

Impact of a large hydraulic barrage on the trace metals concentration in mesozooplankton in the Kochi backwaters, along the Southwest coast of India

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Abstract

This study delineates the impact of a man-made hydrological barrage [Thannermukkom barrage (TB)] on the concentration of selected trace metals (Fe, Zn, Cu, Co, Cr, Mn, Ni, Pb) in mesozooplankton from the Kochi backwaters (KBW). The overall results point out that during Pre-Southwest Monsoon (PRM), the concentration of trace metals in mesozooplankton was high in the upstream due to the closure of the barrage, which essentially causes stagnancy of the waters. Trace metal concentrations in the downstream and upstream regions of KBW were found to be lower during Post- Southwest Monsoon (PSWM) compared to the rest of the seasons. In general, trace metals in mesozooplankton from the KBW showed the following order of concentration: Fe>Mn>Zn >Ni>Cu>Cr>Co>Pb. A comparison with earlier data across the globe showed that trace metal concentration in mesoplankton in the KBW is lower than the values reported from other parts of the world.

Keywords: trace metals, mesozooplankton, Thannermukkom barrage, Kochi backwaters, India

1. Introduction

Reports indicating the rise in trace metal concentrations in biological components have fascinated the attention of several researchers (Marshall and Mellinger, 1980; Austin et al., 1985; Rejomon et al., 2008a; Paimpillil et al., 2010; Vilhena et al., 2014; Srichandran et al., 2016). Researchers are very keen to understand the trace metals level in plankton due to their possible transfer into the higher trophic levels in the aquatic food web (Whitton, 1984; Schindler, 1987; Kelly, 1988; Kahle and Zauke, 2003; Robin et al., 2012; Vilhena et al., 2014; Srichandran et al., 2016). Trace metals enter into waterways through various sources. Waste discharge from the industrial processes viz., mining, smelting, refining, etc., are the potential sources of trace metals (Fe, Zn, Mn, Ni, Cu, Cr, Co, Pb, Hg) to the aquatic environment (Denton et al., 1997; Rejomon et al., 2008a,b; Robin et al., 2012; Vilhena et al., 2014; Srichandran et al., 2016). Domestic wastewater, sewage sludge, urban runoff, and leachate from solid waste disposal sites are obvious sources of heavy metals into rivers, estuaries, and coastal waters (Mance, 1987; Ho et al., 2007; Rejomon et al., 2008a,b; Robin et al., 2012). Other potential sources include the combustion of fossil fuels, ports, harbors, marinas, and mooring sites, recreational boating, fishing and shipping activities, etc., (Denton et al., 1997; Rejomon et al., 2008a,b; Robin et al., 2012).

Trace metals are persistent contaminants of fresh, estuarine, and marine waters. At optimum levels, trace metals are essential for living beings to maintain normal yet complex physiological functions related to their growth and development. Some of these trace metals like Fe, Mn, Cu, and Zn are essential for metabolic activities in organisms, whereas, other metals like Cr, Pb, Co, and Ni are intensely toxic even in low concentration under certain conditions (Phillips and Rainbow, 1989; Fatoki and Mathabatha, 2001; Rainbow, 2002). The accumulation of heavy metals can lead to many abnormalities in organisms including humans, due to biomagnification (Liang et al., 2004; Kumari, 2016). Trace metals are preferentially transferred from dissolved to the particulate phase (Gangaiya et al., 2001) and this causes the elevation of metal concentrations in estuarine and marine organisms through the food web. High levels of trace metals in water can be potentially harmful either due to their direct effect on plankton or indirectly through the transfer of the pollutants to other trophic levels (Rezai et al., 2003; Paimpillil et al., 2010; Robin et al., 2012; Srichandran et al., 2016).

Fishes are an important nutritional resource for humans, particularly in rural economies in developing countries (Welcomme et al., 2010) and they are sustained mainly by plankton (especially mesozooplankton >200µm) present in the aquatic ecosystems. Plankton are the major transporter of the trace metals to the higher trophic levels in the aquatic food web and mesozooplankton play a key intermediate role in the transfer of material from lower to higher trophic levels (Anger, 2003; Beaugrand, 2004; Jyothibabu et al., 2006; Lampert and Sommer, 2007; Jagadeesan et al., 2013,

Jagadeesan et al., 2017, Arunpandi et al., 2017). Copepods usually contribute more than 60% of the mesozooplankton community in Indian waters (Roman et al., 2000; Chen et al., 2011; Jagadeesan et al., 2013, Jagadeesan et al., 2017, Arunpandi et al., 2017; Jagadeesan et al., 2019). Quantification of the trace metal concentrations in mesozooplankton can determine the state of environmental contamination and flow of the metals to the higher-level organisms through the lower level food web (Bryan, 1980; Ibrahim and Joseph 1995; Srichandran et al., 2016).

The construction of dams and barriers across rivers and estuaries is the common world over and they are built mainly for the benefit of agriculture, aquaculture, domestic, and industry. However, such environmental modifications eventually cause large alterations in the natural hydrography, biota, and biogeochemistry of the water body including the adjacent coastal marine environments (Acharyya et al., 2012; Ozhukayil, 2015; Bharathi et al., 2018). These man-made engineering structures disturbs the natural balance of the environment and increase the concentrations of dissolved pollutants such as trace metals and pesticides and transfers them to biological components higher in the food chain (Ozhukayil, 2015). Kochi backwaters (KBW) is the largest estuarine system (256 km²) along the south-west coast of India (Qasim 2003). In KBW, heavy monsoonal rainfall and freshwater influx strongly impact its eco-biology, especially during the Southwest Monsoon (SWM, June- September), wherein salinity may drop to near-zero values (Jyothibabu et al., 2006; Haridevan et al., 2015; Sooria et al., 2015; Arya et al., 2016; Arunpandi et al., 2020). Thannermukkom barrage (TB) in the KBW was operational from 1976 and it is situated 45 km southward from the Kochi inlet to prevent saltwater intrusion into the paddy fields in the upstream region. TB is usually fully open only during the SWM to avoid flooding in the upstream of the KBW at that period (Haridevan et al., 2015; Arunpandi et al., 2020). During the Pre- Southwest Monsoon (PRM) and Post-Southwest Monsoon (PSWM) period TB is mostly closed, results in the interruption of the physical connection between the upstream of the KBW and the Arabian Sea. Therefore, periodic flushing of the upstream of KBW associated with the tidal activity is no longer possible when TB is closed during the non-monsoon periods, which favour the accumulation of pollutants there (Haridevan et al., 2015).

Several earlier studies have reported the trace metals levels in water, sediment, bivalves, and fishes from Indian waters including the KBW (George and Kureishy, 1979; Ouseph 1992; Balachandran et al., 2003; Kaladharan, 2011; Anu et al., 2014; George et al., 2016; Gandhi et al., 2017). However, quantifications of the trace metal concentrations in mesozooplankton are limited in Indian waters (Rejomon et al., 2008a&b; Paimpillil et al., 2010; Robin et al., 2012; Srichandran et al., 2016) and meager in KBW. Besides, the quantification of trace metals concentrations in mesozooplankton related to the seasonal operation of the TB is not available. Considering all these, this study aims (a) to quantify

the trace metals concentration in mesozooplankton in the KBW with seasonal hydrography and (b) to investigate the impact of TB on the spatial variation of trace metal concentration in the mesozooplankton during different seasonal hydrographical settings.

2. Materials and methods

2.1. Study area

The KBW is located between 09°00' -10°40'N and 76°00'-77°30'E along the southwest coast of India, extending from Azhikode in the North to Alleppey in the south. The total area of the KBW is about 256 sq.km (Pillai 1991). The annual rainfall over the region is 3200 mm, which brings in approximately 20,000 mm³ of freshwater into the KBW (Balachandran et al., 2008). Six rivers, Periyar, Muvattupuzha, Pamba, Meenachil, Manimala, and Achankoil drain into the KBW. Generally, KBW is considered to be eutrophic, with significantly high nutrients and phytoplankton biomass throughout the year (Jyothibabu et al., 2006; Haridevan et al., 2015; Sooria et al., 2015; Anjusha et al., 2018; Arunpandi et al., 2020) Also, it acts as a nursery for many estuarine molluscs, crustaceans, finfishes and support mangroves along its shoreline, thereby providing shelter to juveniles of many fishes (George, 1973; Menon et al., 2000; Thomson, 2002). Thannermukkom barrage (TB) is kept open during SWM and closed during the PRM period. When TB is closed, the KBW is physically divided into two separate environments; brackish water downstream region and nearly freshwater upstream region (Fig. 1).

2.2. Sampling and methods

Sampling was carried out from 6 locations during April, July, and December of 2015 representing Pre-southwest Monsoon (PRM), Southwest Monsoon (SWM), and Post-Southwest Monsoon (PSWM), respectively. These 6 locations are grouped into downstream (locations 1 and 2), midstream (locations 3 and 4), and upstream (locations 5 and 6). The sampling was carried out using a speed boat to cover the entire sampling in the KBW within one tidal phase. The vertical distribution of salinity and temperature was measured using a Seabird CTD (SBE 19 plus V2) profiler. Turbidity was measured using a turbidity meter (Eutech instruments TN-100). Dissolved oxygen (DO) concentration was measured by Winkler's method (Grasshoff and Kremling, 1983). Nutrients (nitrate, phosphate, and silicate) were analysed using standard procedures (Grasshoff and Kremling, 1983). Following McLusky (1993), salinity levels in the KBW were categorised into five Viz., euhaline (salinity > 30), polyhaline (salinity 18-30), mesohaline (salinity 5-18), oligohaline (salinity 0.5-5), and limnetic (salinity < 0.5).

Mesozooplankton samples were collected by the horizontal towing of the 200µm WP2 net. Samples collected were kept in a cold box and transported to the laboratory. In the laboratory, sub-samples (5%) were preserved with formalin for the estimation of the dominant groups, and the remaining were rinsed with Milli-Q water to remove salts (Rejomon et al., 2008a). After proper washing, these samples were observed under a stereo zoom microscope to remove non-planktonic particles, and then the samples were dried in an oven (65° C) for 24 hours (complete dry). Dried samples were powdered and 300mg of the dried samples were stored in a vacuum desiccator till further processing. 300mg samples were digested for three hours at 80°C with 3ml of HNO₃ and the digested samples were made up to 25ml with HCl (0.1N) (Rejomon et al., 2008a,b). The same procedure was performed for blanks (without mesozooplankton). The digested samples were analysed using an Atomic Absorption Spectrophotometer (PerkinElmer Analyst-700) for measuring the concentration of trace metals (Fe, Zn, Cu, Mn, Ni, Co, Cr, and Pb) against the standards. Replicate measurements of the desired metals were carried out for accuracy. The procedure of analyzing dissolved metal concentrations was tested using the maximum residual levels in the plankton samples, recommended by earlier studies (Rejomon et al., 2008a; Rejomon et al., 2008b; Paimpillil et al., 2010).

2.3. Statistical analysis

The spatial and temporal difference in the hydrographical parameters and the concentration of trace metals were tested with ANOVA. Initially, datasets were tested for their distribution and homogeneity. For the normal distribution, parametric ANOVA was performed, whereas, non- parametric ANOVA was used for the other case (Kruskal-Wallis). The normality test, Parametric ANOVA, and Non-Parametric ANOVA were performed in the XL-Stat Pro software package.

2.3.1. Principal component analysis

The interrelationships of the metal levels and hydrographical parameters were analysed using the Principal Component Analysis (PCA) ordination method. This biplot shows the interrelationship between the metals and their spatial distribution. Hydrographical and trace metal concentrations were Z score transformed before the analysis of PCA. The ordination significance of the PCA analysis was tested using the Monte-Carlo permutation test with 499 replicates. PCA was performed in Canoco 4.5 software package.

3. Results

3.1. Environmental parameters

3.1.1. Physical variables

The temperature varied from 27.3°C to 32.8°C in the study region. The spatial difference of temperature was negligible and found to be <2°C between the downstream and upstream locations, whereas the temporal variation in temperature was noticeable (Table 1). The water column was warmer during PRM than the other seasons (SWM and PSWM). Salinity showed significant spatial and temporal differences, varying from limnohaline to polyhaline levels (from 0.1 to 21.01 in the surface) in the downstream, limnohaline to mesohaline levels (from 0.25 to 12.15) in the midstream, and limnohaline to oligohaline levels (from 0.08 to 4.9) in the upstream. In all the locations, water column salinity was high during the PRM, followed by the PSWM and the SWM. In the downstream location, surface salinity was at polyhaline levels in station 1 during the PRM and mesohaline during the PSWN, but it transformed into limnohaline during the SWM. In the midstream, salinity was mesohaline during the PRM and the PSWM, but it changed to limnohaline during the SWM. In the upstream, salinity was oligohaline during PRM and PSWM, while salinity during the SWM period was < 0.1 (Fig. 2, Table 1). Regardless of seasons, the water column was more turbid in the downstream locations (from 10.2 to 15.7 NTU), followed by upstream locations (from 3.34 to 13.34 NTU in the surface) and midstream (from 2.8 to 11.3 NTU) locations. In all three locations, the turbidity was highest during the PRM and the SWM, but the water column was relatively clear during PSWM (Table 1).

3.1.2. Dissolved oxygen (DO) and nutrients

A high concentration of dissolved oxygen and nutrients were found in the KBW throughout the study. Spatially, the DO concentration was higher in the upstream regions than in the midstream and downstream (Table 1). Seasonally, the DO level was higher during the SWM in the upstream ($8.5 \pm 0.4 \text{ mg.L}^{-1}$) compared to the PRM and the PSWM. The concentration of nitrate was higher during the SWM especially in the downstream ($15.9 \pm 2.5 \text{ }\mu\text{M}$) and was lower during the PSWM and the PRM (Table 1). Spatially silicate was high in the upstream region, and the high phosphate was found during the PSWM in the downstream ($3.14 \pm 0.2 \text{ }\mu\text{M}$) region. The concentration of silicate and phosphate was noticeably high during the SWM (Table 1).

3.2. Dominant mesozooplankton

During the PRM, the upstream was dominated by copepods, cladocerans, and colony-forming rotifers; midstream by copepods, cladocerans, and planktonic molluscs; downstream by copepods and chaetognaths (Fig. 3a). During the SWM, the upstream was dominated with rotifers, copepods, and cladocerans, and the midstream was dominated cladocerans than copepods. In the downstream, copepods and cladocerans were dominant followed by rotifers (Fig. 3b). During PSWM, copepods

were more abundant in the downstream, and the midstream was characterised by a high abundance of copepods, cladocerans, chaetognaths, and decapods (Fig. 3c). Overall, the copepods in the upstream were dominated by cyclopoids and the downstream by calanoids.

3.3. Trace metals concentration in mesozooplankton

Eight trace metals were measured in mesozooplankton samples collected from the KBW and their concentrations are given in Fig. 4 and Table 2. Fe concentration ranged from 6057 to 15284 $\mu\text{g/g}$. It showed significant spatial and temporal differences during the study period. During the PRM, Fe was higher in the upstream ($14834 \pm 123 \mu\text{g/g}$) and a comparable concentration in the midstream and downstream (Table 2). During the SWM, Fe concentration in the upstream and midstream was lower than the PRM; but, noticeably high ($15284 \pm 168.6 \mu\text{g/g}$) in the downstream. During the PSWM, Fe was higher in the upstream ($13561 \pm 197.2 \mu\text{g/g}$) and lower in the midstream (Fig. 4 and Table 2).

The concentration of Zn ranged between 10.1 $\mu\text{g/g}$ and 47.3 $\mu\text{g/g}$. Regardless of the seasons, Zn was high in the bar mouth, followed by the middle reaches of the estuary and upstream locations. The spatial difference in Zn was found to be significant during the study period (Fig. 4). Cu concentration ranged between 1.5 and 13.2 $\mu\text{g/g}$ and showed clear spatial and temporal differences in the study area. Overall, the highest concentration was found in the upstream during the PRM and the lowest in the downstream during the PSWM (Fig. 4 and Table 2).

Co concentration varied from 0.22 to 3.7 $\mu\text{g/g}$. During the PRM and the PSWM, Co concentration was high in the upstream with low seasonal differences. The spatial difference in Co concentration was significant during the PRM and PSWM, and its spatial difference was minimal during the SWM (Table 2). Cr ranged from 0.32 to 4.35 $\mu\text{g/g}$. Spatially, Cr was higher in the upstream compared to the midstream and downstream regions. Overall, Cr was higher in the midstream and upstream than in the downstream during the PRM and the PSWM. Its highest concentration ($4.35 \pm 0.18 \mu\text{g/g}$) was in the Kochi inlet during the SWM (Fig. 4 and Table 2).

Mn concentrations ranged between 21 and 177 $\mu\text{g/g}$. Its lower values were in the downstream during PSWM and the higher level in the upstream during the SWM. In all seasons, the spatial variation in Mn concentration was significant. During the PRM and the PSWM, Mn was higher in the upstream, followed by the midstream and downstream. The spatial distribution of Mn during the SWM varied from the PRM and PSWM, with the maximum level (177.8 ± 3.21) in the downstream and minimum level ($35.6 \pm 4.5 \mu\text{g/g}$) in the upstream (Fig. 4).

Ni concentration ranged from 2.2 to 14.6 $\mu\text{g/g}$. In the entire study area, Ni was higher during the SWM compared to the PRM and the PSWM. During the PRM, Ni was higher in the upstream, but it

was higher in the downstream during the SWM and the PSWM (Table 2). Pb concentration ranged from 2.1 to 4.4 $\mu\text{g/g}$. Relatively, Pb concentration was found higher in the upstream during the PRM and the PSWM but it was high in downstream during the SWM. The spatial and temporal differences in Pb was insignificant (Fig. 4 and Table 2).

In general, the trace metal concentrations in mesozooplankton in the KBW showed the following order: Fe>Mn>Zn >Ni>Cu>Cr>Co>Pb. Fe was higher during the PRM compared to SWM and PSWM. Zn was higher in SWM compared to other seasons. Spatially, all the trace metals were high in the upstream locations during the PRM, followed by the midstream. During the SWM, the highest concentration of metals was found in the upstream. Similarly, during the PSWM, the highest trace metal concentration was found in the upstream except for Zn and Ni, which were the highest in the downstream.

3.4. Principal component analysis

The interrelationships between hydrographical variables and trace metals concentration to their spatial and temporal distribution are presented as a biplot. During the PRM, the downstream was characterised by increasing gradients of salinity and phosphate. Upstream locations were oriented to the right side of the plot with the increasing gradients of DO and silicate, and decreasing gradients of salinity and phosphate, indicating their low saline conditions. The axes of Ni, Fe, Cu, Cr, and Mn showed a positive relationship with the increasing gradient of silicate and decreasing gradients with salinity, indicating their high concentrations in the upstream and low concentration in the downstream. The Zn axis was oriented to the left-hand side of the plot with increasing gradients of salinity in the downstream, indicating their high concentration in the downstream. During the PSWM, salinity and phosphate axes were oriented to the right-hand side of the plot with Zn, which indicates their high concentrations in the downstream. The axes of the other metals were oriented to the left-hand side of the plot and in the opposite direction to the salinity axis, representing their high concentration in the upstream locations. During the PRM and PSWM, most of the trace metals concentration was high in the upstream, associated with the fully closed or partially opened conditions of TB. During the SWM, the trace metals concentrations were high in the downstream locations, related to the river flow during the SWM period (Fig. 5).

4. Discussion

4.1. Environmental parameters

The water column temperature in the KBW was higher during the PRM, as compared to monsoon periods, due to low wind speed, clear sky, and high solar insolation (Table 1) (Jyothibabu et al., 2006;

Haridevan et al. 2015). Salinity showed clear gradients from the downstream to upstream regions (Table 1). Heavy river influx during the SWM significantly alters the salinity in the KBW and hence freshwater dominates and limnohaline or oligohaline salinity levels prevail in the entire system. During the PSWM and PRM period, river influx to the KBW is less, and seawater incursions dominate then, causing euhaline/polyhaline conditions in the downstream, mesohaline conditions in the midstream, and limnohaline levels in the upstream locations (Jyothibabu et al., 2006; Haridevan et al. 2015). Spatial and temporal variations of the salinity pattern were similar to the previous studies (Jyothibabu et al., 2006; Haridevan et al. 2015; Jagadeesan et al. 2017).

Regardless of the samplings, turbidity was high in the downstream locations compared to the midstream and upstream. During the PRM, turbidity was spatially high in the downstream compared to midstream and upstream, which can be attributed to tidal resuspension (Menon et al., 2000). During the SWM, turbidity increased two to three-folds higher levels, as compared to PRM, which was caused by the floodwater associated with the heavy rainfall (Jyothibabu et al., 2006; Nasir, 2010) (Fig. 2b). Nitrate concentration in the KBW is in the eutrophic levels which are noticeably higher than other similar estuaries (Jyothibabu et al., 2006; Madhu et al., 2007; Shoji et al., 2008; Jagadeesan et al., 2017). Silicate concentration was higher in the upstream, and phosphate in the downstream; this pattern of distribution is typical of the study region (Jyothibabu et al., 2006). Dissolved oxygen concentration remains always high in the KBW (Table 1) and the high primary production and the shallowness of the system could be the possible reasons (Qasim, 2000; Jyothibabu et al., 2006). The seasonal hydrographical setting in the downstream of the KBW showed partially mixed conditions during PRM and PSWM and strongly stratified salt wedge conditions during the SWM. Midstream was weakly stratified during PRM and well mixed during the SWM. Regardless of the seasons, the upstream water column was well-mixed and this kind of spatial and seasonal hydrographical setting is typical of the KBW (Qasim, 2000; Jyothibabu et al., 2006). The stratification and mixing state of the estuarine conditions could alter the biogeochemistry of the system (Sujatha et al., 2009).

4.2. Dominant mesozooplankton in KBW

The changes in the hydrographical parameters alter the mesozooplankton composition in KBW (Qasim, 2000; Jyothibabu et al., 2006). Based on the salinity tolerance and hydrography, mesozooplankton composition differed in KBW (Fig.3). Oligohaline and limnohaline levels of salinity with small phytoplankton (cyanobacteria- *Microcystis*) favour the growth of the cladocerans and Rotifers in the upstream locations (Haridevan et al., 2015; Anjusha et al., 2018; Arunpandi et al., 2020). Mesohaline levels of the salinity with a composite of diatoms, dinoflagellates, and cyanobacteria favours the growth of the copepods, and some extend to cladocerans (Arunpandi et al., unpublished

data). Polyhaline levels of the salinity in the downstream region with the diatoms and dinoflagellates result in high dominance of the copepods and reduce the cladoceran and rotifer abundances (Haridevan et al., 2015; Anjusha et al., 2018).

4.3. Trace metals concentration in mesozooplankton

Mesozooplankton species composition, diversity, and proliferation of certain forms could be the reason for the reported variations of metal concentrations in the mesozooplankton (Gavis et al. 1981; Brand et al. 1983; Brand et al. 1986). Trace metals in mesoplankton increases through the direct assimilation, biological uptake, grazing (Rejomon et al., 2008b; Wang and Fisher, 1998). A comparison of the trace metal values of the present study with the earlier studies from various parts of the world (offshore, coastal waters, and estuarine regions) has been presented in Table 3. During the open phase of TB agricultural waste inputs and sewage water pollute the upstream region and increase the trace metal concentration in the entire KBW (Balachandran et al. 2008) especially Fe and Zn.

The overall maximum concentration of Fe in this study were recorded during the downstream locations during the SWM season (Table 2). However, Fe concentration was high in upstream locations during the PRM and PSWM period. Fe concentration in mesozooplankton was higher than other trace metals in KBW, this was agreed with the results from the other Indian estuaries and coastal waters (Table 3). Fe concentration was reported 94 to 50942 $\mu\text{g/g}$ (Table 3) in diverse regions of the world and Indian waters (Ho et al., 2007; Vilhena et al., 2014; George and Kureishy, 1979; Sen and Qasim, 1985; Rejomon et al., 2008a; Rejomon et al., 2008b; Paimpillil et al., 2010; Srichandran et al., 2016). The values recorded in this study (6057 $\mu\text{g/g}$ to 15284 $\mu\text{g/g}$) was lower than the values of Rejomon et al., (2008b) and Paimpillil et al., (2010), whereas they were higher than the values of George and Kureishy, (1979), Rejomon et al., (2008b) and Srichandran et al., (2016). The quantity of the Fe in the mesozooplankton differed with the quantity of the entry and rate of uptake and feeding mode of the organisms (Srichandran et al., 2016).

Similarly, Zn concentration was high during SWM and noticed maximum levels in the downstream (Table 2). Zn concentration in plankton samples varied from 38 $\mu\text{g/g}$ to 625 $\mu\text{g/g}$ in other parts of the world estuaries and coastal waters (Martin and Knauer, 1973; Greig et al., 1977; Everaarts et al., 1993; Zauke et al., 1996; Kahle and Zauke, 2003; Ho et al., 2007; Vilhena et al., 2014). Zn values from 0.62 to 7546 $\mu\text{g/g}$ in Indian estuaries and coastal waters (Table 3). The Zn values recorded in the present study from the KBW range from 10.1 to 47.3 $\mu\text{g/g}$ (Fig. 4 and Table 2), which was lower than the values reported earlier from this region, it depends upon the source, dispersion with space, and time.

During the closed phase of TB, increasing trace metal concentration is due to the tidal activity which spread pollutants from downstream and midstream towards the upstream region of KBW (Balachandran et al. 2008). Cu enters into estuaries through the anthropogenic wastes, applications of fertilizers, pesticides. During the PRM and the PSWM, Cu concentrations were higher in the upstream compared to downstream, which was linked to the high agricultural activities in the upstream (Robin et al., 2012) and the stagnant nature of water there due to the close of the TB. Cu concentration in plankton recorded was from 0.2 to 228 $\mu\text{g/g}$ in Indian waters and other parts of the world (Table 3). The Cu values observed in the present study varied from 1.5 to 13.2 $\mu\text{g/g}$ (Table 2). The reported values are relatively high compared to Robin et al., (2012) from the coastal region of the Arabian Sea. Mn concentration in plankton recorded from other parts of the world range from 510 to 1064 $\mu\text{g/g}$ (Ho et al., 2007; Vilhena et al., 2014); reports from India varied from 0.13 to 552 $\mu\text{g/g}$ (George and Kureishy, 1979; Paimpillil et al., 2010; Robin et al., 2012; Srichandran et al., 2016). The concentration found in this study showed a range from 21 to 177.8 $\mu\text{g/g}$, which was lower than the earlier records in this region (Table 2 and Fig. 4).

Human activities such as dredging, refining, fossil fuels, fertilizers, and pesticides in agriculture and electroplating industries contain a variety of heavy metals (Co, Cr, Ni, and Pb), and their release in the aquatic environment increase the toxic metals (Ozhukayil, 2015). Co and Cr concentration was highly accumulated in mesozooplankton during the closed phase of TB (PRM and PSWM) and the maximum was in upstream, water stagnant region. Co concentration from the mesozooplankton samples in the KBW ranged from 0.22 $\mu\text{g/g}$ to 3.7 $\mu\text{g/g}$. This concentration was lower than in other parts of the world (Ho et al., 2007) and other India estuaries and coastal waters (Table 3). The concentration of Cr in plankton in the present study varied from 0.32 to 4.35 $\mu\text{g/g}$, which is lower than the other regions of the world (Greig et al., 1977; Ho et al., 2007; Vilhena et al., 2014) as well as in India (Table 3).

Ni concentration in the present study ranged from 2.2 $\mu\text{g/g}$ to 14.6 $\mu\text{g/g}$. The highest concentration was recorded during the SWM when the river influx was the highest. The present observation is comparable to many earlier reports (Table 3). Ni concentration reported from other parts of the world varied from 4.5 $\mu\text{g/g}$ to 64 $\mu\text{g/g}$ (Table 3) and from the Indian waters from 3 $\mu\text{g/g}$ to 81 $\mu\text{g/g}$ (George and Kureishy, 1979; Sen and Qasim, 1985; Rejomon et al., 2008a; Rejomon et al., 2008b; Paimpillil et al., 2010; Srichandran et al., 2016).

Pb concentration in plankton, reported globally, ranges from 0.7 to 81 $\mu\text{g/g}$ (Table 3). As per earlier reports from Indian waters, Pb concentration in plankton varies from 3 to 119 $\mu\text{g/g}$ (George and Kureishy, 1979; Rejomon et al., 2008a; Paimpillil et al., 2010; Robin et al., 2012; Srichandran et al., 2016). In the present study, Pb concentration in plankton was found to be from 2.1 to 4.2 $\mu\text{g/g}$ (Fig. 4

and Table 2), which is much lower than the past reports (Table 3). The highest value of Pb was found during the PRM when the TB was closed. The results of the PCA plots represent the interrelationships of the hydrographical variables and trace metals concentration (Fig. 5). Positive relationships of the metals Cu, Mn, Cr, Pb, and Co with each other and negative relationship with salinity in the PCA plots of PRM and PSWM points out runoff as the sources of these metals.

The overall results show that the complete closure of TB during the PRM and the PSWM alter the hydrography and increase the accumulation of trace metals (Table 2) in the upstream. The periodic opening of TB results in flushing and exchanges of the water masses between the downstream and upstream by the tidal activity, which may reduce the accumulation of pollutants in the upstream. Trace metals concentration in mesozooplankton in the study area were found less than that in the other Indian estuaries and many other parts of the world. Based on the present study, longterm monitoring of trace metal pollutants and the scientific management practice of TB to regulate the flushing characteristics of the KBW are strongly suggested to avoid any future disastrous effect on human beings through heavy metal contamination in the future.

5. Conclusion

This study showed how TB influences the concentration of eight trace metals (Fe, Mn, Ni, Cu, Cr, Co, Pb, Zn) in mesozooplankton in the KBW. The trace metals concentration varied within and between the zooplankton samples. The concentration of trace metals in mesozooplankton during the PRM showed higher values in the upstream of the KBW due to the closure of TB, which inhibited the free flow of water. During the SWM, when TB was open, most of the trace metals were found in higher concentrations in the downstream of KBW. During PSWM, a lower trace metals concentration was found in the study area compared to the other seasons. When TB was closed during PRM, the lack of flushing in the upstream increased the trace metal concentration. However, the overall concentration trace metals in mesozooplankton in the KBW was found to be lower than in the many other Indian estuaries and other parts of the world.

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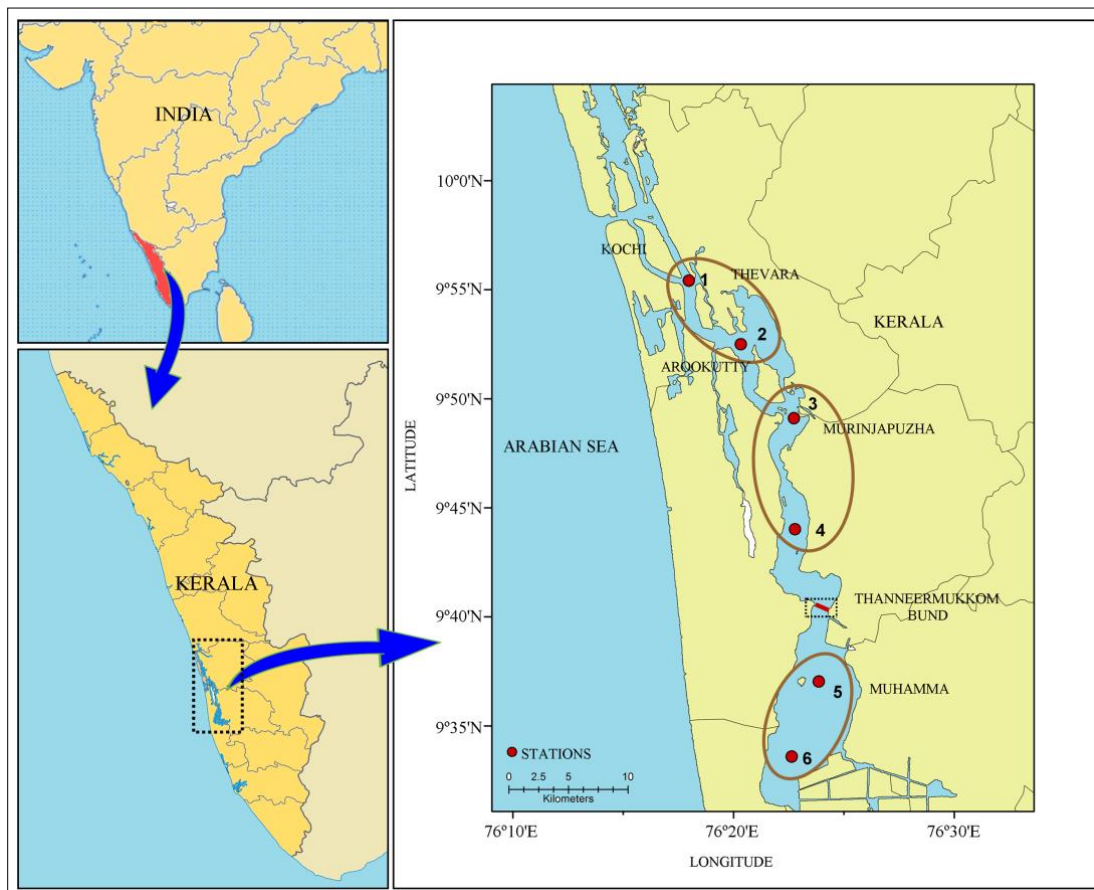


Fig. 1. Sampling locations in the Kochi backwaters, along the southwest coast of India. The brown oval shapes indicate the stations in three groups. Station 1 and 2 in the downstream, station 3 and 4 in the midstream and 5 and 6 in the upstream.

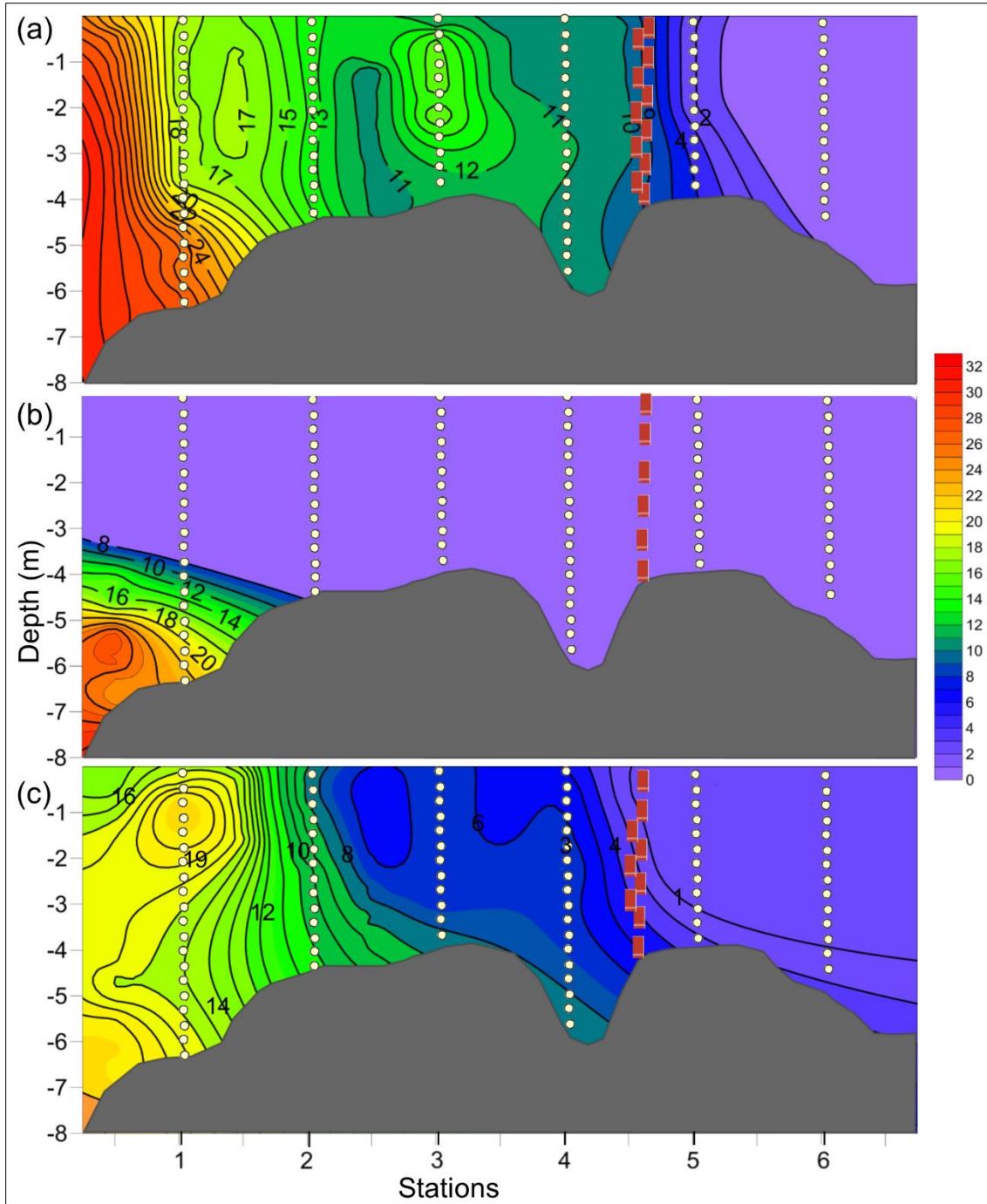


Fig. 2. Seasonal vertical distribution of salinity in the selected stations at Vembanad estuary. (a) PRM- Pre- Southwest Monsoon, (b) SWM- Southwest Monsoon, (c) PSWM- Post- Southwest Monsoon. White dots indicate the Vertical CTD data points and vertical red bricks indicate the bund (Thaneermukkom) across the Kochi backwaters.

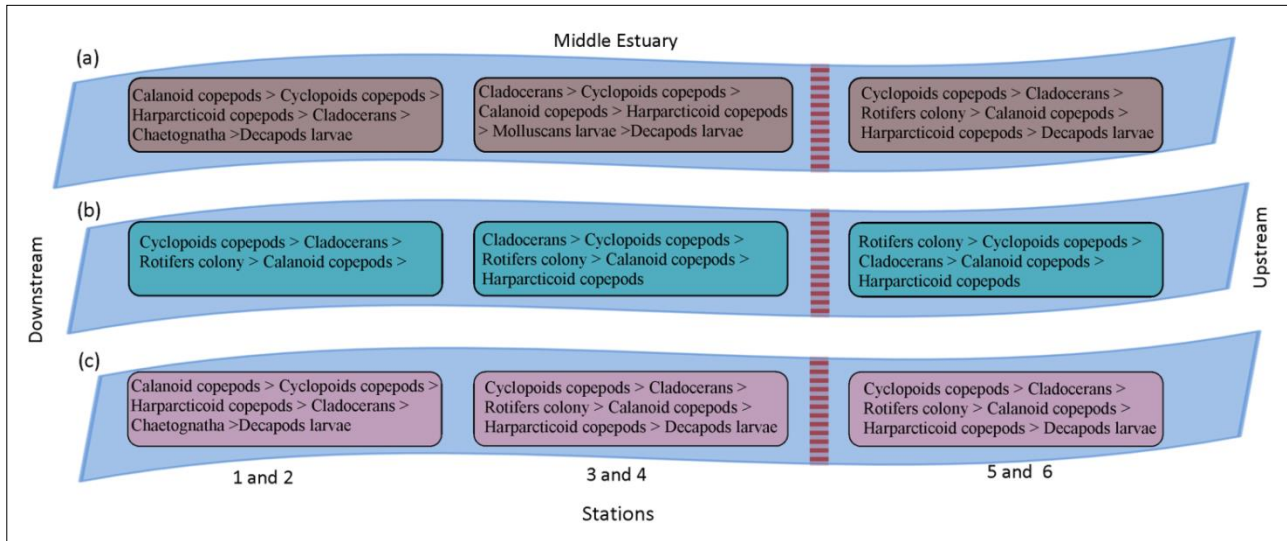


Fig. 3. Seasonal distribution of most dominant mesozooplankton communities in the Vembanad estuary. (a) PRM- Pre- Southwest Monsoon, (b) SWM- Southwest Monsoon, (c) PSWM- Post- Southwest Monsoon. Vertical red-coloured bricks indicate the bund (Thanermukkom) across the Kochi backwaters.

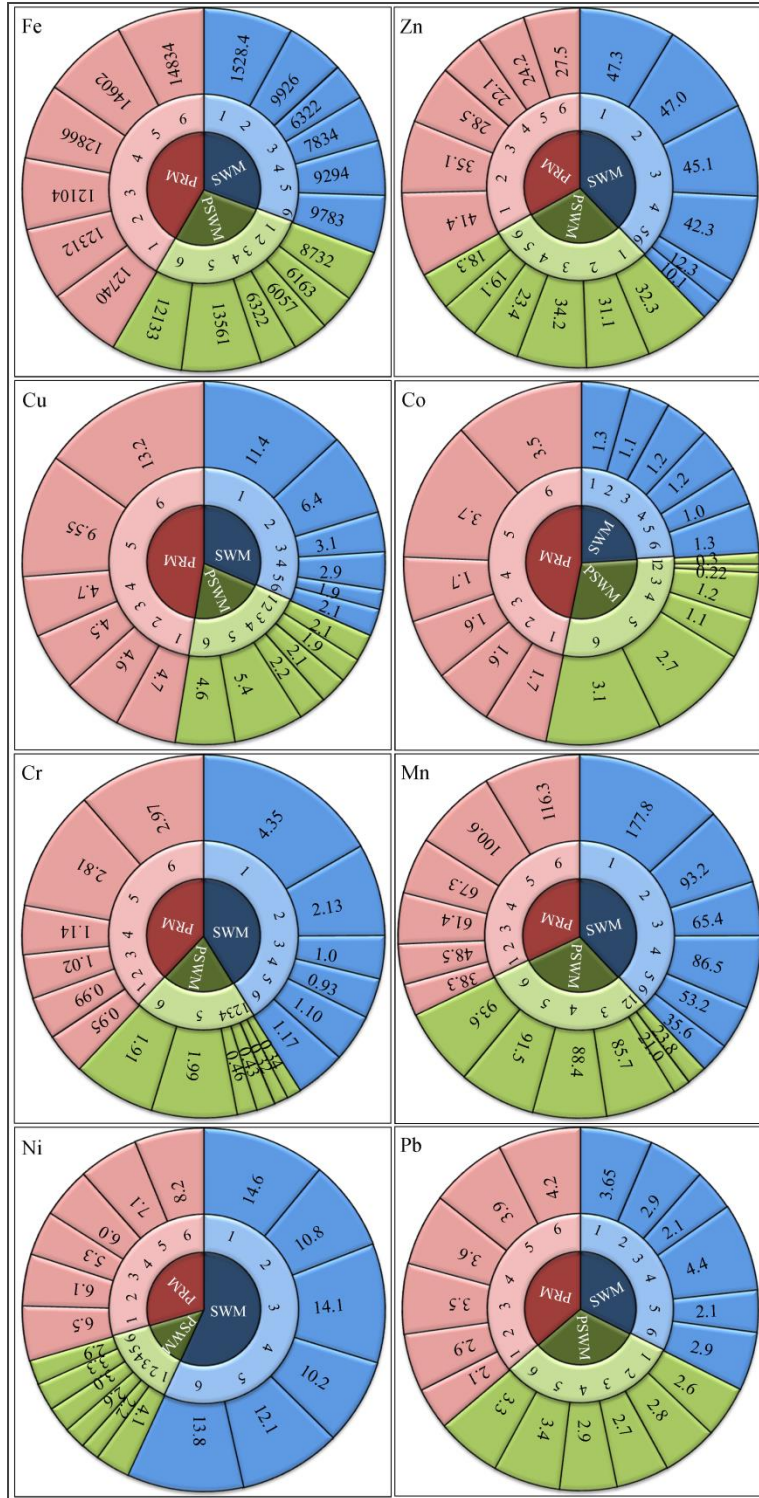


Fig. 4. Detected trace metals ($\mu\text{g/g}$) mean concentrations in the collected mesozooplankton samples. Inner circle indicates seasons (SWM- Southwest Monsoon, PSWM- Post- Southwest Monsoon, and PRM- Pre – Southwest Monsoon.); middle circle indicates stations and outer circle indicates the average concentration of trace metal in each station.

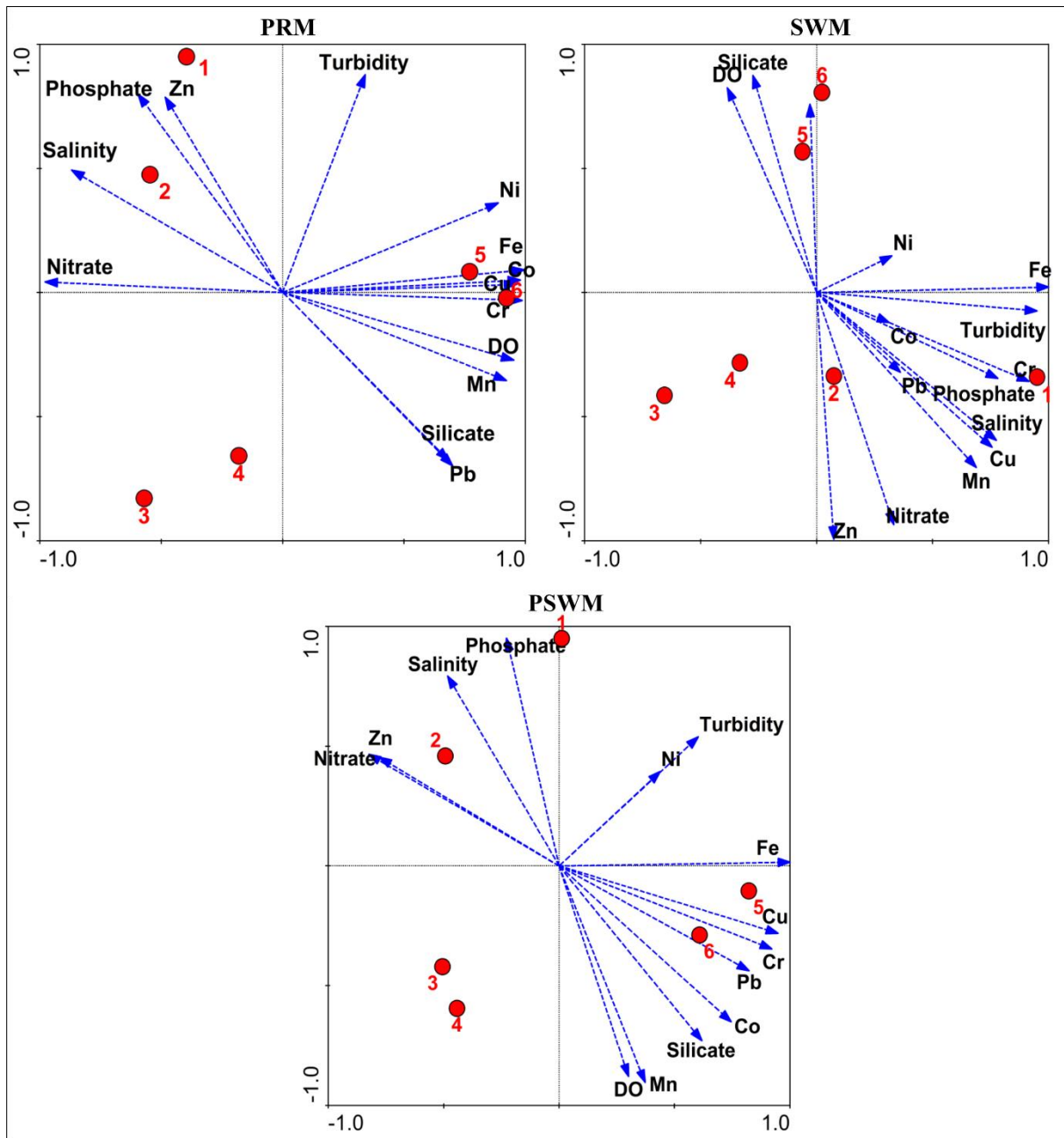


Fig. 5. PCA biplot represents the interrelationships between the hydrographical parameters and trace metal concentration during the Pre- Southwest Monsoon (PRM), Southwest Monsoon (SWM), and Post- Southwest Monsoon (PSWM). PCA biplot stations are in red circles, while the parameters show up as blue-dotted arrows. The direction of the arrows represents their increase in that direction.

Table 1- Physico-chemical parameters of surface water of the study region

Stations	Temperature (°C)	Salinity	Turbidity (NTU)	DO mg/L	Nitrate (µM)	Phosphate (µM)	Silicate (µM)
PRM							
1	28.5	21.01	13.62	4.47	1.95	2.05	20.00
2	29	15.27	15.7	4.76	0.81	1.12	14.4
3	30.3	12.15	2.79	5.31	3.46	0.82	22.00
4	31.2	10.99	3.14	5.13	9.06	0.32	28.15
5	32.2	4.91	12.4	5.24	10.93	0.24	38.65
6	32.8	1.01	13.34	6.00	9.55	0.15	41.25
SWM							
1	28.2	0.11	12.88	5.68	17.75	3.25	71.15
2	29.1	0.1	10.21	6.15	14.1	3.41	68.65
3	27.26	0.34	9.27	6.38	10.25	0.75	76.4
4	30.41	0.25	8.8	7.85	8.6	0.92	92.1
5	30.64	0.08	9.89	8.47	1.5	1.05	101.6
6	30.92	0.08	12.15	8.54	1.2	1.17	107.2
PSWM							
1	28.42	14.4	10.2	4.1	8.55	3.29	31.5
2	29.1	7.58	10.63	5.73	6.23	3.0	48.24
3	29.19	6.35	5.16	6.21	6.62	0.59	54.77
4	30	4.63	7.3	6.86	5.13	0.63	76.9
5	30.16	0.64	10.22	7.04	1.40	0.73	96.48
6	30.3	0.12	11.2	7.01	0.78	0.79	99.43

Table 2- Trace metals (dry weight- $\mu\text{g/g}$) concentration in mesozooplankton. SWM- Southwest Monsoon, PSWM- Post- Southwest Monsoon, PRM- Pre- Southwest Monsoon

Stations	Fe	Zn	Cu	Co	Cr	Mn	Ni	Pb
PRM								
1	12740 \pm 124.4	41.4 \pm 1.3	4.7 \pm 0.67	1.7 \pm 0.5	0.95 \pm 0.11	38.3 \pm 6.5	6.5 \pm 2.1	2.1 \pm 0.8
2	12312 \pm 185.3	35.1 \pm 0.8	4.6 \pm 0.42	1.6 \pm 0.3	0.99 \pm 0.7	48.5 \pm 7.9	6.1 \pm 1.9	2.9 \pm 0.3
3	12104 \pm 264.7	28.5 \pm 1.1	4.5 \pm 0.44	1.6 \pm 0.7	1.02 \pm 0.12	61.4 \pm 9.7	5.3 \pm 1.2	3.5 \pm 0.4
4	12866 \pm 267.6	22.1 \pm 0.9	4.7 \pm 0.61	1.7 \pm 0.7	1.14 \pm 0.4	67.3 \pm 5.4	6.0 \pm 1.7	3.6 \pm 0.3
5	14602 \pm 100.5	24.2 \pm 1.6	9.55 \pm 0.12	3.7 \pm 0.6	2.81 \pm 0.16	100.6 \pm 1.54	7.1 \pm 2.4	3.9 \pm 0.8
6	14834 \pm 123	27.5 \pm 1.1	13.2 \pm 0.23	3.5 \pm 0.8	2.97 \pm 0.23	116.3 \pm 1.89	8.2 \pm 2.1	4.2 \pm 0.6
SWM								
1	15284 \pm 168.6	47.3 \pm 2.4	11.4 \pm 2.1	1.3 \pm 0.5	4.35 \pm 0.18	177.8 \pm 3.21	14.6 \pm 4.1	3.6 \pm 0.7
2	9926 \pm 184.1	47.0 \pm 1.9	6.4 \pm 1.9	1.1 \pm 0.6	0.21	93.2 \pm 3.02	10.8 \pm 1.5	2.9 \pm 0.4
3	6322 \pm 234.6	45.1 \pm 1.6	3.1 \pm 1.6	1.2 \pm 0.6	1.0 \pm 0.18	65.4 \pm 2.98	14.1 \pm 0.9	2.1 \pm 1.1
4	7834 \pm 197.4	42.3 \pm 1.2	2.9 \pm 0.77	1.2 \pm 0.8	0.93 \pm 0.22	86.5 \pm 3.25	10.2 \pm 3.2	4.4 \pm 2.9
5	9294 \pm 138.9	12.3 \pm 0.9	1.5 \pm 0.23	1.0 \pm 0.1	1.10 \pm 0.24	53.2 \pm 1.36	12.1 \pm 2.7	2.1 \pm 1.5
6	9783 \pm 157.8	10.1 \pm 1.5	2.1 \pm 0.51	1.3 \pm 0.4	1.17 \pm 0.17	35.6 \pm 4.5	13.8 \pm 1.5	2.9 \pm 0.4
PSWM								
1	8732 \pm 256.4	32.3 \pm 2.1	2.1 \pm 0.6	0.3 \pm 0.1	0.34 \pm 0.1	23.8 \pm 7.5	4.1 \pm 1.3	2.6 \pm 0.8
2	6163 \pm 175.4	31.1 \pm 1.6	1.9 \pm 0.4	0.22 \pm 0.1	0.32 \pm 0.9	21.0 \pm 3.2	2.2 \pm 2.9	2.8 \pm 0.4
3	6057 \pm 236.8	34.2 \pm 2.3	2.1 \pm 0.5	1.2	0.43 \pm 0.5	85.7 \pm 2.5	2.6 \pm 0.1	2.7 \pm 0.9
4	6322 \pm 267.3	23.4 \pm 2.7	2.2 \pm 0.4	1.1 \pm 0.2	0.46 \pm 0.8	88.4 \pm 5.3	3 \pm 0.1	2.9 \pm 0.7
5	13561 \pm 197.2	19.1 \pm 1.5	5.4 \pm 0.6	2.7 \pm 0.4	1.99 \pm 0.2	91.5 \pm 1.0	3.3 \pm 0.7	3.4 \pm 0.6
6	12133 \pm 287.3	18.3 \pm 1.2	4.6 \pm 0.9	3.1 \pm 0.7	1.91 \pm 0.3	93.6 \pm 8.7	2.9 \pm 1.0	3.3 \pm 0.7

Table 3- Concentration of Trace metals ($\mu\text{g/g}$, dry weight) in the plankton samples taken from the earlier reported (maximum) values. The (-) symbol indicates ‘not reported’

No.	Source	Fe	Zn	Cu	Co	Cr	Mn	Ni	Pb	Place
1	Martin and Knauer, 1973	-	116	13	-	-	-	-	3.6	Monterey (CA, USA)
2	Greig et al., 1977	-	625	54.4	-	35.2	-	4.6	81	New York Bight, Atlantic coast of the USA
		-	136	39.3	-	4.7	-	4.5	22.6	Long Island Sound estuary, New York
3	George and Kureishy, 1979	6930	938	228	26	nr	249	81	119	Coastal Bay of Bengal
4	Sen and Qasim 1985	94	31	5	4	nr	7	3	nr	Indian Ocean
5	Everaertset al., 1993	-	580	92	-	-	-	-	54	The Banc d'Arguin, Mauritania
6	Zauke et al., 1996	-	524	34	-	-	-	-	2.7	Central North Sea
7	Kahle and Zauke, 2003	-	518	26	-	-	-	-	0.7	Weddell Sea
8	Ho et al., 2007	37,702	307	122	13	96	816	64	-	The South China Sea
9	Rejomon et al., 2008a	14,073	2000	46.2	24	-	-	29.5	6.6	Western Bay of Bengal
10	Rejomon et al., 2008b	44,894	7546	84.9	46.2	-	-	62.8	19	Coastal Bay of Bengal
		3423	502	29.4	19.5	-	-	25.3	3	Off shore Bay of Bengal
11	Paimpillil et al., 2010	50,962	7066	78	34	-	552	54	20	Off Visakhapatnam, Bay of Bengal
		22,291	3379	73	26	-	438	45	7	Off Chennai, Bay of Bengal
12	Robin et al., 2012	-	2.08	0.2	-	-	0.66	-	7.9	Cochin Coast, Arabian Sea
		-	0.62	0.32	-	-	0.13	-	2.69	Alleppy Coast, Arabian Sea
13	Vilhena et al., 2014	21887	38	16	-	16.61	510	7.5	10	Eastern Amazon, Para estuary
		33435	102	17	-	32	1064	6.5	36	Mocajuba estuary
14	Srichandran et al., 2016	6388	1407	14.4	0.65	4.55	49.7	3.1	4.16	Off Rushikulya estuary, Odisha, east coast of India
15	Present study (2015)	15,284	47.3	13.2	3.7	4.35	177.8	14.6	4.2	Kochi backwaters, Kerala-India