

## Dynamics of trace metals in sediments of a seasonally hypoxic coastal zone in the southeastern Arabian Sea

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### Abstract:

This study examined the effect of water column hypoxia on the distribution and geochemical fractionation of trace metals in the seasonally hypoxic coastal environment in the southeastern Arabian Sea. Water and surface sediments were collected fortnightly from the Alappuzha mud bank between April and August 2016, which covered the pre-upwelling and upwelling seasons. The water column was warm and well-oxygenated during April-May. During June-August, the incidence of cold and hypoxic water indicated strong coastal upwelling prevailed in the entire study domain. The Fe and Mn content in sediments gradually decreased, because of the reductive dissolution and subsequent release of metals under hypoxia. The concentration of metals such as Ni, Zn and V decreased substantially under oxygen deficiency, whereas Cr showed marked enrichment in sediments. Although the geochemical forms of trace metals displayed the dominance of residual fractions (inert), the reactive non-residual metal forms (exchangeable, Fe/Mn (oxy) hydroxide, and organic matter/sulphide bound) showed considerable variability under hypoxia. The shift from Fe/Mn (oxy) hydroxide bound to organic matter and sulphide bound was evident during hypoxia. Cr exhibited strong affinity towards organic matter and sulphide, and Pb and Zn showed relatively high association towards the Fe/Mn (oxy) hydroxide phase. Even with such a phase shift induced by the hypoxic conditions, the concentrations of these metals remained within the normal background levels, indicating the pristine nature of the mud bank environment.

**Keywords:** geochemistry; trace metals; upwelling; hypoxia; organic matter; bioavailability.

## 1. Introduction

Coastal regions experiencing upwelling can be considered ideal sites to understand dissolved oxygen control over the accumulation of trace elements and organic matter (Castillo et al., 2018). Sediments deposited under coastal upwelling areas accumulate many bioactive and redox-sensitive trace metals (Nameroff et al., 2002; Bonning et al., 2004; 2005). Metals exist in sediments in different phases (e.g. organic matter bound, Fe/Mn (oxy) hydroxides bound, carbonates, sulphides, and residual) based on the prevailing environmental conditions and affinity of metals towards various carrier phases (Malandrino et al., 2009; Dang et al., 2015). Even though most of these metals (Fe, Mn, Zn) are involved in metabolic processes, trace metals are of particular concern owing to their persistence, bioavailability, and toxicity (Dhanakumar et al., 2013).

Metal fractions in the coastal environment are mainly controlled/regulated by organic matter/organic ligands (Canfield, 1994; Chakraborty et al., 2016; Helmond et al., 2018; Zhang et al., 2014), Fe and Mn (oxy) hydroxides, and the rate of formation of authigenic minerals (Canfield, 1994; Chakraborty et al., 2016; Helmond et al., 2018). The degradation of organic matter in a water column is more efficient in oxygenated conditions than in hypoxic or anoxic conditions (Jahnke et al., 1982; Henrichs and Reeburgh, 1987), which leads to the enrichment of organic matter bound metals in the sediments (Munoz et al., 2012; Boning et al., 2009; Helmond et al., 2018). Periodic hypoxia or anoxia in the sediment-water interface can alter the sedimentary redox conditions, causing repeated dissolution and re-precipitation of metals bound to Fe/Mn (oxy)hydroxides (Chakraborty et al., 2016, 2018). Hypoxic bottom water decreases oxygen penetration to the sediment. It decreases electron acceptors, accelerating the release of metals from sediments, and enhancing their potential bioavailability (Eggleton and Thomas, 2004; van der Geest and Leon Paumen, 2008). Thus, depending on the biogeochemical variability across the sediment-water interface (such as dissolved oxygen, pH, grain size, and organic matter), the sediments may act as a sink or source of metals (Gleyzes et al., 2002; Atkinson et al., 2007). Metals can thus enter the food chain in the aquatic environment and become available for accumulation in biota.

Coastal upwelling and mud banks are two concurrent coastal oceanographic phenomena operating along the southwest coast of India. The southwest coast of India experiences basin-wide coastal upwelling during the southwest monsoon season (June-September) when the cold, nutrient-rich, and oxygen-depleted waters are brought to the surface, thereby significantly enhancing the biological production (Gupta et al., 2016; Naqvi et al., 2000). Mud banks are unique seasonal oceanographic phenomena occurring during the southwest monsoon season at specific locations along the southwest coast of India. They appear as semi-circular patches of calm nearshore waters (water

depth 10 m) when the rest of the coastal environment is highly turbulent due to high monsoonal waves (height = 2-5 m ). A fluid mud layer at the bottom of mud banks continuously attenuates the incident waves to create a calm environment conducive to fishing (Jyothibabu et al., 2018; Gireeshkumar et al., 2020). The coastal waters become productive during the upwelling period, showing a substantial increase in the abundance and biomass of phytoplankton and zooplankton (Arunpandi et al., 2017; Karnan et al., 2017; Madhu et al., 2020, 2021). A shift in the dominance of microbes based on their preferences to sustain low oxygen conditions was also observed (Anas et al., 2018; Parvathi et al., 2019).

Varying levels of dissolved oxygen in the sediment-water interface from the pre-upwelling and upwelling period (well-oxygenated to hypoxic) influence the geochemical partitioning of trace metals. Mud banks can be considered a natural mesocosm to understand the trace metal cycling and biogeochemical processes operating under seasonal oxygen deficiency. Nearshore hypoxia triggers the reductive dissolution of metal oxides, resulting in influxes of trace metals to the overlying water column, which may significantly impact the water column productivity and ecosystem functioning. Understanding the labile metal fractions or potential bioavailability of trace metals in nearshore sediments is crucial for the sustainable development of the coastal environment, especially in specialised coastal systems such as mud banks (Prasannakumar et al., 2018). This time-series monitoring of the Alappuzha mud bank from April (pre-upwelling) to August (upwelling) portrays the transition of a coastal environment (sediment) from normoxic to suboxic condition (Gireeshkumar et al., 2017; Mathew et al., 2019, 2020), which may have a significant influence on the dynamics of trace metals. This study focuses on the variations in trace metal concentrations and their geochemical forms under varying redox conditions in surface sediments to describe the factors influencing metal cycling in this dynamic nearshore region.

## **2. Materials and Methods**

### *2.1 Study area*

The study region considered herein is situated on the southwest coast of India; it is influenced by the Asian monsoon characterised by seasonally reversing winds and coastal circulation. The west coast of India resembles an eastern-boundary-type upwelling environment during the southwest monsoon (Naqvi et al. 2009) when the surface current flows equatorward. Upwelling brings oxygen-poor, nutrient-rich subsurface waters to the coastal region, which turn hypoxic by late summer due to exhaustion of oxygen by heterotrophic microorganisms (Naqvi et al., 2010). The eastern Arabian Sea is the only region where upwelling occurs with high freshwater inputs. A low salinity lens on the

surface also contributes to the development and sustenance of intense oxygen deficiency at considerably shallow depths. Hypoxia in the bottom waters significantly affects the geochemistry of the sediment, and a corresponding decrease in the Fe and Mn concentration proportional to oxygen depletion was observed in the study region (Mathew et al., 2019, 2022).

## *2.2 Time-series sampling from the study domain*

Fortnightly observations were made at three locations (M1, M2, and M3) in and around the Alappuzha mud banks covering the pre-upwelling (April to May) and upwelling (June to August) seasons of 2016. Station M2 (water depth = 7 m) represents the Alappuzha mud bank (tranquil waters with a fluid mud layer at the bottom), while station M1 (water depth = 7 m) is a non-mud bank region located 7 km north of M2. Station M3 is situated at a water depth of 13 m (Fig. 1). A CTD profiler (SBE 19 plus) was used to record the salinity (accuracy of  $\pm 0.0005$  S/m in terms of conductivity) and temperature (accuracy of  $\pm 0.0005^\circ\text{C}$ ). Water samples were collected at all stations at every 3 m intervals using a 5 L Niskin sampler and sub-sampled to measure dissolved oxygen (DO). Sediments were collected using a Van Veen grab ( $0.04\text{ m}^2$ ). Several deployments per station were performed to reduce bias due to the washout of supernatant water and possible disturbance of the surface sediment during the grab operation, obtaining well-preserved sediment samples. The surface layer (1-3 cm) was carefully skimmed off using a pre-cleaned scoop and transferred to a clean high-density polyethylene (HDPE) bottle in an inert atmosphere. The samples were stored in ice till analysis.

## *2.3 Laboratory analysis*

### *2.3.1 Dissolved oxygen and bulk sediment characteristics*

Dissolved oxygen was analysed using Winkler's method with an automatic titration system (Metrohm 865 Dosimat plus) following standard procedure with a detection limit of  $2\ \mu\text{M}$  (Grasshoff et al., 1999). Sediment texture was determined following pipette analysis (Folk, 1980) using wet sediments following treatment with 1 M HCl and  $\text{H}_2\text{O}_2$  (30 %) to remove carbonates and organic matter. Sediment samples were washed with distilled water, dried at  $50^\circ\text{C}$ , weighed, and treated with sodium hexametaphosphate (overnight) to disperse the sediment particles, and separated following pipette analysis. Vacuum dried samples were powdered with a mortar and pestle. For total organic carbon (TOC) analysis, sediments were pre-treated with 1 M HCl (for removal of carbonates), washed with deionised water (to remove salts), and freeze-dried. TOC, total nitrogen (TN), and total sulphur (TS) were determined using a Vario EL III CHNS Analyzer with detection limits of 0.07 %, 0.01 %, and 0.01 %, respectively. The sediment samples (0.3 g) for total metal analysis were digested with a mixture of extra-pure acids,  $\text{HNO}_3\text{-HCl-HF}$  (7:2:1), in a microwave digester (Milestone Ethos Easy).

After cooling, the extract was filtered and diluted to 50 ml. Metal concentrations (Fe, Mn, Zn, Ni, Co, Cr, Pb, Cd, and V) were determined using inductively coupled plasma-optical emission spectrometer (ICP-OES; Thermo Scientific i-CAP 7000 Series). Triplicate analyses were conducted, and the average values were reported as total metal concentrations. The accuracy of trace metal analysis was validated using standard reference material for marine and estuarine sediments (BCSS-1) from the National Research Council of Canada. The recoveries were within the acceptable range ( $\pm 5\%$ ).

### 2.3.2 Metal fractionation

Sequential extraction was performed using a three-stage modified procedure recommended by BCR (1999). Solid-phase trace metals are classified into four geochemical forms, namely, water-soluble, exchangeable, and associated with carbonates (Exch), reducible trace metals associated with Fe/Mn hydroxides (Red), trace metals associated with organic matter, and sulphide (Oxi) and metals incorporated into the structural component of the sediment or residual fraction (Res). The sequential extraction method used in this study is described in detail by Nemati et al. (2011).

Freeze-dried and homogenised sediment samples were extracted with glacial acetic acid for 16 hours to extract exchangeable fractions. For a reducible fraction (Red), the residue from step 1 was resuspended in 0.5 M hydroxyl ammonium hydrochloride (pH 1.5) for 16 hours. The oxidisable fractions (Oxi) were extracted by treating the residue from step 2 with  $H_2O_2$ , evaporated, and treated with 1 M ammonium acetate solution (pH 2) and shaken for 16 hours. The obtained residue was finally subjected to microwave-assisted tri-acid digestion (Milestone Ethos Easy, USA) using a mixture of  $HNO_3$ :  $HCl$ :  $HF$  (7:2:1) to extract the residual fraction (Red). All extraction was conducted on end over a shaker at  $25^\circ C$ , and the subsequent residue was washed with deionised water to remove traces of the solvent mixture. All fractions were analysed using graphite furnace atomic absorption spectrophotometer (GFAAS; Thermo Scientific iCE 3000 Series, GFS 35). A certified reference material (BCR 701, Sigma Aldrich, USA) was used to ensure the accuracy of the sequential extraction. The recovery was checked by comparing the total trace metal data with the sum of metal concentrations obtained from each sequential extraction step. The recoveries for both the methods mentioned above were within the acceptable range ( $\pm 5\%$ ). Triplicate extractions were performed, and the average values were reported.

## 3. Results

### 3.1 Upwelling induced nearshore hypoxia

The water column temperature data displayed the incursion of cold subsurface water with time, which indicates upwelling (Fig. 2a). The water column remained warm on the surface ( $32^\circ C$ ) and well

mixed till the end of May. The strengthening of south-westerly winds was associated with the upwelling of relatively cold (26 °C) bottom waters at M3 on 2 June 2016, which gradually progressed to the coastal locations (M1 and M2). The subsurface water temperature decreased by 3°C during the initial phase of upwelling, and it further intensified as the southwest monsoon progressed. The time evolution of water column DO indicates a progressive decline in the concentration and devolvement of water column hypoxia in tandem with the upward propagation of colder waters (Fig. 2a). The DO of bottom water was <40 µM below the well-oxygenated surface layer (i.e., 2 m below the surface layer at M1 and M2, and 4 m below at M3) during the southwest monsoon and sustained throughout the study period (Fig. 2c).

### 3.2 Bulk sedimentary characteristics

The dominance of clay (>80%) over silty-clay fractions was the characteristic change associated with the formation of mud banks and a fluid mud layer, just above the sediment bed, especially at M2 (Fig. 3a). The mud bank formation also coincided with the enrichment of TOC (2.79% ± 0.21%), TN (0.37% ± 0.02%), TS (0.9% ± 0.16%) and TP (0.21% ± 0.08%) in sediments (Fig. 3b).

### 3.3 Trace metals in sediments

Iron was the most dominant metal in mud bank sediments and exhibited a significant positive correlation with DO ( $r=0.45$ ,  $p<0.05$ ) (Supplementary material Table S1). Fe concentration showed a considerable decrease during the southwest monsoon, especially at M3. The removal of Mn was more pronounced (Mn vs DO  $r=0.57$ ,  $p<0.01$ ; Supplementary material Table S1) during hypoxia when its pre-monsoon levels (138-150µg/g) decreased considerably to 70-74µg/g during the peak monsoon period (Fig. 4). Ni, V, and Zn were positively correlated with DO ( $p<0.05$ ) and had the lowest values during hypoxia (37.12-81.13 µg/g, 79.21-96.87µg/g, and 45.72-67.91µg/g, respectively). Cr (136.11-242.82µg/g) was enriched during hypoxia, whereas Co (11.00-14.53µg/g), Pb (12.15–23.53µg/g), and Cd (0.12-0.37µg/g) did not show any variations (Fig. 5).

### 3.4 Trace metal fractionation

The abundance of different geochemical forms of trace metals varied significantly during the well-oxygenated and hypoxic periods. Different trace metals exhibited a heterogeneous response to the hypoxia at the sediment-water interface. The lithogenic fraction was predominant among the geochemical forms of all trace metals considered herein (Ni:76- 87%; Zn:69-86%; Cr:60-83%, Co:82-92%; Pb:53-94%). The labile form of Ni exhibited high affinity towards organic matter (oxidisable; 12-23 %), followed by the reducible fraction (<1 %) (Fig. 6). Among the bioavailable forms of Zn, the reducible fraction accounted for 5-15% of total Zn. It decreased gradually, whereas the oxidisable

fraction, (4 to 25 % of total Zn), demonstrated an increasing trend during hypoxia (Fig. 7a). Pb did not display a seasonal trend; however, its the geochemical forms, especially major labile forms (reducible and oxidisable) varied with DO. The reducible fraction was dominant among the labile forms (1 to 38 %), and the oxidisable fraction accounted for 5-14 % of total Pb (Fig. 7b).

Cr showed significant enrichment during hypoxia and displayed a similar trend to the metals mentioned above. Its reducible fraction (1-13 % of total Cr) decreased gradually during the upwelling (hypoxic) period. In contrast, the oxidisable fraction (15-27 % of total Cr) increased during the bottom water hypoxia (Fig. 8a). For Co, the reducible fraction was lower, contributed 0-6 % of total Co, and the oxidisable fraction contributed 7-13 % of total Co (Fig. 8b). The exchangeable fraction was considerably low for all the trace metals (Ni < 1 %, V < 6 %, Zn < 2 %, Cr < 1 %, Co < 1 %, and Pb < 1 %).

#### **4. Discussion**

Upwelling was persistent in the study region from June onwards, which brought hypoxic waters (< 62  $\mu\text{M}$ ) to the subsurface layer in the shallow depths (Gireeshkumar et al., 2017; Mathew et al., 2019), and it was sustained for a long period, especially at M3. The low salinity lens in the surface waters formed through intense precipitation in the coastal zone led to strong thermohaline stratification and contributed to the sustenance of severe oxygen deficiency at considerably shallow depths (Naqvi et al., 2006; Naqvi and Unnikrishnan, 2009). The development of water column hypoxia, nutrient enrichment, and high primary productivity in mud bank has been investigated in previous studies (Gireeshkumar et al., 2017; Mathew et al., 2019). The study region experienced relatively weak winds (< 5 m/s) during pre-upwelling (April to May), while considerably strong winds (6-7 m/s) were prevalent during the onset of the southwest monsoon (Smitha et al., 2014). There was substantial rainfall over the study region (average of  $7.7 \pm 5.8$  mm/day) during the monsoon period, with a significant peak during June (average of  $15.1 \pm 5.8$  mm/day) (Madhu et al., 2021). The formed mud banks acted as a calm region even during monsoon due to the thick fluid mud layer, which decreased the wave energy (Jyothibabu et al., 2018; Shynu et al., 2017).

The redox condition of the sediment and adsorbing/scavenging phases such as clay minerals, Fe/Mn (oxy)hydroxides and organic ligands are the main influencing factors of trace metal accumulation in the sediments (Zhang et al., 2014). Therefore, the main variables explaining metal dynamics are organic enrichment, oxygen, and sediment texture. In mid-June, dissolved oxygen values in the subsurface waters decreased considerably, reaching the lowest (< 20  $\mu\text{M}$ ) in the study region during July. The offshore station M3 continued to remain hypoxic thereafter (July-September),

whereas its incursion towards the shallow depths of the mud bank (M1 and M2) occurred only during severe atmospheric depressions (Muraleedharan et al., 2017a). The chlorophyll *a*, and nutrients data obtained in this study is already presented in Gireeshkumar et al. (2017) and Mathew et al. (2019). Chlorophyll *a* content was low (<3 mg/m<sup>3</sup>) during May and June (especially in the offshore M3 station), and it increased to high concentrations (>12 mg/m<sup>3</sup>) by end-July due to the nutrient injection through upwelling. Dinoflagellate blooms were also reported in the study region from August onwards (Madhu et al., 2020; Madhu et al., 2021), and subsequent decomposition of organic matter increased the oxygen demand of already oxygen-deficient water. Mud bank sediments are mostly clayey and have high metal binding capacity due to the large surface area (McCave, 1984; Horowitz and Elrick, 1987).

Fe concentration in this study (average of  $6.35 \pm 0.61$  wt.%) is much higher than the continental margin ( $2.92 \pm 0.78$  wt.%) and the suboxic region ( $3.42 \pm 1.08$  wt.%) around the world (Raiswell and Canfield, 1998), which is unique to the mud banks (Mathew et al., 2020, 2022). Dissolved oxygen exhibited significant positive correlations with Mn ( $r=0.57$ ,  $p<0.01$ ) and Fe ( $r=0.45$ ,  $p<0.05$ ) (Supplementary Material, Table S1). Mn occurs in sediments as discrete oxide particles, coatings on particles, and Mn<sup>2+</sup> adsorbed on organic materials (Feely et al., 1982; Graham et al., 1976). In the surface sediment, Fe and Mn concentration decreased proportional to decrease in oxygen content, and it was characterised by a more pronounced decrease in Mn concentration (Fig. 4). When the overlying water column was well oxygenated, oxygen in the sediment surface was used for the oxidation of organic matter. In contrast, reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup> occurred in the deeper layers to release electrons that diffused and re-oxidised Mn<sup>2+</sup> to Mn<sup>4+</sup> on the surface (Froelich et al., 1979; Schulz et al., 2006). However, hypoxia favours the reduction of Mn<sup>4+</sup> to Mn<sup>2+</sup>, which in turn releases into the water column, decreasing Mn concentrations in the surface sediments. The re-oxidation rate of Fe is higher than that of Mn, and the diffusive flux of Fe from the deeper layers through the dissolution of Fe(oxy)hydroxides could be re-precipitated even during mild oxygen deficiency (Krom and Berner, 1980; Jensen et al., 1995; Slomp et al., 1996). The temporal variations of Fe and Mn during hypoxic/suboxic events indicated that the metal oxide reduction is a significant pathway of organic matter mineralisation in sediments (Canfield et al., 1993; Thamdrup and Canfield, 1996; Berg et al., 1998; Vandieken et al., 2006).

Sedimentary trace metals exhibited different seasonal features concerning the oxygen deficiency in the water column. A marked reduction of Zn, V, and Ni, corresponding to hypoxia ( $r=0.43$ ,  $0.45$ , and  $0.43$  respectively,  $p<0.05$ ) (Supplementary Material, Tables S1 and S2), indicated the association of these metals with Fe/Mn (oxy) hydroxides. The reductive dissolution of this primary



binding phase during hypoxic events might dislodge the scavenged metals to the overlying water column or convert metals into more soluble sulphide forms (Chakraborty et al., 2018; Gallon et al., 2004; Schaller et al., 1997). On the contrast, Cr enrichment was evident during the same period; Cr enrichment under reducing conditions has been established (Guo et al., 1997) as reduced Cr (III) is more stable than Cr (VI). A slight decrease in total Cr values during peak upwelling indicated the reductive dissolution of Red-Cr corresponding to oxygen deficiency (especially at M2 and M3).

#### *4.1 Trace metal fractionation in sediments*

The non-residual forms of Ni predominated by Oxi-Ni (Fig. 6) showed close correlation with TOC ( $r=0.66$ ;  $p<0.01$ , Supplementary Material, Table S2), indicating that organic matter is the major controlling factor for bioavailability. Ni is involved in the enzymes participating in photoautotrophic production (especially in diatoms); therefore, most highly productive upwelling zones (Peru, Namibia, Chile, and the Gulf of California), a close association of Ni and organic matter has been observed, and it is often considered a reliable indicator of organic matter sinking flux (Twining et al., 2012; Boning et al., 2015). Red-Ni displayed a significant negative correlation with Exch-Ni ( $r= -0.52$ ;  $p<0.05$ ) (Supplementary Material, Table S2), which may be due to the reductive dissolution of Ni during hypoxia and subsequent release into the pore water or the overlying water column.

Among the non-residual fractions, Pb was more concentrated ( $> 30\%$ ) in the reducible form (Fig. 7b), indicating its dependence on Fe/Mn (oxy)hydroxide (Chakraborty et al., 2015; Belzile et al., 1989). Under the oxic condition, Pb forms stable complexes with Fe/Mn (oxy) hydroxides, whereas hypoxic conditions lead to the dissolution of metal oxides releasing Pb in the reducible form (Gallon et al., 2004, Chakraborty et al., 2016; Chakraborty et al., 2018). Red-Pb content decreased considerably during persistent hypoxia (24 June-10 July). Subsequent hypoxia for a short duration showed a spike in this fraction, which may be due to the re-precipitation of authigenic Fe oxides (poorly crystalline oxides) with high scavenging capacity. The significant correlation of Fe with Exch-Pb ( $r=0.88$ ,  $p<0.01$ , Supplementary Material, Table S3) substantiates the loss of Pb in exchangeable form by dissolution and its association with organic matter/sulphide. Similarly, non-residual Zn was mainly concentrated in the reducible fraction (Fe/Mn (oxy) hydroxides), followed by oxidisable and exchangeable fractions (Fig. 7a). Both reducible and exchangeable fractions of Zn were low during intense hypoxia, which may be attributed to their weak adsorption as a coating to metal oxides. However, increase in Oxi-Zn could be attributed to the adsorption of released Zn to oxidisable phases. The positive correlation of Oxi-Zn with chlorophyll *a* ( $r=0.48$ ,  $p<0.05$ , Supplementary Material, Table S1) suggests increased association of Zn with freshly derived organic matter during enhanced biological productivity.

Under the oxic condition, Cr (IV) (chromate ion,  $H_xCrO_4^{-2+x}$ ) is thermodynamically stable (Richard and Bourg, 1991), and it prefers to bind with organic phases and gets weakly adsorbed to Fe/Mn (oxy) hydroxides. Approximately 20 % of the metal concentration (30-50  $\mu\text{g/g}$ ) was bound in this fraction (Oxi-Cr), and it increased gradually with upwelling intensity, especially at M1 (Fig. 8a). However, Red-Cr decreased considerably corresponding to decreasing DO values (Chakraborty et al., 2018) owing to the reduction of Fe/Mn (oxy)hydroxides. Oxi-Cr exhibited a significant positive correlation with TS ( $r=0.52$ ,  $p<0.01$ ) (Supplementary Material, Table S4). Under reducing conditions, the rapid reduction of highly soluble Cr (IV) (Guha et al., 2001; James, 2002) to less mobile Cr (III) occurs, which is favoured by the presence of organic matter (Chakraborty et al., 2018), sulphide, and Fe(II) (Schaller et al., 1997). The association of reduced chromium with iron sulphide (Lakatos et al., 2002) is also probable. Thereby, stable Cr (III) forms dominant in sediments during peak upwelling, leading to the enrichment of overall Cr concentration (Fig. 8b). The non-residual fraction of Co prefers to adsorb on the surface of Fe/Mn (oxy) hydroxides (Chakraborty et al., 2012) and organic matter, while Oxi-Co showed significant positive correlation with clay ( $r=0.48$ ,  $p<0.05$ ) and a negative correlation with DO ( $r=-0.54$ ,  $p<0.05$ , Supplementary Material, Table S5).

In marine ecosystems, metal contamination harms flora and fauna. Total metal concentrations, except for Cr and Ni, in mud bank sediments are substantially below the threshold limits (for instance, Pb concentration is 20  $\mu\text{g/g}$ , while threshold limit is 60  $\mu\text{g/g}$ ) specified by sediment quality guidelines (SQGs) (MacDonald et al., 1996; SEPA, 2002). Under reducing conditions, Cr (III) predominant in the sediment is rarely found in the dissolved form, and it cannot easily pass through cell membranes, while major component of Ni is in the residual fraction. This clearly shows that even though Cr and Ni concentrations in clayey mud bank sediments are high, their potential bioavailability is limited.

Benthic fauna in oxygen-deficient zones exhibit morphological and physiological adaptations to maximise oxygen uptake (Childress and Seibel, 1998; Levin, 2003), they generally show reduced diversity and biomass under oxygen deficiency (Rowe 1971; Levin et al., 2009). On the west coast of India, under oxygen deficiency, standing stock of macrobenthos, species number and diversity of polychaetes were decreased (Joydas and Damodaran, 2014); furthermore, substantially low benthic biomass has been reported from 20 m depth contours along the southwest coast of India (Jeyaraj et al., 2007). Therefore, the enrichment of toxic organic matter bound metals (especially Cr and Ni) may not pose any large-scale impact on benthic fauna due to its low biomass and abundance in the mud bank sediments.

## 5. Conclusions

This study investigated seasonal variations and geochemical fractionation of trace metals in the surface sediments of a seasonally hypoxic (upwelling) coastal environment to understand hypoxia-induced changes in trace metal fractions. The incidence of cold and hypoxic waters indicated strong coastal upwelling in the study region during the southwest monsoon. The reduction in the concentrations of Fe and Mn during hypoxia periods indicated the dissolution of Fe/Mn (oxy) hydroxides in the surface sediments. Concentrations of trace metals such as Ni, V, and Zn decreased gradually in sediments, while that of Cr was considerably enriched. Geochemical fractionation revealed that these variations follow their preference for binding sites during hypoxia. Ni and Cr exhibited strong affinities towards organic matter and sulphides. Pb and Zn were characterised by their relatively high affinity towards the Fe/Mn (oxy) hydroxide phase under hypoxia. Reductive dissolution of reducible fractions led to decreased Ni, Zn, V, and Pb levels. Stable Cr (III) bound to organic matter was enriched, though all values were within threshold limits. Hypoxia in the sediment-water interface shifts the Fe/Mn (oxy) hydroxide bound metals to organic matter and sulphide bound, which is relatively more bioavailable. However, it possesses less/no harm to the biota due to the low trace metal concentration in the sediment, the dominance of stable forms, and the relatively fewer benthic fauna during the oxygen deficiency. However, the labile fractions can affect biota in future if (i) the metal concentrations increase due to anthropogenic activities or (ii) the intensity of hypoxia continues to increase.

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## **Figure Captions**

**Figure 1** Map of the study region showing locations of sampling stations (M1, M2, and M3) in Alappuzha mud banks. The discontinuous white line indicates the approximate boundary of the persistent mud bank site. The red dots (upper left panel) reported mud bank locations along the southwest coast of India

**Figure 2** Vertical profiles of temperature (a), salinity (b) and dissolved oxygen (c) during the study period.

**Figure 3** (a) Distribution of sand, silt and clay in surface sediments (b) distribution of Total Organic carbon (TOC), Total Nitrogen (TN), Total Sulfur (TS) and Total Phosphorus (TP) in surface sediments of the Alappuzha mud bank.

**Figure 4** Seasonal variability of Fe and Mn in surface sediments.

**Figure 5** Distribution of trace metals in surface sediments of the Alappuzha mud bank.

**Figure 6** Geochemical forms of Ni in surface sediments.

**Figure 7** Geochemical forms of Zn (a) and Pb (b) in surface sediments.

**Figure 8** Geochemical forms of Cr (a) and Co (b) in surface sediments.

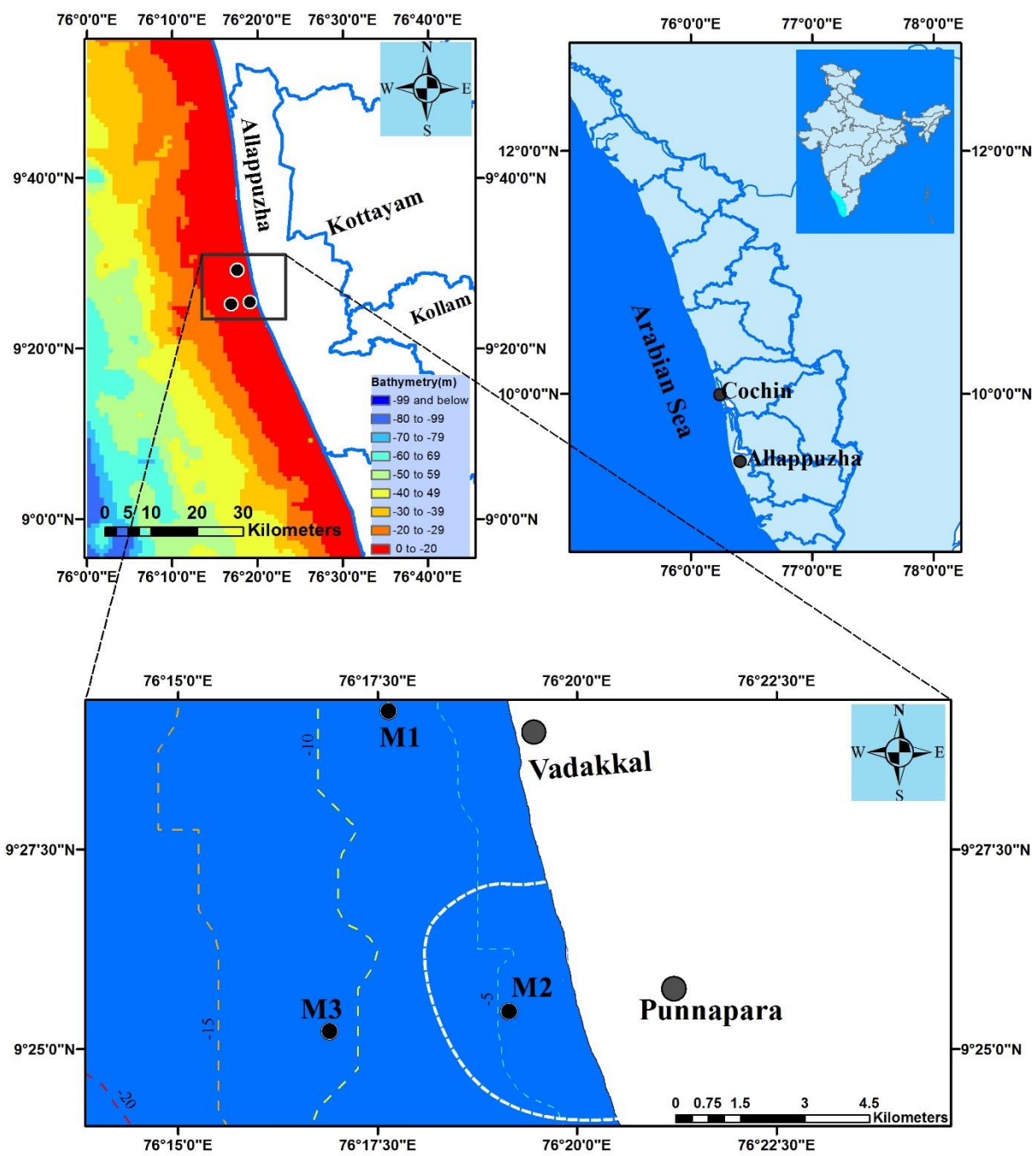


Figure 1

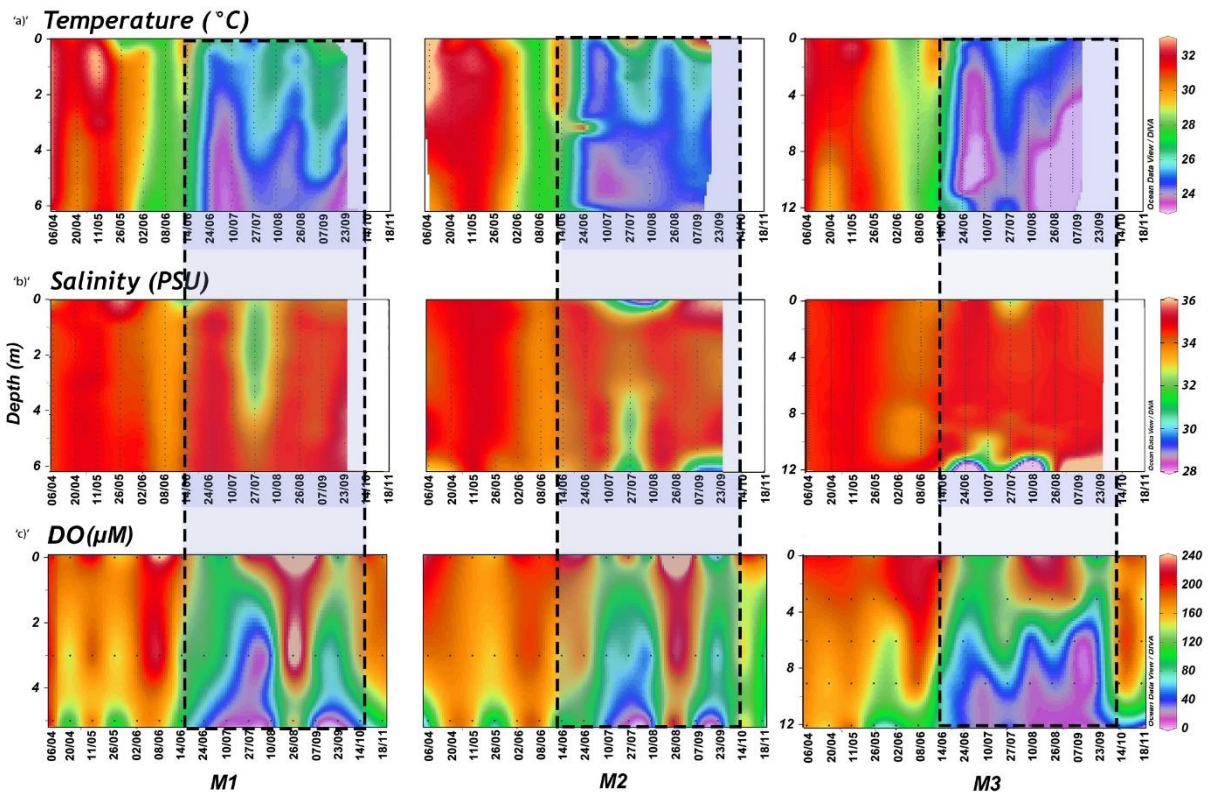


Figure 2

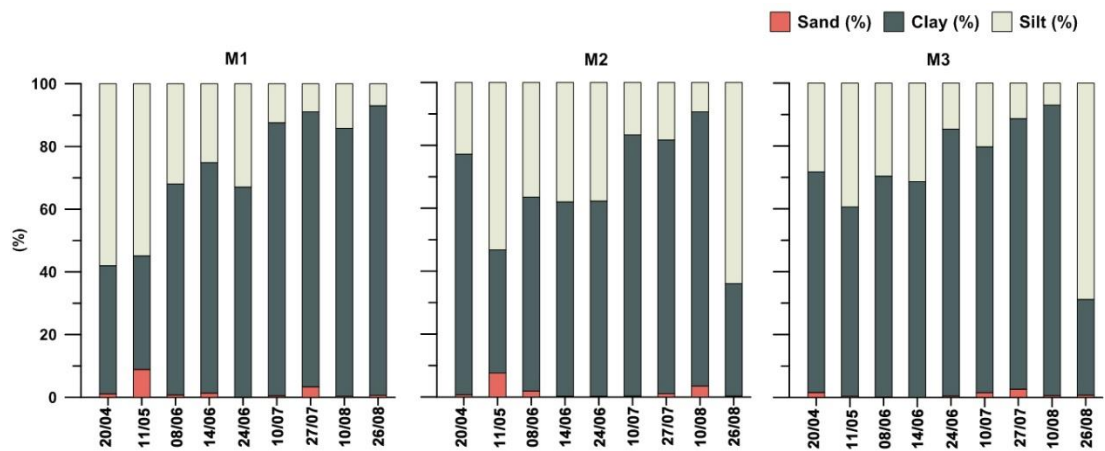


Figure 3a

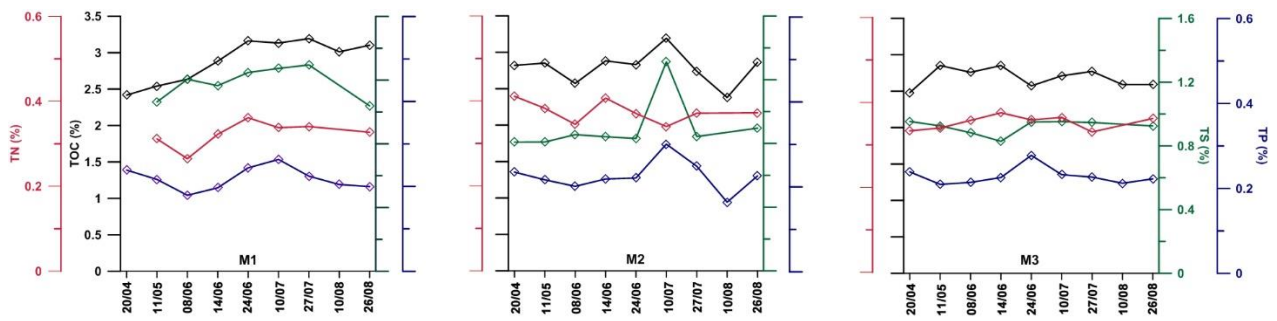


Figure 3b

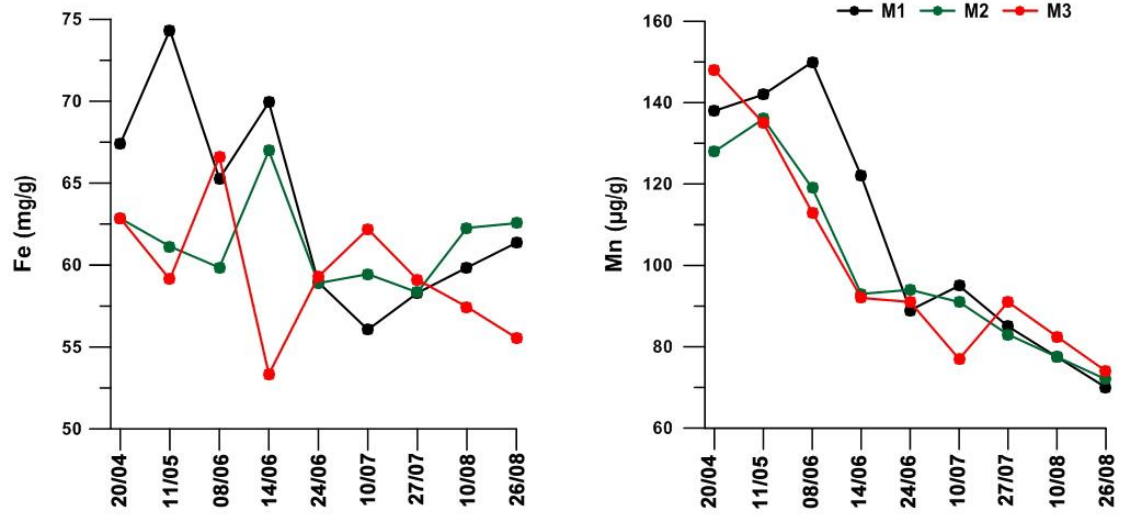


Figure 4

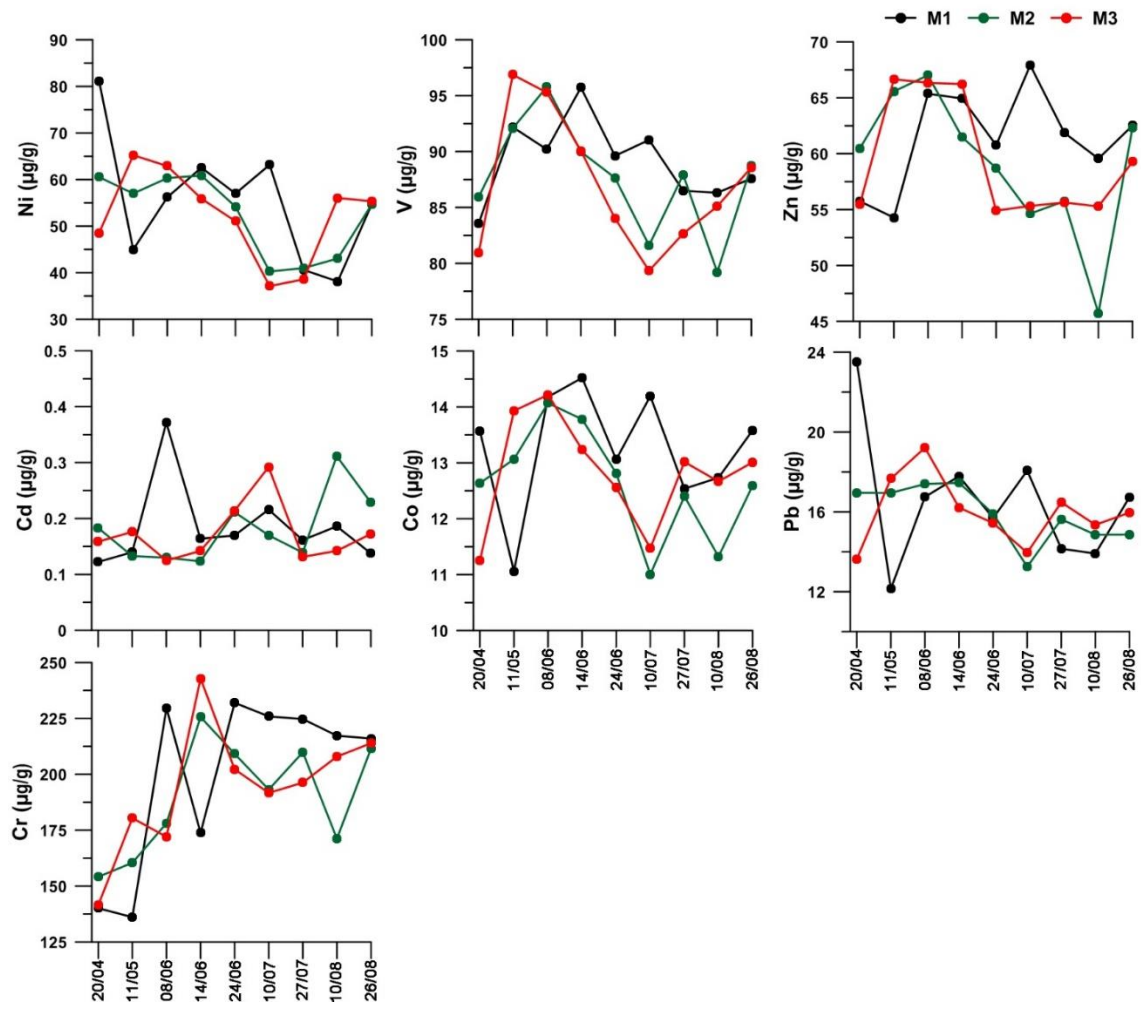


Figure 5

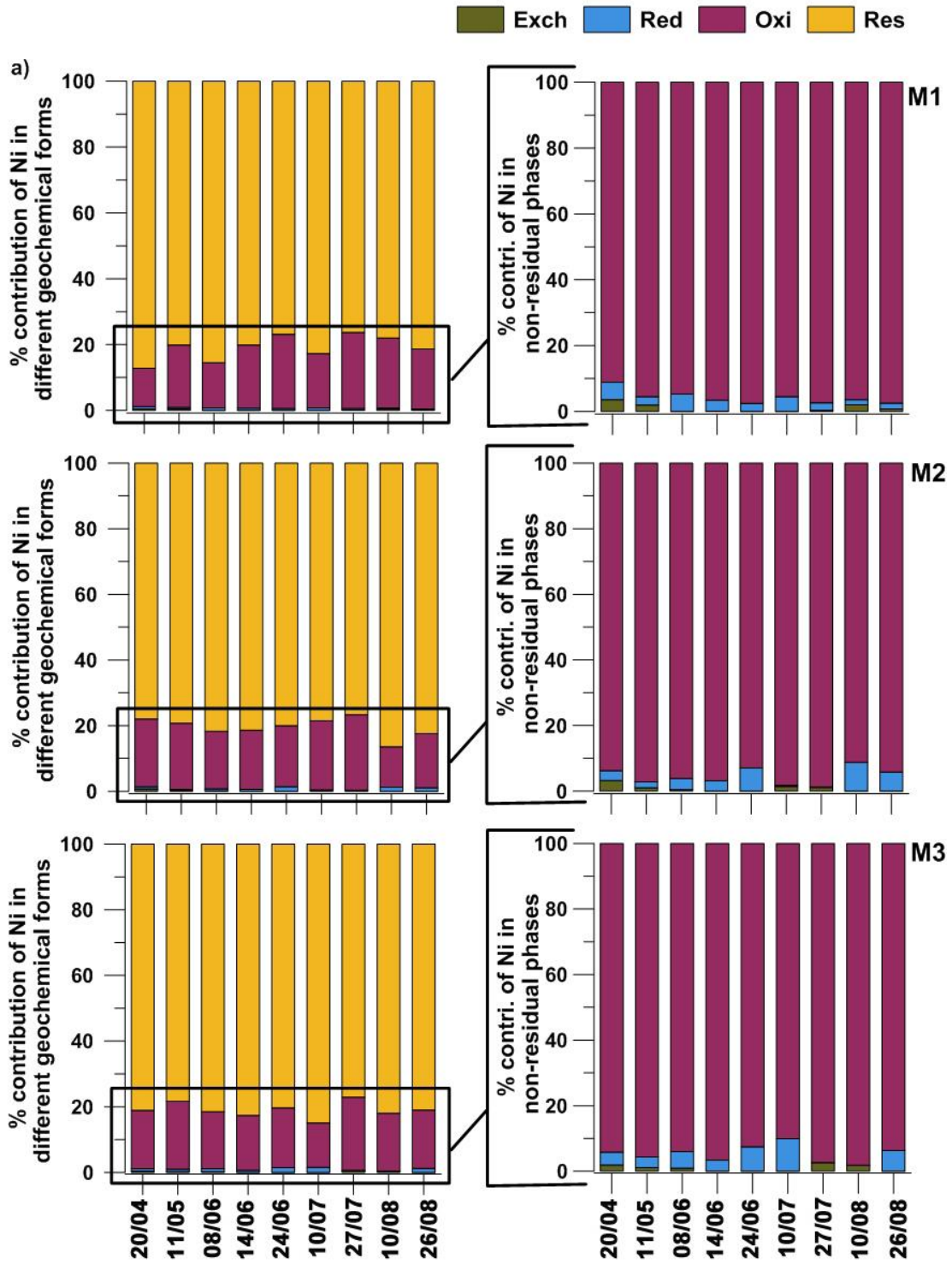


Figure 6



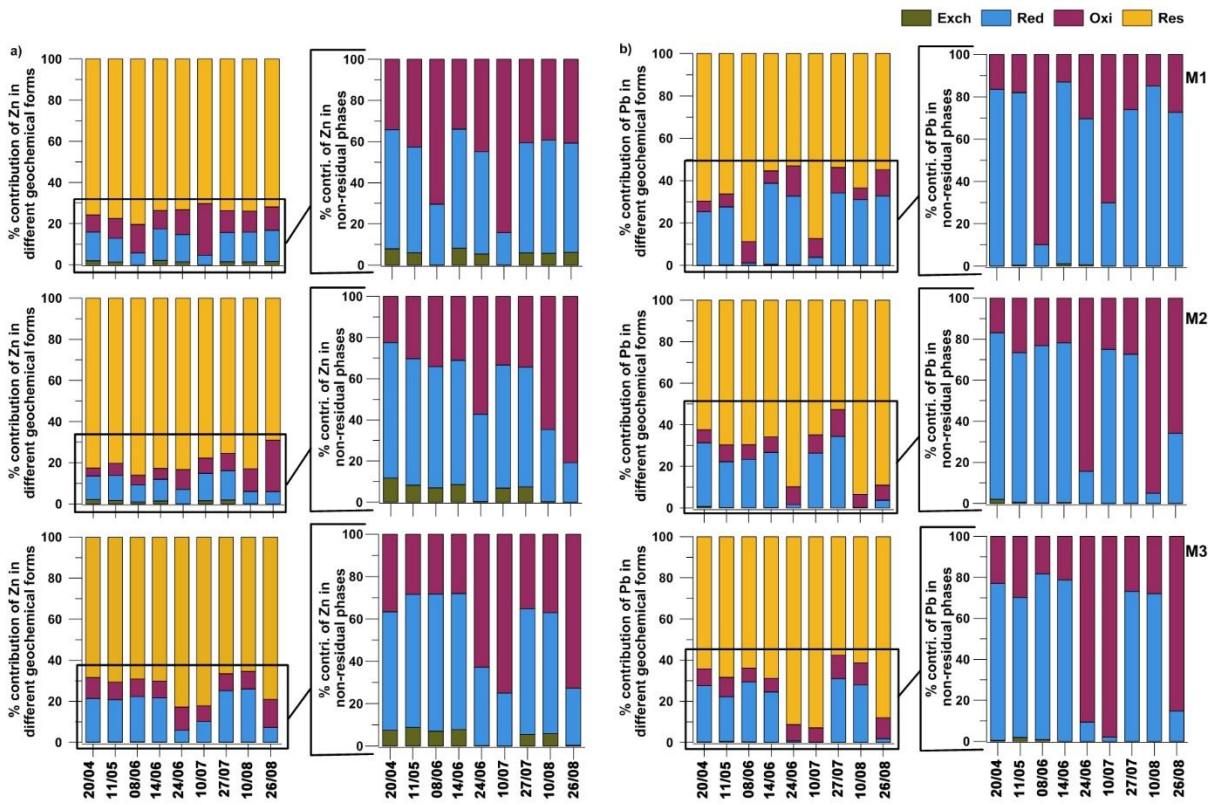


Figure 7

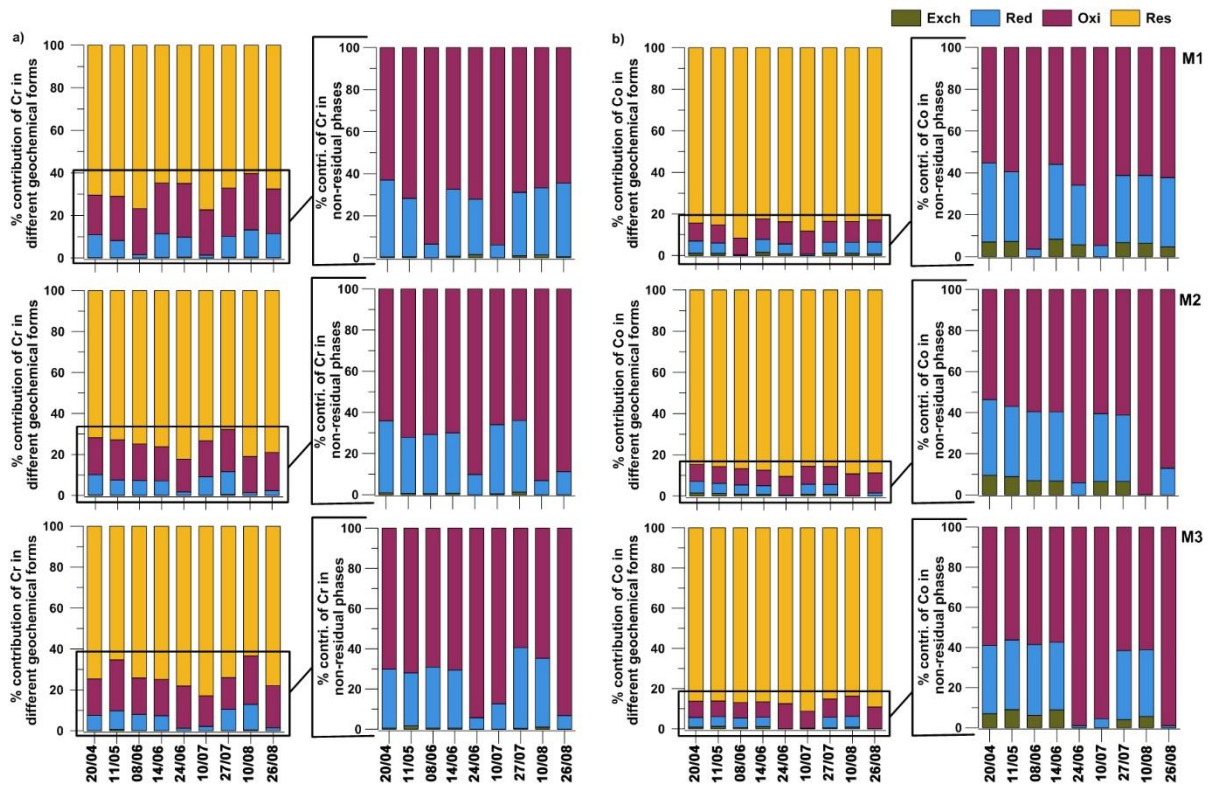


Figure 8