oxygen deficiency observed in the region.

4.3 Release of phosphorus from the sediments into the water column during LSM

P_{Fe} was significantly low along the WCSI during LSM compared to SIM. Temporal variability in oxygen levels of bottom water can have major consequences for Fe and Mn concentration in the sediments (Kristensen et al., 2003; Middelburg and Levin, 2009). Ferric oxides, hydroxides and oxyhydroxides (Fe oxides) provide sorption sites for phosphorus. Though phosphorus itself is not oxidized or reduced, it undergoes redox cycle together with Fe oxides. Under anoxic conditions, iron(III) oxides are reduced to iron(II) oxides, which add excess Fe(II) in the water phase along with observed phosphate (Krom amd Berner, 1980; Slomp et al., 1996; Jensen et al., 1995). Therefore, Fe oxides play important role governing the cycling of P in the sediments. In the present study, an enrichment of PO_4 in the subsurface waters of the inner (20–30 m) and outer (30–100 m) shelf was observed during LSM with respect to SIM (ΔPO_4). We also noticed simultaneous depletion of P_{Fe} in the surface sediments during LSM in contrast to SIM (ΔP_{Fe}) coinciding with ΔPO_4. The relationship obtained (Fig. 9) shows significant statistical correlation for inner shelf ($n=7$, $r=0.81$, $P<0.05$) and outer shelf ($n=7$, $r=0.59$, $P<0.10$) (Fig. 9). A concomitant increase of Fe is also observed in the subsurface water of the inner shelf during LSM. The effusion of phosphate to the water column from the surface sediments of the inner shelf is further evident from the >2 µM contours of PO_4 observed in the near bottom water along 11–16° N (Fig. 2). These results provide evidence for mobilization of PO_4 from the sediments together with Fe as a result of reductive dissolution of Fe(III) oxides/hydroxides to Fe(II) oxides/hydroxides during periods of intense oxygen deficiency observed along WCSI during LSM. High fluxes of phosphate and Fe under hypoxic and anoxic conditions have been reported from other marine environments including ocean-margin settings (Ingall and Jahnke, 1997; Aigar, 2001; Conley et al., 2002; Mort et al., 2010) and coastal regions (Kemp et al., 2005; Jordan et al., 2008). Our observations are the first from Indian Ocean region identifying the relationship of hypoxia with mobilization of phosphorus from sediment to water. This supports the hypothesis proposed earlier on the possible mechanism of removal of phosphorus from the sediment to the water column by Naqvi et al., (2006). The schematic diagram (modified from Peña et al., 2010) explains the major processes along the suboxic inner shelf of the WCSI during LSM (Fig. 10). Though we made the first documentation of the relationship between phosphorus species in the sediment and PO_4 in the overlying water and its release mechanism, it needs to be established with laboratory based studies and regional monitoring of coastal water along with the surface sediments.

4.4 Influence of the hydrographical characteristics on the phosphorus speciation in the sediments along the ECSI

The eastern continental shelf is a zone of weak upwelling and hence, remains less productive compared to its western counterpart. The substantial lithogeneous input through major rivers supports high sedimentation, fast burial of organic matter and subsequently a better preservation of organic matter. The surface sediments show higher abundance of labile organic matter along ECSI compared to WCSI (Jacob et al., 2008). P_{det} was the dominant phosphorus species constituting ∼50% of TP along ECSI. The dominance of P_{org} (>30% of TP) and the low C/P and C/N ratios (Table 1) found in the region indicates high organic matter preservation (Ingall and Van Cappellan, 1990). Phosphorite deposits of Cretaceous-Eocene age with high P_2O_5 (>18%) have been recovered from the shelf off Chennai (13° N) along the ECSI. During the Cretaceous, India was situated south of the equator and hence the eastern margin of India might have experienced coastal upwelling which led to the formation of phosphorites along the margin (Rao et al., 1998). But we observed low TP in the surface sediments of the ECSI than the sediments of the WCSI. In the ECSI, the abundance of P_{aut} was also lower than the WCSI which may be due to the low productivity in the region. Hence, the characteristic hydrographical features of the region such as high terrigeneous input, low production in the surface euphotic layers and greater preservation of labile organic matter in the sediments are also reflected in the speciation of phosphorus in the surface sediments of the ECSI.

5 Conclusions

The present study examines the phosphorus speciation along with the geochemical characteristics (TOC, TN and TP) of the surface sediments, and the hydrographical characteristics of the WCSI during (LSM) and before (SIM) the prevalence of seasonal oxygen deficiency associated with upwelling along the region. The hydrography, geochemical characteristics and the phosphorus geochemistry of the surface sediments of the WCSI were found different during both the sampling periods. During LSM, the WCSI experienced upwelling and the associated oxygen deficiency with hypoxic conditions along the outer shelf and suboxic conditions along the inner shelf. High PO_4, NO_2 and Fe were also observed in the subsurface intermediate water column during LSM. The WCSI was found to be oligotrophic and oxygen rich during SIM. Geochemical characteristics of sediment were also different during LSM and SIM with high latitudinal enrichment of TOC, TN and TP along 13–17° N during LSM where intense seasonal suboxia was observed. P_{aut} and P_{org} were the dominant species during LSM while P_{det} was the dominant species during SIM. Significant seasonal variations were observed for P_{Fe} which was considerably higher along the WCSI during SIM while it was depleted during LSM. The excess of PO_4 in the subsurface water during LSM compared to SIM (ΔPO_4) was positively correlated with the depletion of P_{Fe} in the surface sediments during the same period (ΔP_{Fe}). The present study provides observational evidence for the proposed mechanism of release of PO_4 in presence of redox conditions prevailing along the shelf during LSM. The redox condition promoted reduction of Fe(III)-oxy-hydroxides to Fe(II)-oxy-hydroxides which releases phosphorus to the overlying water column, leading to a higher dissolved PO_4 concentrations in the shelf water during LSM. This provides new idea about the relationship of the seasonal oxygen deficiency and phosphorus mobilization observed in the sediment column from the region.

The high lithogenic input along the ECSI was reflected in the dominance of P_{det} in the surface sediments. The high P_{org}, low C/P and C/N ratios along ESCI suggest rapid burial and preservation of organic matter due to the high sedimentation rate along the region. Hence, the differences in the hydrographical conditions and the productivity patterns of the two regions are found to exert a major influence on the phosphorus geochemistry of the surficial sediments of the western and eastern continental shelves of India.

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Table 1. Distribution of C/N and C/P in the surface sediments along the WCSI and ECSI.

		Latitude (° ′ N)	Longitude (° ′ E)	C/N	C/P
Western Continental shelf (Late Summer)	Inner shelf	9 56.52	75 48.94	4.64	173.34
		11 30.09	75 0.05	5.63	116.13
		13 0.36	74 24.17	7.17	207.77
		14 58.85	73 44.87	8.30	319.00
		17 03.45	72 48.57	6.66	237.54
		18 51.96	71 59.81	7.85	249.63
		20 59.42	69 32.76	6.35	151.76
	Outer shelf	8 03.11	76 41.66	7.62	159.28
		9 55.90	75 36.42	8.28	56.56
		11 29.82	74 42.13	8.46	84.65
		12 59.93	73 55.38	7.89	91.73
		15 00.00	72 59.05	13.35	267.13
		16 59.81	71 57.58	9.21	156.36
		18 59.82	70 0.45	9.65	324.70
		21 01.86	69 4.43	3.72	63.33
Western Continental shelf (pre-monsoon)	Inner shelf	9 59.06	75 48.78	4.81	152.60
		11 30.57	75 09.94	6.36	249.00
		13 00.32	74 24.19	8.57	229.34
		14 58.00	73 42.00	7.25	212.80
		17 00.03	73 00.24	9.06	488.42
		18 46.67	71 46.26	6.07	80.09
		20 59.85	69 30.52	5.23	135.94
	Outer shelf	9 59.48	75 38.30	6.14	304.44
		11 28.90	74 43.31	7.12	67.98
		12 59.33	73 54.45	8.90	147.68
		14 59.86	73 00.24	15.71	194.22
		16 59.80	72 04.34	7.56	99.36
		19 00.05	70 00.83	700	93.38
		20 59.31	69 10.16	7.60	190.43
		22 00.96	68 00.44	13.26	188.63
Eastern Continental shelf	Inner shelf	11 00.00	80 03.35	5.30	168.21
		13 00.00	80 23.21	2.88	72.87
		17 00.00	82 32.97	2.99	58.97
		18 57.48	84 47.47	2.70	71.96
		20 29.91	87 30.23	4.19	131.23
	Outer shelf	11 00.00	80 12.58	2.76	58.81
		13 00.00	80 36.76	6.59	92.49
		15 1.51	80 23.01	2.78	56.51
		20 30.09	88 19.79	5.04	131.68

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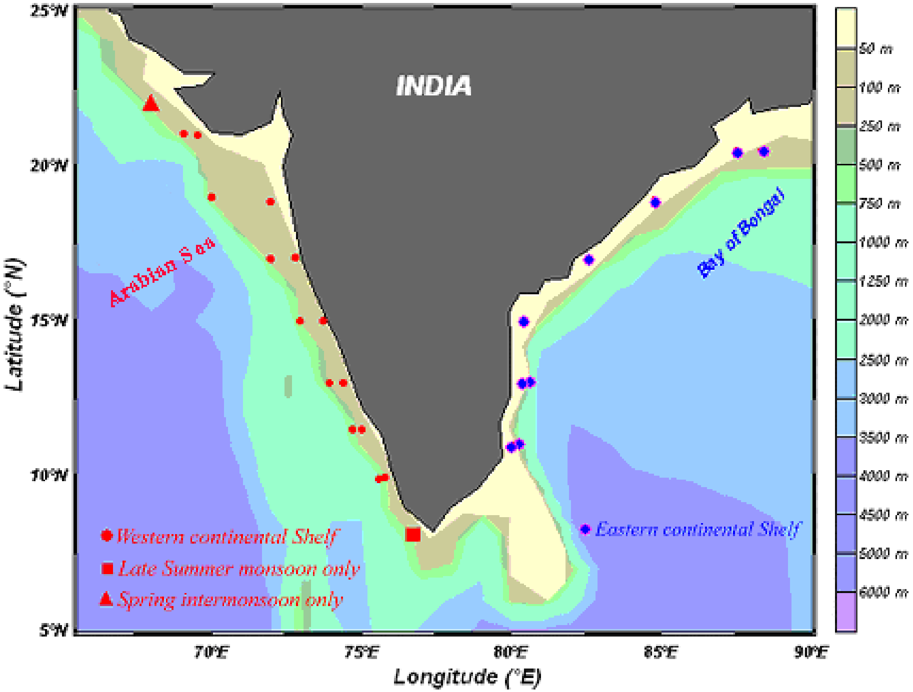

Fig. 1. Sampling locations along the WCSI and ECSI.

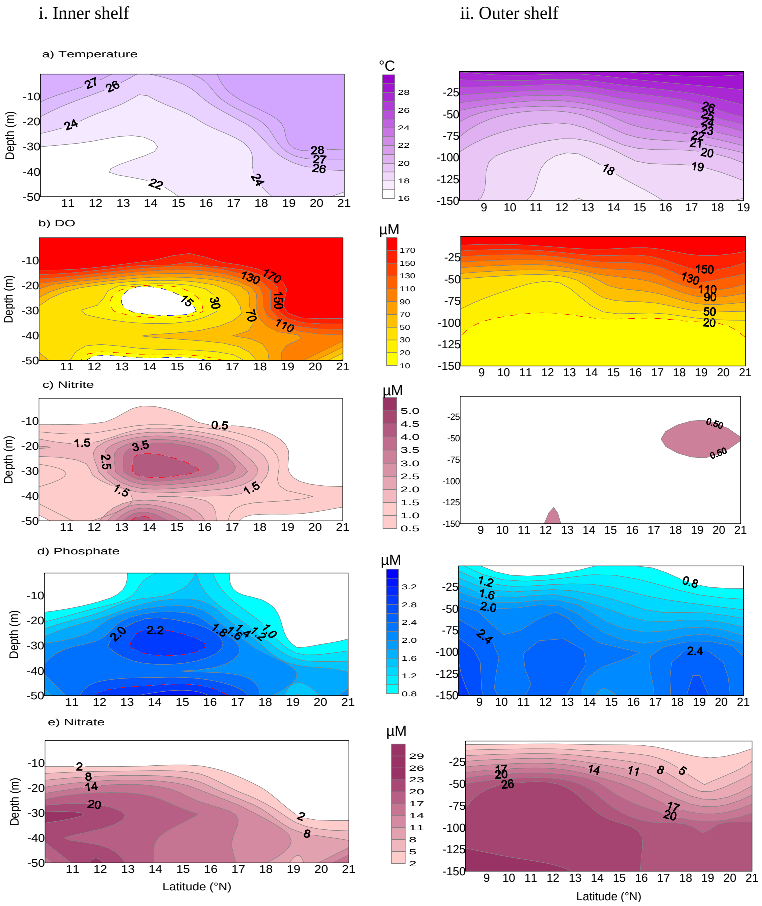

Fig. 2. Distribution of temperature, dissolved oxygen and dissolved inorganic nutrients along the WCSI during LSM.

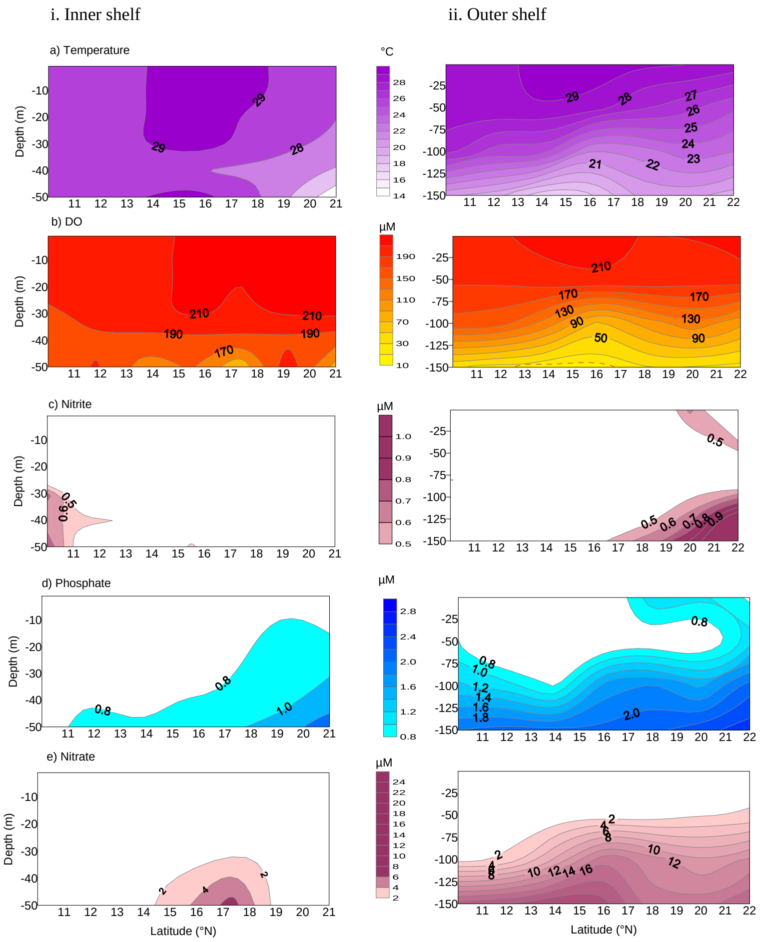

Fig. 3. Distribution of temperature, dissolved oxygen and dissolved inorganic nutrients along the WCSI during SIM.

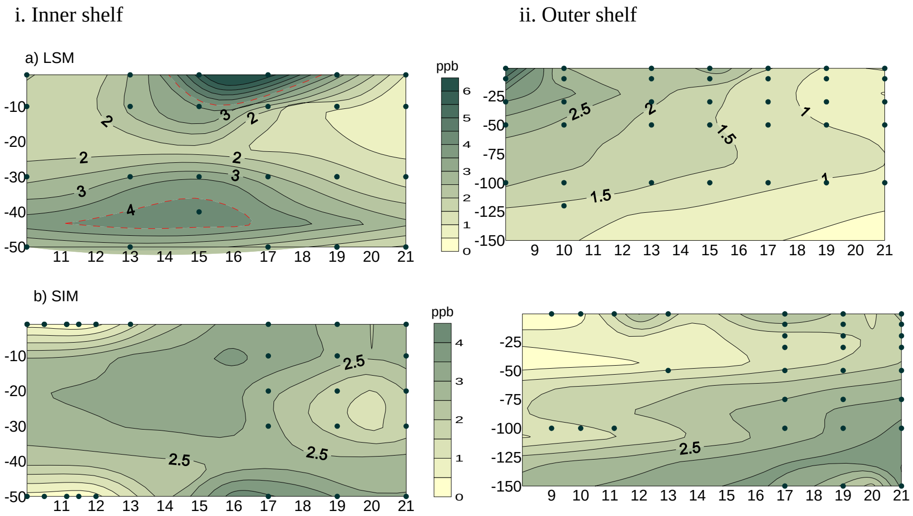

Fig. 4. Distribution of dissolved iron (Fe) along the WCSI.

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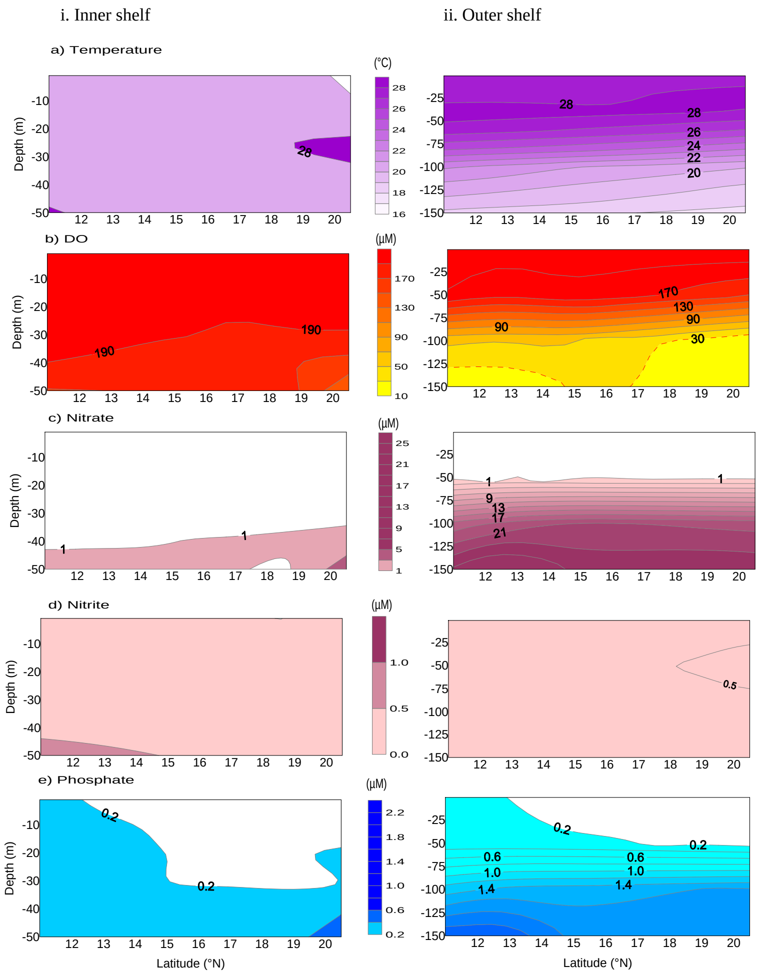

Fig. 5. Distribution of temperature, dissolved oxygen and dissolved inorganic nutrients along the ECSI.

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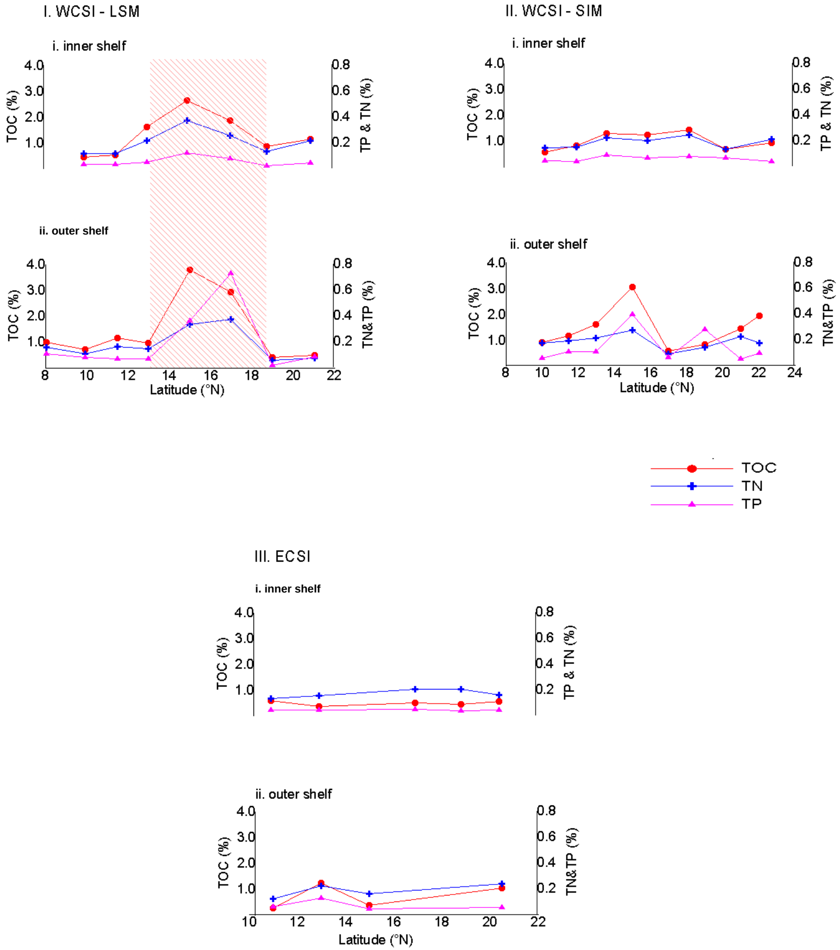

Fig. 6. Distribution of TOC, TN and TP in the surface sediments of WCSI during **(a)** LSM **(b)** SIM and along **(c)** ECSI.

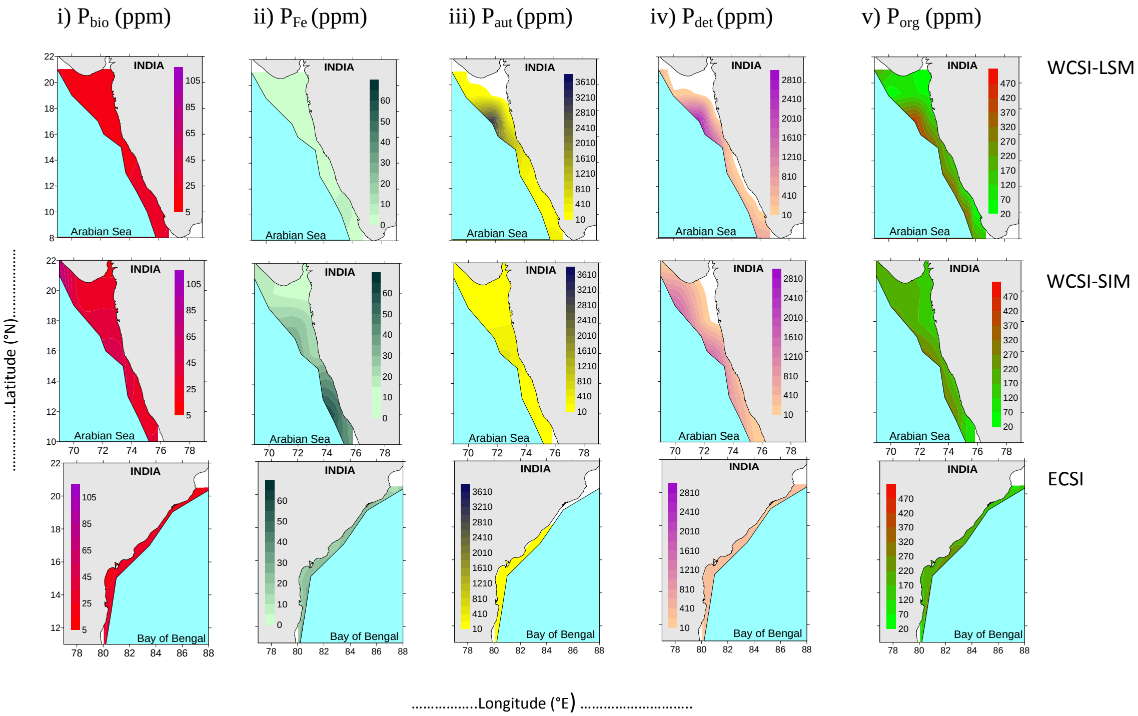

Fig. 7. Distribution of the phosphorus species in the surface sediments of WCSI and ECSI during the sampling periods.

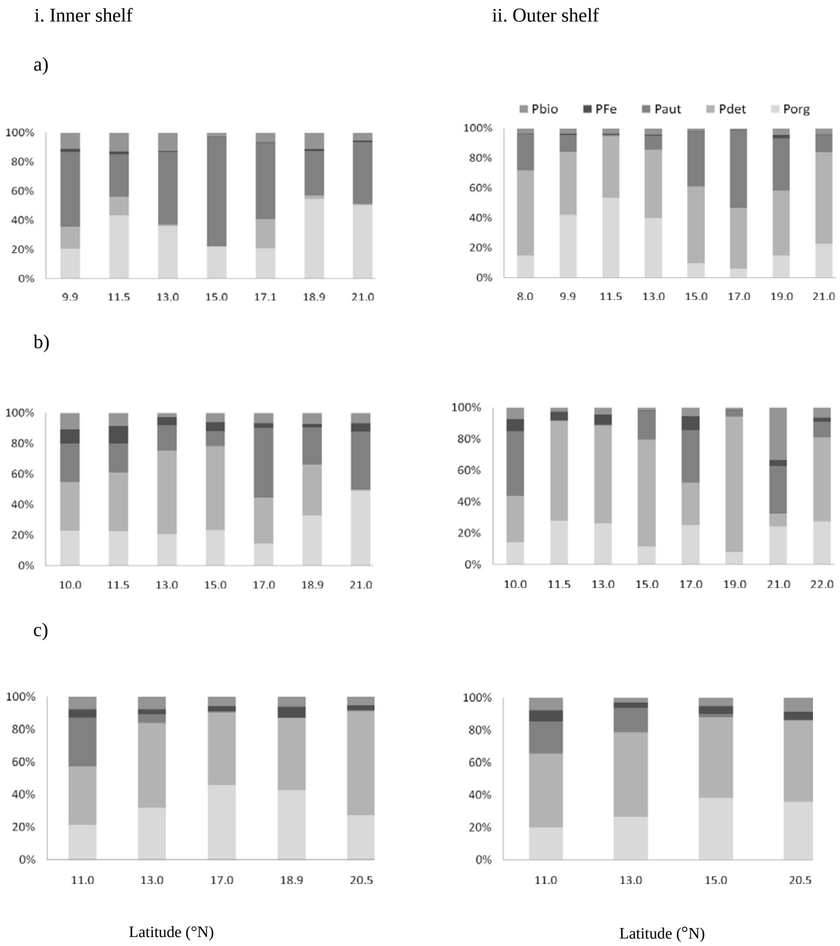

Fig. 8. Percentage contribution of the phosphorus species to TP in the surface sediments along the WCSI during **(a)** LSM **(b)** SIM and along **(c)** ECSI.

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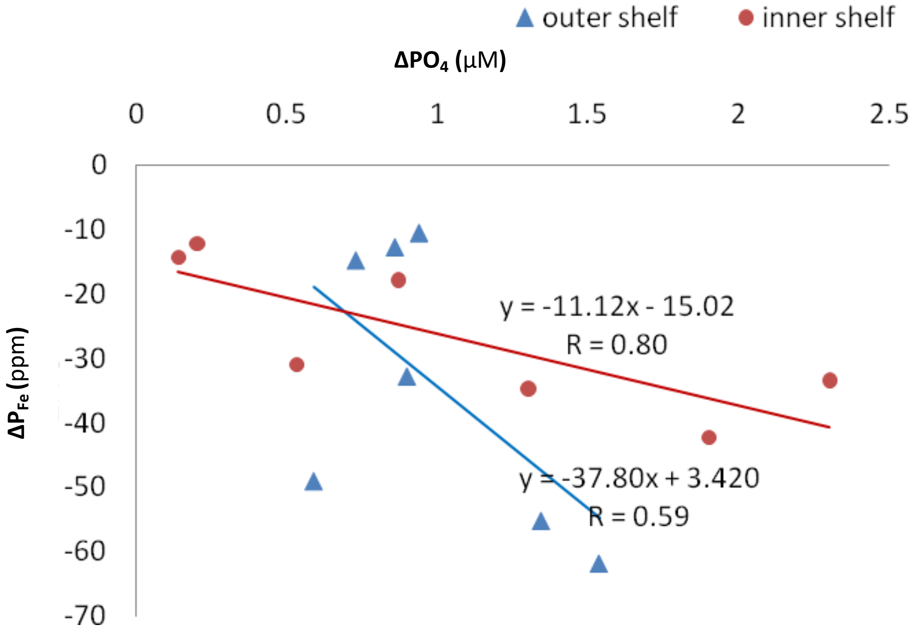

Fig. 9. Correlation of the enrichment of PO_4 in the subsurface waters (ΔPO_4) vs. depleted P_{Fe} in the surface sediments (ΔP_{Fe}) along the WSCI during LSM.

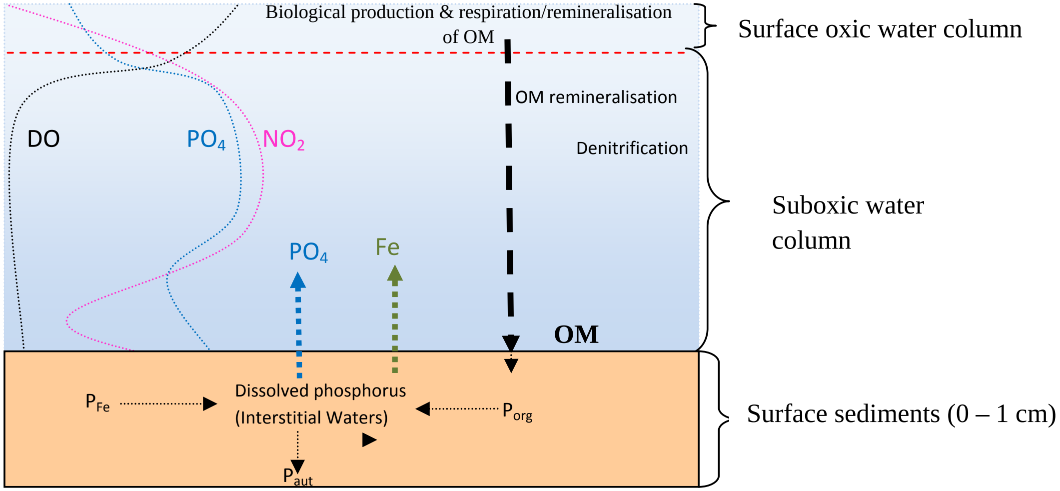

Fig. 10. Schematic representation of the major processes along the suboxic inner shelf of the WCSI during LSM.