

Input-export fluxes of heavy metals in the Cochin estuary, southwest coast of India

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Abstract

Cochin estuary (CE) is one of the largest tropical estuaries along the southwest coast of India, sustaining rich bio-resources. Several studies enlighten the environmental changes in the CE caused by anthropogenic activities. In the present study, an attempt has been made to quantify the heavy metal (dissolved and particulate) fluxes brought by the six rivers into the CE with their exchange into the coastal ocean through the major inlet at Cochin during a steady flow period (October-November 2015). The water flux across the inlet was quantified using an Acoustic Doppler Current Profiler. The measured daily input of dissolved metals from the rivers was 2.43×10^3 kg Fe, 334 kg Zn, 259 kg Ni and 83 kg Cr, while that of particulate metals were 85.30×10^3 kg Fe, 8.6×10^3 kg Mn, 236.9 kg Cr and 111.9 kg Zn. The net export of metals through the Cochin inlet (per tidal cycle) was 3.3×10^3 kg Fe, 515 kg Cr, 150 kg Zn and 5 kg Ni in dissolved form and 3.32×10^5 kg Fe, 1747 kg Mn, 1636 kg Cr, 1397 kg Zn and 586 kg Ni in particulate form. The high concentrations of metals during ebb tides are clear indications of their contribution from the industrial conglomerates (industrial units of metallurgy, catalyst, fertilizer, and pesticides) located in the Periyar River. The significance of this study is that the export fluxes may increase further during the summer monsoon (June-September), which may impact the abundant fishery emanating in the coastal environment during the period due to intense upwelling.

Keywords: Acoustic Doppler Current Profiler; Biogeochemistry; Cochin estuary; Fluxes; Heavy metals; Time-series measurement

1. Introduction

The usage of heavy metals for a variety of human applications such as industries, domestic, agriculture, medicine, and technology has a consequence of widespread spillage, causing potential impacts on the environment and health, as they are persistent, toxic, non-biodegradable, and bioaccumulative and thereby harm living organism such as plants, microbes, fishes, animals, and humans at high concentration (Kennish, 1991; Buchman, 2008). The term "heavy metals" refers to elements with densities greater than 5g/cm^3 and usually indicates metals and metalloids associated with pollution and toxicity. Rock weathering and volcanic eruptions are natural sources of metals, whereas mineral extraction, mining, industries, agricultural practices, and various other developmental activities are considered anthropogenic sources of heavy metals. Much of the metals mobilized during natural crustal weathering and anthropogenic activities are dispersed by rivers, transporting the materials towards the land/sea margins through estuaries (Masson et al., 2006). Although these elements are toxic to estuarine and marine organisms above a threshold availability (Buchman, 2008), many are essential to metabolism at lower concentrations (Briffa et al., 2020). Heavy metals such as Fe, Co, Zn, Cu and Ni serve as essential micronutrients whose availability influences the physiological state and biochemical activity of aquatic organisms (Riba et al., 2003; Sparks, 2005; Khan et al., 2014). Heavy metals such as Cd and Pb have no known nutritional, biochemical or physiological functions in organisms and may significantly affect biotic communities (Sparks, 2005; Nordberg et al., 2015).

Estuaries characterized by strong gradients in pH, dissolved oxygen, freshwater discharge (salinity), and suspended particulate matter play an essential role in transporting materials to the coastal environment (Elliott and McLusky, 2002) by acting as a natural geographical barrier (Brinat et al., 2021). The estuarine physicochemical gradients, biogeochemical processes, and organism physiology coordinate metal's fate and potential effects in estuaries (Machado et al., 2016). The fate of heavy metals reaching the coastal environment is of concern where the anthropogenic activities are extensive. Therefore, export fluxes of materials across an estuary can be used to understand how the human-induced perturbations may impact the health of a coastal marine ecosystem (Che et al., 2003; Zwolsman and Van Eck, 1999; Briant et al., 2021).

The partitioning of metals between different phases is strongly influenced by attributes such as pH, redox potential, particle size and its distribution, and the important metal-binding phases such as organic matter (OM), iron and manganese oxyhydroxides and acid-volatile sulphur (Chapman et al., 1999, Simpson et al., 2007). Under hypoxic conditions, oxidation of organic matter and reductive dissolution of iron and manganese oxyhydroxides result in the metal release from labile metal forms

and stabilize metal sulphides (Machado et al., 2016). Upwelling that occurs during the southwest monsoon season (June to September) results in nutrient enrichment and hypoxia along the southwest coast of India, leading to high water column productivity (Naqvi et al., 2000). The influx of upwelled waters is evident in and around the estuarine inlet during the southwest monsoon season. A seasonal change in dissolved oxygen significantly influences metal's geochemical forms in sediments (Gupta et al., 2016; Cyriac et al., 2021). Studies on the input and fate of heavy metals in monsoonal estuaries are poorly constrained owing to the uncertainties associated with the cycling of metals (Samanta et al., 2018). Estimates of the river input and exports are essential to assess the anthropogenic loading of metals and their fate on the ecology of the coastal environment (Nriagu and Pacyna, 1988; Pacyna et al., 1995; Samanta et al., 2018).

. Cochin estuary (CE), one of the most productive estuarine systems along the southwest coast of India, sustaining numerous aquatic plants and shellfishes (Qasim, 2003), is a part of the Vembanad wetland system, which has been designated as a Ramsar site in November 2002 (Balachandran et al., 2008). The construction of the Cochin shipyard, followed by intense and large-scale constructional activities, reclamation, and aquaculture farming, has resulted in the massive destruction of mangrove vegetation in most areas. Paddy cum prawn culture is prevalent in various regions of the estuary. CE has been a deteriorating water body over the last few decades following widespread reclamation (Gopalan et al., 1983) and increased dumping of effluents (0.104×10^6 m³/day) from industries and sewage (260 tons/day) from domestic sectors (Balachandran et al., 2006; Martin et al., 2012; Anu et al., 2014; George et al., 2016). Chemical industries of the Kerala state (~70%) are mainly located on the banks of the rivers Periyar and Chitrapuzha. They manufacture a range of chemicals and petrochemical products, which include fertilizers, pesticides, rare earth elements, rubber processing chemicals, zinc/chrome products, paints, pigments, phenolics, acids, batteries, oil, greases, mercury, and leather products (Joy et al., 1990). Another industrial unit located at Piravam on the Muvattupuzha Riverbank is the Hindustan Newsprint factory. These industries discharge concentrated toxic effluents daily after little treatment into the rivers (Balachandran et al., 2008). Moreover, wastes from aquaculture fields (62 km²), agricultural areas (80 km²), coconut husk retting yards, fish processing plants, and animal bone processing units have increased the organic pollution in the estuary

The hydrography of the Cochin estuary has deteriorated due to the loading of pollutants exceeding its carrying capacity (Menon et al., 2000; Balachandran et al., 2001, 2005; Miranda et al., 2008). Despite several studies on the eutrophication (Gupta et al., 2009; Lallu et al., 2014), organic contaminants (Ramzi et al., 2017; 2018; 2020), and heavy metals (Balachandran et al., 2005;

Chakraborty et al., 2014a, b; Sarkar et al., 2016; Salas et al., 2007), estimation of input fluxes of metals into the estuary and net export of pollutants into the coastal waters have never been attempted so far for the CE. Therefore, the present study is the first attempt to study the input-export fluxes of heavy metals in the CE. The objective is to identify the primary sources of heavy metals (Fe, Zn, Mn, Cr, Cu, Ni, Pb and Cd) in the estuary and their impact on the coastal environment. The input of heavy metals in dissolved (D) and particulate (P) forms entering the CE through 6 rivers and their exchange through the Cochin inlet were measured simultaneously based on cross-sectional surveys using an Acoustic Doppler Current Profiler (ADCP).

2. Study region and Methodology

2.1 Regional Setting

Cochin estuary (Fig. 1) is the second-largest estuary along the west coast of India that spreads over 250 km² (10°10' N, 76° 15' E in the north to 09° 30' N, 76° 25' E in the south) and has a length of ~80 km, oriented parallel to the coastline and connected to the Arabian Sea at Munambam and Cochin (Srinivas et al., 2004). The Cochin inlet is 450 m wide and 10-16 m deep, while the rest of the estuary is generally shallow (2-6 m). Tides in the estuary are mixed semi-diurnal with an average tidal amplitude of 1m (Qasim and Gopinathan., 1969). The hydrography of the CE is significantly influenced by freshwater influx from six rivers viz: Periyar-R₁, Muvattupuzha-R₂, Meenachil-R₃, Manimala-R₄, Pampa-R₅ and Achankovil-R₆ (Qasim 2003; Srinivas et al., 2003, Balachandran et al., 2002). The annual rainfall over the area is around 320 cm, 75% of which nearly occurs during the summer monsoon (June to September) characterized by high river discharge, while post-monsoon (October-January) and pre-monsoons (February-May) are considered as moderate and minimum discharge periods, respectively. There is strong stratification at the inlet during heavy discharge periods, while well-mixed condition prevails during the post and pre-monsoon periods (Bincy et al., 2013). Cochin estuary has distinct zones based on the tidal excursions; a dynamic central zone sandwiched between two relatively weak zones on the north and south (Balachandran et al., 2005)

2.2 Sampling and analysis

A total of 14 locations, six stations in the rivers (R₁ to R₆) and eight stations in the estuary (S₁ to S₈) were selected for this study (Table 1; Fig. 1). Estuarine stations were selected in such a way that S₁ and S₂ receive freshwater from R₁; S₄, S₅ and S₆ receive freshwater from R₂; S₇ receives freshwater from R₃-R₆, and S₈ receives freshwater from R₆. S₃ is the Cochin inlet through which the materials are exchanged with the sea (Shivaprasad et al., 2013). Water samples from near-surface and near the bottom from 6 rivers (R₁ to R₆) and 7 estuarine stations (S₁, S₂, S₄, S₅, S₆, S₇ & S₈)

were collected during 28-30 October 2015. As the flushing time of CE for the wet season is ~ 2.5 days (Vinita et al., 2015), the time-series measurements at Cochin inlet, S₃ were conducted on 3-4 November 2015), assuming that the freshwater will reach the inlet in three days. Water samples were collected from S₃ every 3 hours (for 27 h) from the near-surface, middle (7m) and bottom (15m).

Water samples collected from each location using a 5L Niskin sampler (Hydro-Bios, Kiel-Holtenau, Germany) was used for the estimation of pH, salinity, dissolved oxygen, dissolved/particulate heavy metals and suspended particulate matter (SPM). Salinity was measured using a conductivity-temperature-depth profiler (CTD 19 plus, Sea-Bird Electronics, conductivity ± 0.001 S/m). In the laboratory, samples with salinity < 2 were measured using a DIGI AUTO Salinometer (Model TSK, accuracy ± 0.001). Dissolved oxygen was analyzed following Winkler's method (Grasshoff et al., 1999) with a lower detection limit of 2 μ M. pH was measured using a pH meter (Eutech pH 2700, accuracy ± 0.001). Water samples for heavy metals were passed (1L) through a pre-weighed 0.45 μ m cellulose acetate filter paper (Millipore), dried at 60°C and weighed to quantify the suspended particulate matter (SPM). The filtrate was preserved at pH < 2 using con. HNO₃ and extracted with a mixture of 2% Ammonium Pyrrolidine Dithio Carbamate (APDC), 2% Disodium Diethyl Dithio Carbamate (DDDC) and Chloroform (pH adjusted to 4.5 with ammonium acetate). The metals retained in the organic layer were extracted with 0.1 N HNO₃ and used to estimate dissolved metals (Grasshoff et al., 1999). The filter paper (stored at -20° C) was digested using a 5:2 mixture of HNO₃ + HClO₄ in a Teflon vessel on a hot plate (Fabunmi et al., 2015). The heavy metals in the dissolved and particulate fractions were analyzed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Scientific iCAP 7000 Series). 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, and the recoveries are within the acceptable range ($\pm 5\%$). Analytical precision was monitored by running triplicates and relative standard deviation (RSD) was <5% for all the metals. The detection limits for Zn, Ni, Fe, Mn, Cr, Pb, Cu, and Mg were 0.19, 0.18, 0.12, 0.07, 0.21, 0.53, 0.18, and 0.05 mg/L, respectively. All analyses were carried out in triplicates, and the average value is reported.

A tide gauge (SBE 26 plus) was moored at S₃ to record the water level variation at 10-min intervals during 3-4 November 2015. For the flux measurements, the instantaneous cross-sectional flow through each of the six rivers was measured using an Acoustic Doppler Current Profiler (ADCP-Teledyne River Ray-600 KHz) with bottom-track capability. The instantaneous cross-sectional flow through the Cochin inlet was measured at 3hr. intervals for 27hrs. using ADCP on 3-

4 November 2015. The water flux obtained from ADCP was post-processed into the surface, mid and bottom fluxes using MATLAB.

The particulate metal input fluxes (kg/d) were computed by multiplying the average of particulate metal concentrations ($\mu\text{g/g}$) in each river collected during 28-30 October 2015 by the freshwater flow of each river (m^3/s) obtained from ADCP and unit conversion to kg/d. The dissolved metal input fluxes were computed as the product of the average monthly concentration of heavy metals ($\mu\text{g/L}$) obtained from the Central Water Commission (CWC, 2014) and the freshwater flow from each river (m^3/s) obtained from ADCP. The product of metal concentration ($\mu\text{g/L}$) and water flux (m^3/s) measured at each depth gives the instantaneous metal transport (mg/m^3), which is integrated over a tide (24 hours 50 minutes) to compute the net flux (kg/tidal cycle) across the Cochin inlet. During the computation, the water flux and metal concentration at the 25th hour were calculated by triangular interpolation of the 24th and 27th values of water flux and metal concentration.

2.3 Data Processing

Graphical representation and statistics

Graphic representation of metal data and SPM was achieved using Ocean Data View 4.8.1 (Schlitzer, 2018) and Grapher 8.1.388 (Golden Software, Inc Golden, CO 80401-1866 USA). Descriptive statistics, Pearson's correlation analysis, Dixon test for outliers and One Way ANOVA were performed using XLSTAT 2014.

Data Normalization

Geochemical normalization of an element is estimated as the ratio of the concentration of the element in the sample to the concentration of the same element in the global shale or the primitive mantle of the earth (Nath et al., 2000). The pollution status of an environment can be evaluated based on the normalization factors. Thus, the normalization factor (NF) less than 1 refers to low contamination, $\text{NF} < 3$ refers to moderate contamination, $\text{NF} > 3$ indicates severe contamination and $\text{NF} > 6$ shows extreme contamination. The elemental concentrations are normalized with those of Post Archean Australian Shale reference material (PAAS).

Sediment Quality guidelines

Sediment quality guidelines put forward by National Oceanic and Atmospheric Administration (NOAA) were used to assess whether the concentrations of heavy metals in sediments/SPM could have adverse biological impacts. Long et al., 1995 suggested two guideline values, namely, the ER-L (effective range limit) and ER-M (effective range: medium), delineating three concentration ranges

of a particular metal. If a metal occurs in concentrations below ER-L value, effects on the biota would rarely be observed. At concentrations \geq ER-L but $<$ ER-M, the biota could "occasionally" be affected by the pollutant, whereas at concentrations \geq ER-M, effects would be expected to occur "frequently."

3. Results and Discussion

3.1 General characteristics

Hydrography is an important factor controlling the distribution of heavy metals in an estuary. The freshwater discharges into the CE through 6 rivers obtained from ADCP are presented in Fig. 2a. The high discharge through R₆ may be associated with unexpected landslides. The tides at S₃ (Fig. 2b) showed a maximum tidal range of 0.56 m. Salinity in the upper estuary was $<$ 1 (Table S1, Supplementary Information), while S₃ remained high saline with moderate variation (Fig. 2c) in the surface (3.23-31.68), mid-depth (13.23-33.48) and bottom (31.98-33.78) respectively. The water column at the S₃ was stratified, and a well-mixed condition was observed during 30-33hrs. The variation in salinity at the S₃ is found to follow the tidal rhythm (Balachandran et al., 2001; Shivaparasad et al., 2013).

Both riverine and estuarine stations are slightly acidic in nature. The spatial variation was less for pH (5.24 ± 0.16) in the rivers. However, pH (5.6 ± 0.34) showed significant spatial variation ($p < 0.01$) in the estuary. S₃ was slightly alkaline (average pH: 7.58 ± 0.26 at the surface, 7.80 ± 0.22 at mid-depth & 7.89 ± 0.14 at the bottom) due to the influx of saline water from the Arabian Sea. The upstream and estuary were well-oxygenated (DO $>$ 6mg/l) (Table S1 and S2, Supplementary Information) during the study period, with significant spatial variation in the estuary ($p < 0.01$). The DO (mg/l) at S₃ showed a vertical gradient with surface av: 6.20 ± 0.36 , mid-depth av: 5.28 ± 0.55 and bottom av: 4.9 ± 0.49 . Histograms showing distribution, frequency of sample and sample size are now included as supplementary graphs (Fig S11-S14).

3.2 Suspended Particulate Matter (SPM)

SPM showed significant spatial variation ($p < 0.01$) in the rivers (30.15 ± 19.07 mg/L) with maximum in R₆ (Table S1, Supplementary Information). The northern rivers (R₁ & R₂) were relatively less turbid compared to the southern rivers (R₃, R₄, R₅ and R₆). High SPM (66.7 mg/L) in R₆ may be associated with a landslide before the field survey. SPM was relatively lower (12.28 ± 3.19 mg/L) in the estuary (except at the inlet, S₃) with significant spatial variation ($p < 0.01$). The increase in SPM was noticed towards the south of the estuary with a maximum (18.94 mg/L) at S₈ (Table S3, Supplementary Information). SPM at the Cochin inlet (S₃) varied over a tidal cycle (Fig. 3), with a

surface maximum (86.94 mg/L) at the end (39 hrs.) and minimum (5.83 mg/L) at the start (33 hrs.) of the ebb tide. SPM in mid-depth (38.63 ± 25.64 mg/L) was higher than in the surface, and a peak was observed during peak flood (27-30 hrs.) when there was a reversal of water currents at the surface and mid-depth (Fig. S1, Supplementary Information) directed towards the estuary. The SPM in the bottom (241.68 ± 258.04 mg/L) was higher at 12, 24 and 39 hrs., soon after the peak ebb, with a maximum (718.5mg/L) at the lowest low tide at 24 hrs. The resuspension of sediments during ebbing may have contributed to higher SPM at the bottom. These results agree with the previous study (Vinita et al., 2017) that the variations in SPM at Cochin inlet (S₃) may be due to the combined effect of river discharge and tides

3.3 Heavy metal distribution

Rivers

The concentration of heavy metals with their spatial variation in rivers is provided in Table S1, Supplementary Information. Dissolved metals ($\mu\text{g/L}$): DZn (1.35 ± 1.25), DFe (41.27 ± 9.87) and DMg (10.37 ± 4.95) observed in the 6 rivers were comparable with earlier reports. These values are also well within the permissible drinking water limit (Table S5, Supplementary Information) recommended by the Bureau of Indian Standard (BIS 10500-2012). The concentrations of DCu, DMn and DPb in rivers were below measurable levels (nd). However, the particulate metals in the rivers ($\mu\text{g/g}$): PZn (51.33 ± 51.48), PCr (298 ± 746.39), PMn (347.36 ± 566.55), PNi (15.67 ± 54.28), PFe (5.03 ± 1.97) % and PMg (0.37 ± 0.26) % were several times higher than the dissolved metals. The results of ANOVA revealed significant spatial variation for DFe ($p < 0.05$) and PZn ($p < 0.05$) in rivers. The values of PFe, PCr, and PMn in Periyar and PCr in Muvattupuzha river were higher than PAAS and those reported for Upper Crust (UC) and World Rivers SPM concentration (WRSPM) standards (Table S6, Supplementary Information), probably due to laterite-rich low and midland soils of Kerala (Nath et al., 2000). Lateritic soil is the most predominant soil type in the Ernakulam district. Lateritic soil is encountered in Muvattupuzha, Kothamangalam, Kunnathunadu and parts of Aluva taluks. Laterite is a polymetallic ore, as it is the essential repository for aluminium and a source of iron, manganese, nickel, and chromium (District Survey Report, 2016). The high Chromium in rivers might be derived from various anthropogenic activities in river basins (e.g., fertilizer residues from farmlands and plantations, domestic sewage from settlement clusters). Higher PFe and PCr in bottom may be resuspended from sediments underneath. Under highly oxygenated conditions in rivers, Fe and Mn exist as oxides and hydroxides which are insoluble in water, get precipitated and may lead to lower soluble Fe and absence of soluble Mn in all the six rivers. Elevated concentration of PCr (in rivers, R₁ and R₂) and its association with particulate Fe

and Mn suggest coprecipitation of Cr with Fe-Mn oxyhydroxide. The above results showed that SPM is a major carrier of heavy metals into the CE.

Heavy metals in the Cochin estuary

The concentration of heavy metals with their spatial variation in the estuary is provided in Table S2, Supplementary Information. The dissolved metals ($\mu\text{g/L}$) in the estuary varied as DZn (10.84 ± 23.74), DFe (74.48 ± 29.53) and DMg (8.94 ± 1.19) and showed significant spatial variation for DZn and DFe ($p < 0.01$). Dissolved heavy metals measured were within the permissible limit of BIS 10500-2012 for drinking water. The particulate metals were higher than dissolved fractions and varied as PZn (176.88 ± 396.71) $\mu\text{g/g}$, PCr (131.35 ± 255.76) $\mu\text{g/g}$, PMn (47.06 ± 85.26) $\mu\text{g/g}$, PCu (24.48 ± 76.03) $\mu\text{g/g}$, PPb (15.09 ± 39.20) $\mu\text{g/g}$, PFe (6.85 ± 4.42) % and PMg (0.42 ± 0.25) %. PZn ($p < 0.01$) and PFe ($p < 0.01$) showed significant spatial variation in the estuary. Even though spatial variation was less for Pb, Cr, Ni and Cu in the estuary, the concentrations of PZn, PCu and PPb were very high in the north estuary (S_1 and S_2), even higher than the WRSPM/PAAS standards and are mainly related to untreated effluent discharge from various industries located on the banks of Periyar. A high concentration of PPb in S_5 confirms its addition through non-point sources. The possible sources of lead in this region may be paints, petroleum products, and sewage discharge. PFe was uniformly high in the estuary with a maximum in S_6 , possibly due to sewage disposal and land use pattern. A high concentration of PCr higher than WRSPM/PAAS standards observed S_6 and S_7 indicates additional input from anthropogenic activities. The possible source of Cr and Pb in S_7 can be fertilizer residues from farmlands and plantations nearby, and at S_6 can be domestic sewage. The other possible sources of lead in S_7 may be paints, petroleum products, and sewage discharge. The only exception was Mn and Cr (in S_2), which are deposited relatively faster during their transport downstream. S_4 (lower reaches of R_2) and S_8 (lower reaches of R_6) regions exhibited low concentrations of heavy metals. The distribution of particulate heavy metals may be due to the hydrodynamic sorting of minerals associated with it (Balachandran et al., 2005). The denser minerals settle quickly during deposition, while the lighter minerals are transported further downstream. This is supported by a reduction in the suspended solids from (30.15 ± 19.07) mg/l to (12.28 ± 3.19) mg/l towards the estuary. The strong association of Fe, Mn and Cr towards the coarser suspended particles during the present observation might have resulted in their rapid settling and lower particulate Fe, Mn and Cr in the lower reaches of R_2 . Both dissolved and particulate metal levels were comparable with previous reports in CE (Table S7 and S8, Supplementary Information).

Influence of tide on heavy metal concentrations at the Cochin inlet

The intra-tidal variations (27 hrs.) in both dissolved and particulate metal concentrations measured at the Cochin inlet during 3-4 November 2015 are depicted in Fig. 4 and 5. DMg (28.8-947), DFe (9.7-125.3), DCr (2.14-5.55), DZn (nd-6.15) and DNi (nd-0.64) showed moderate concentrations ($\mu\text{g/L}$), while DCo, DCu and DPb were below measurable levels (Table S4, Supplementary Information). DFe, DCr and DMg were present at moderate levels throughout the observation, while DZn and DNi were below detectable levels during certain periods, and an increase in the bottom was noticed during flood tide (15-18hrs. and 27-30hrs.). The pH and salinity were relatively higher (due to flooding), and dissolved oxygen was comparatively higher at the bottom. The degree of desorption of metals from the SPM increases with salinity (Samanta et al., 2018). Elevated values of heavy metal concentrations at higher salinity require an increasing degree of adsorption of one or more of the dissolved major ions (Na, Mg, and Ca) with increasing salinity. A significant negative correlation ($p < 0.05$) exists between DNi and DMg. The adsorption of DMg may be responsible for the dissolution of Ni. However, such a significant correlation between DZn and DMg was absent. When an oxygen gradient exists in addition to the salinity gradient, the redox process has a profound influence on trace metal mobilization (Gerringa et al., 2001). Therefore, further studies are required to determine the causative factor for the dissolution of Zn and Ni at the Cochin inlet. DMn (9.5 $\mu\text{g/L}$), and DCd (3.3 $\mu\text{g/L}$) were present only in one sample and could be due to resuspension. Autochthonous metals can be mobilized under suitable redox conditions (Forstner, 1981). Cd forms soluble complexes such as CdCl_2 and CdSO_4 under high salinity (Machado et al., 2016) may lead to an increase in DCd in the bottom (12hrs.). DMn was present during one ebb tide (36 hrs.) at mid-depth (9.5 $\mu\text{g/L}$), where the waters were oxygenated (5.01-6.34 mg/L) and productive.

The particulate metals exhibited tidal variations for Zn (nd - 1307 $\mu\text{g/g}$), Mn (nd - 3483 $\mu\text{g/g}$), Cr (nd - 148 $\mu\text{g/g}$), Ni (nd - 59.2 $\mu\text{g/g}$), Fe (0.06 - 48.4 %) and Mg (0.02 - 18.1%). Dissolved Zn was uniformly high in the surface except at 24 and 33 hrs., while particulate Zn was high in mid and bottom. Dissolved Ni and particulate metals (Fe, Mn, and Mg) were dominant throughout the tidal cycle. Dissolved Cr was high when SPM was low.

High concentrations of particulate metals (Fe, Mg, Mn, Zn, Cr, Ni, and Pb) in the bottom and mid-depth (Zn, Fe and Mg) at 12 hrs. could be due to high turbidity (SPM 412.1mg/L) towards the end of ebb tide due to sediment resuspension. However, it should be noted that the turbidity increased (SPM 718 and 701 mg/L) again soon after the next ebb tide (i.e., at 24 hrs. and 39 hrs.), though the heavy metals did not show a corresponding increase at the bottom. The ebb during 21-24hr and 33-36hr with a high tidal coefficient may favour the resuspension of denser particles.

Heavy metal concentrations in SPM are related to particles' size, and finer particles accumulate more heavy metals than denser ones (Salas et al., 2017). Low concentrations of dissolved Zn, Fe and Cr in the mid-depth at 27 hrs. may be associated with biological uptake, as evidenced by phytoplankton blooms (Zwolsman and Van Eck, 1993; Luengen et al., 2007). The nutrients brought from the estuary by the preceding tide (24hr.) to the sluggish waters (27hrs.) may have favoured high biological production.

Fe in both (D and P) phases displayed a similar trend in its distribution. A peak in the particulate metals (Zn, Mn, Fe and Mg) in the surface during ebb tide (33 hours) when water currents and SPM were minimum could be related to the anthropogenic input. Zn may be bound to Fe-Mn oxyhydroxide during this period. Comparatively high oxygenated condition (6.78mg/l) at the inlet during 33hrs may favour the Fe and Mn to exist in its oxidized state. The redox-sensitive metals such as Fe and Mn showed a significant ($p < 0.01$) positive correlation with heavy metals. Fe-Mn oxyhydroxide revealed its vital role in the linkage of Zn as Fe-Mn oxyhydroxides (Balachandran et al, 2005) in Cochin inlet. Strong interrelationship among Fe, Mn and Zn indicated their common source and identical behaviour (Table S9; Supplementary Information).

Ni in dissolved fraction and Mg in dissolved and particulate forms showed an increase, while all other metals decreased at the inlet. Fe (both dissolved and particulate) concentration in the upstream was high and low at the inlet, indicating a substantial removal of Fe during estuarine mixing (Balachandran et al., 2005; Nair et al., 2013). Mn also displayed a similar trend with a decrease in concentration towards the inlet. A comparison of dissolved and particulate metals with previous reports in the CE (Table S8 and S9, Supplementary Information) shows that dissolved metals remained consistent over the years (Ouseph et al., 1992; Rajamani, 1994; Unnikrishnan, 2000; Balachandran, 2001; Nair et al., 2013; Anas et al., 2015), though there is an increase in the particulate Cu and Fe levels (Paul and Pillai, 1983; Ouseph et al., 1992; Rajamani, 1994; Nair et al., 2013). The above results show that the wide variation in the heavy metal levels at the inlet was caused by the discharge of effluents from industries and its regulation by estuarine processes such as adsorption-desorption and resuspension.

3.4 Water flux

The water flux through the surface, mid and bottom waters at the Cochin inlet at 3-hr. intervals for 27hrs. were represented in Fig. S1, Supplementary Information. The advection of seawater was high during the highest high water (HHW) at 27hrs. The water flux through the Cochin inlet (integration over 25 h) varied from 45.76 (S), 29.44 (M) and -8.18 (B) Mm^3/tidal

cycle. While the surface and mid-depth water flux was seaward (positive), the bottom flow was landward (negative) with a residual flow of 67.10 Mm³/tidal cycle. Inter-tidal and seasonal changes will influence this water exchange at the inlet, as the major controlling factors are the tides and freshwater discharge (Seena et al., 2020).

3.5 Heavy metal fluxes

Input flux of heavy metals

Input fluxes (kgd⁻¹) of dissolved and particulate heavy metals through 6 rivers (R₁ to R₆) are provided in Table 2 (average freshwater discharge from the 6 rivers during 28-30 October 2015 was 58.56 Mm³d⁻¹). The dissolved and particulate heavy metal input fluxes during 28-30 October 2015 was Zn (334.8 and 111.9 kgd⁻¹), Cr (82.9 and 236.9 kgd⁻¹) and Fe (2432.7 and 86301.6 kgd⁻¹). Similarly, the input of particulate Mn was 604.8 kgd⁻¹ and dissolved Ni was 259.3 kgd⁻¹.

Fluxes of heavy metals across the inlet

Net export of most of the heavy metals through the Cochin inlet was observed. The instantaneous fluxes (gs⁻¹) of heavy metals (Zn, Cr, Fe, Ni & Mn) across the inlet (Fig. 6-8) show a temporary reversal (negative) during flood tide (27 hrs.). This indicates an import of water through the surface and mid-depth, though on integrating over 25 hrs., the result was a net export (positive). Ni and Cr transport through mid-depth and bottom were mostly in dissolved form, while the transport of Zn, Fe and Mn fluxes was in particulate form. The instantaneous fluxes, when integrated over a tidal cycle (24 hrs. and 50 min), showed a net export of Fe (3.3 x 10³ kg), Zn (150 kg), Cr (515 kg), Ni (5 kg) and Cd (2.5kg) in dissolved form.

Net export of Fe (3.32 x 10⁵ kg), Zn (1397 kg), Cr (1636 kg), Ni (586 kg) and Mn (1747 kg) in particulate form was observed (Table 2). The export fluxes of particulate Zn were an order of magnitude (≈ 12) high, while particulate Cr, Fe and Mn were ~ 6 , 4 and 3 times higher than their combined river input to the CE. The heavy metal flux data suggest that despite a moderate trapping efficiency, the export fluxes from the CE are high, especially during high and medium flow periods. Except for Hooghly estuary (Samanta et al., 2018), no data is available on the heavy metal fluxes across the estuarine inlets in India. The export fluxes of heavy metals were high during the ebb period (at 12 hours and 24 hours), when the parcel of water containing the effluent reached the inlet. However, the high concentration of metals in the surface did not cause a corresponding increase in the export fluxes during the flood period (33hours), since the currents were directed towards the estuary. DCd showed a net export, probably through remobilization from sediments during ebb tide (12 hr). Dissolution of Zn and Ni from sediments under high salinity during the

flood period leads to higher dissolved flux directed landward and this has reduced the net export of DZn and DNi to the coastal sea. These results indicate that export fluxes of heavy metals from the CE were mainly dependent on the river flow, type of effluents brought by the ebb currents, tides at the Cochin inlet and estuarine processes resuspension and dissolution.

Estuarine processes (weak flushing) can trap a major portion of suspended particle-associated metals within the estuary to limit the export fluxes to the sea (Balachandran et al., 2005; Sebin et al., 2020). This is evidenced from the high concentrations of Zn (391.4 mg/kg), Cr (213.6 mg/kg), Ni (98.3 mg/kg), Cu (118.5 mg/kg), Cd (18.5 mg/kg), Pb (71.6 mg/kg), Fe (4.10 %) and Mn (1605.4 mg/kg) in the mid-estuarine sediments (Balachandran et al., 2005; Martin et al. 2012; Selvam et al., 2012). This indicates moderate pollution as these metals are likely to be transported to higher trophic levels through detrital and deposit-feeders (Machado et al., 2016). Heavy metal contamination has caused changes in a microbial activity affecting the biota (Martin et al., 2008; Miranda et al., 2008; Shoji et al., 2008). The influence of anthropogenic activities on the soft benthic community and frequent fish kills are common in the northern estuary (Martin et al., 2011).

During the southwest monsoon and northeast monsoon season, coastal upwelling was predominant up to the Cochin inlet, characterized by cool and oxygen-deficient, high saline nutrient-rich waters at the bottom (Lallu et al., 2014, Shivaprasad et al, 2013). In this study, the time series observation for 24hrs. at the Cochin inlet showed that oxygen saturation was quickly regained due to the dynamic nature of the estuary (Lallu et al., 2014). The hypoxic condition in the upwelling zone may support the release of metal bound to Fe-Mn oxides and labile organic matter. Since the study was undertaken during the post-monsoon season, the upwelling induced hypoxia was absent in the bottom waters.

The fate of export fluxes of heavy metals is quite a concern, as it is transported to a coastal environment of high fishery potential, especially during the summer monsoon. The ultimate sink of these heavy metals could be their deposition in coastal sediments (Pichaimani et al., 2008). The changes in redox conditions, pH, and dissolved oxygen could be crucial in the depositional environment. They are removed from the dissolved and particulate form to the sediments and vice versa (Machado et al., 2016). Thus, sediments can act as both sink and source metals under changing redox conditions. In the coastal region, the diagenetic changes in sediments (Nath et al., 2000) can release metals back into the water column during periods of hypoxia. However, the heavy metals in coastal sediments are firmly incorporated into clay and organic matter (Balachandran et al., 2003). The continuous exposure of marine organisms to high concentrations of heavy metals exported from the CE may result in bioaccumulation and subsequent transfer to man through the

food web. Exposure to metals in the fish is mainly through their food and, to a limited extent, by direct absorption from the water column (Rejomon et al., 2010). Therefore, the accumulation of heavy metals in planktons, copepods, and benthic organisms will adversely affect fishes. Elevated trace metal concentrations (Fe, Co, Ni, Cu, Zn, and Cd) in the pelagic and demersal fishes from upwelling zones of the southwest coast of India, especially off Kochi, have been reported. The present study indicates that the concentrations of particulate Zn, Cr and Ni in the Cochin inlet are sufficiently high to cause adverse biological effects (Table S10, Supplementary Information). The accumulation of heavy metals in sediments is a long-term source of contamination to higher trophic levels, as they are exposed to detrital and deposit-feeding organisms (Mendil and Uluozlu, 2007).

Conclusions

The present study provides baseline information on the input-export fluxes of heavy metals in the CE. The rivers in the CE contained low concentrations of heavy metals as they were relatively unpolluted, whereas the northern part of CE was significantly polluted due to industrial effluents. The flux measurements at the Cochin inlet further showed that the export of particulate heavy metals is higher than their input fluxes, indicating CE as a significant source of heavy metals in the coastal sea. The freshwater flow, industrial effluents and tides are the major factors influencing the export fluxes of metals from the CE. These fluxes may be much higher during the high flow period. The fate of heavy metals reaching the coastal environment is a matter of concern as it is a region of rich fishery potential.

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Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

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Compliance with ethical standards

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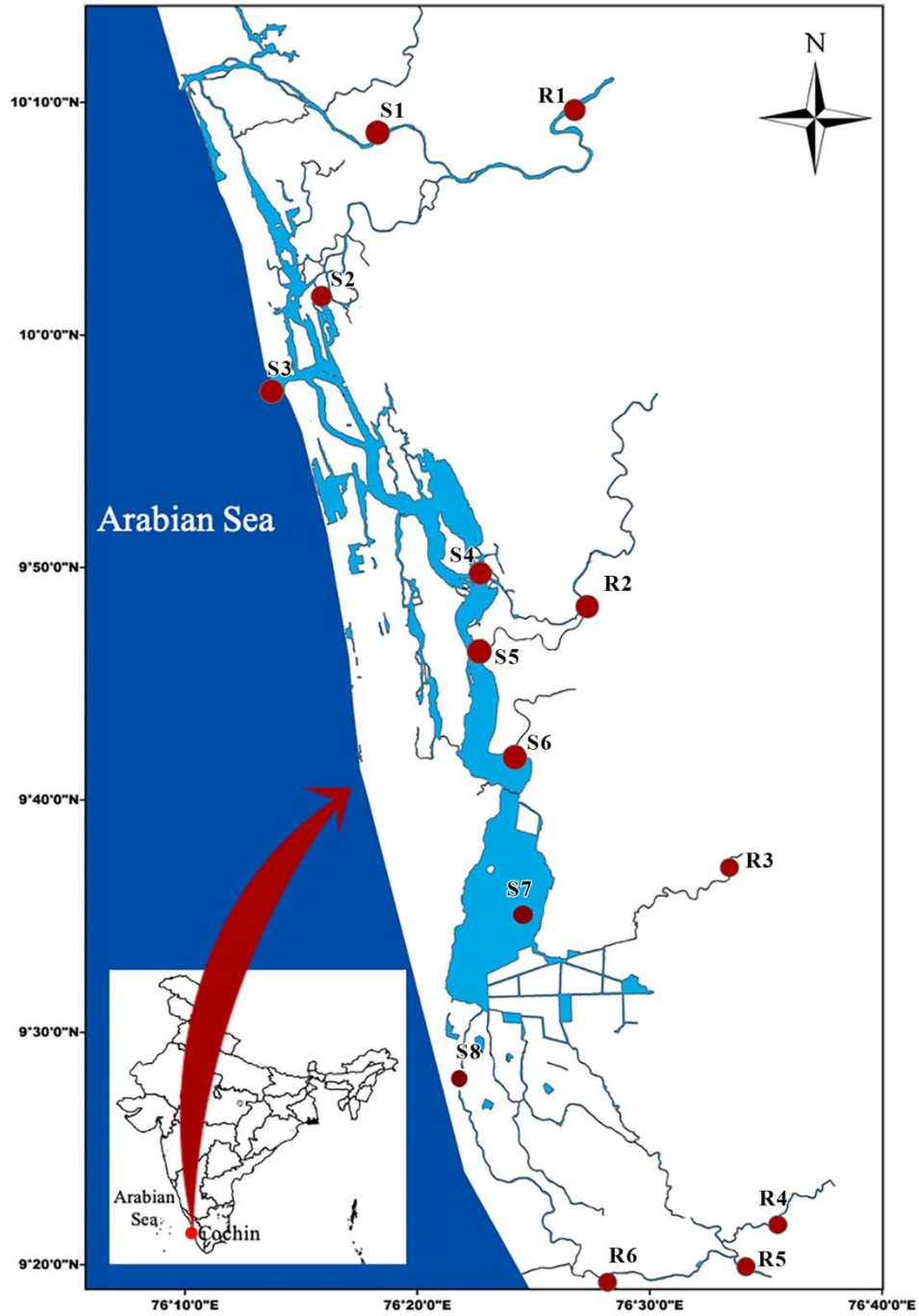


Figure 1 Cochin Estuary and the 6 rivers draining into the system; the red dots symbolize the station locations for the present study.

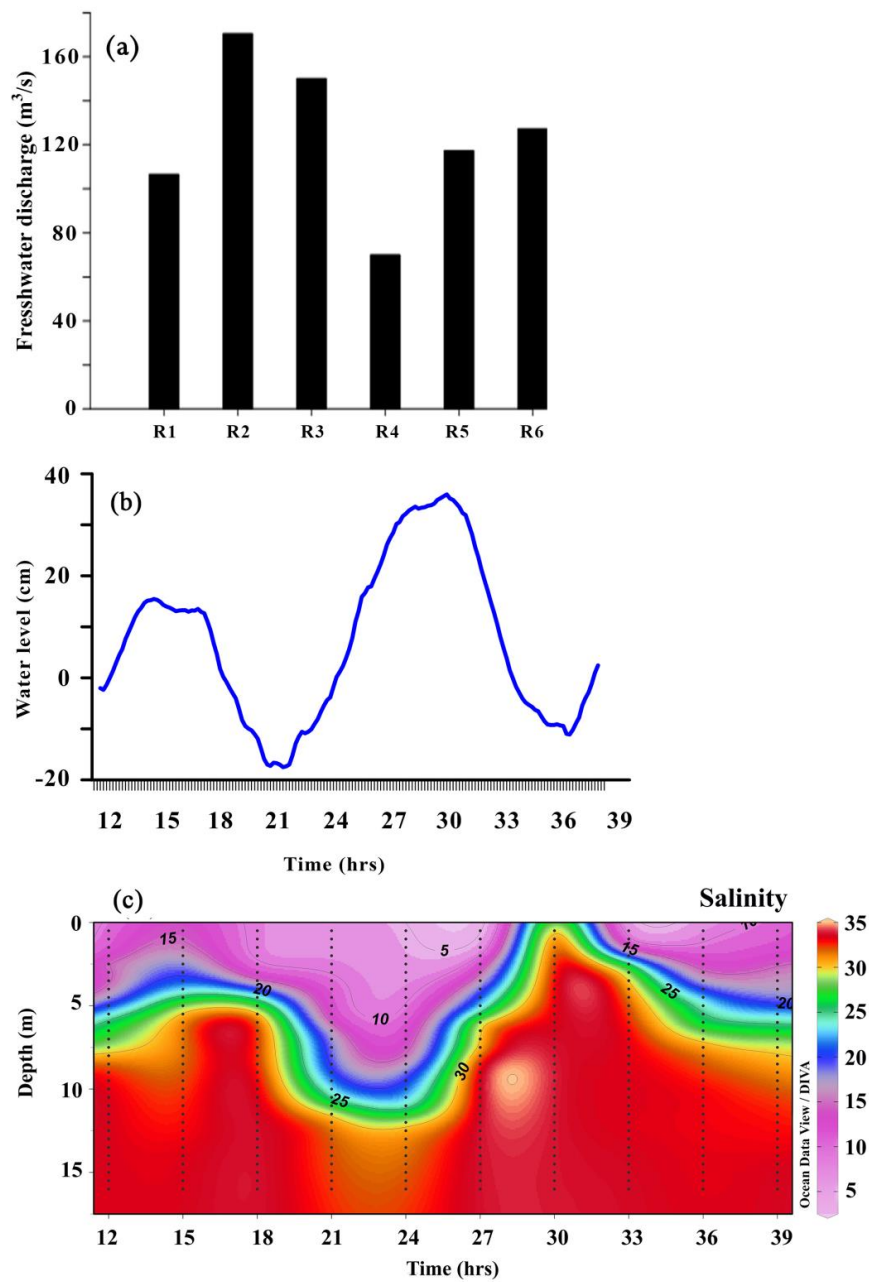


Figure 2 Charts representing (a) Combined freshwater discharge (m^3/s) into the Cochin estuary during 28-30 November 2015, (b) variations in the water level (cm), and (c) salinity profile at Kochi inlet on 3 November 12.00 hours to 4 November 15.00 hours, 2015.

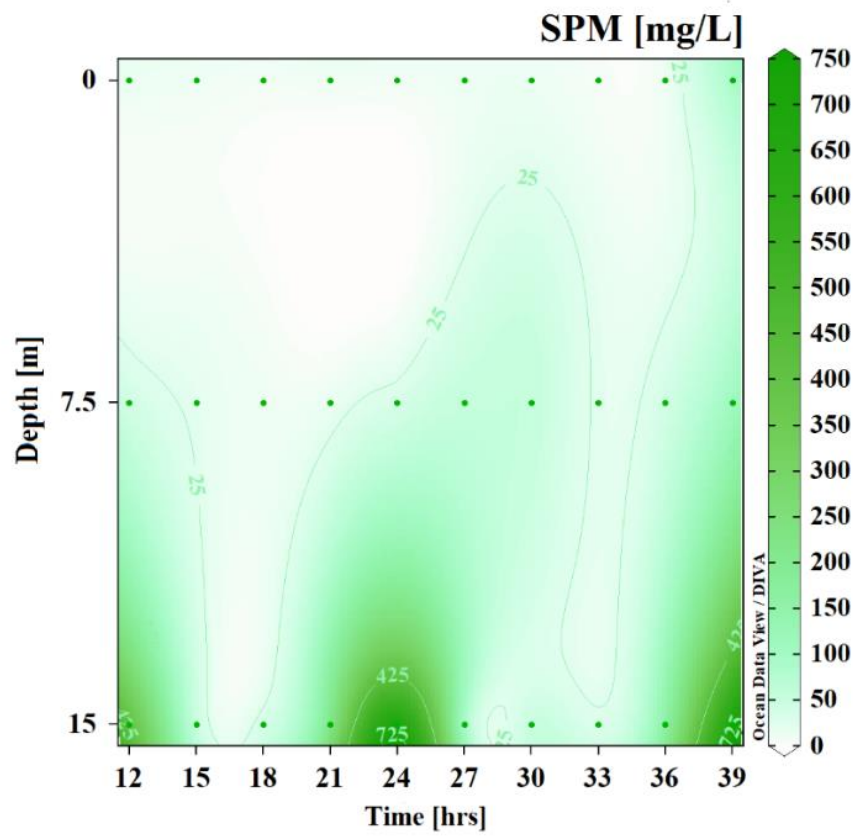


Figure 3 Variation in SPM (mg/L) at Cochin inlet during 3-4 November 2015.

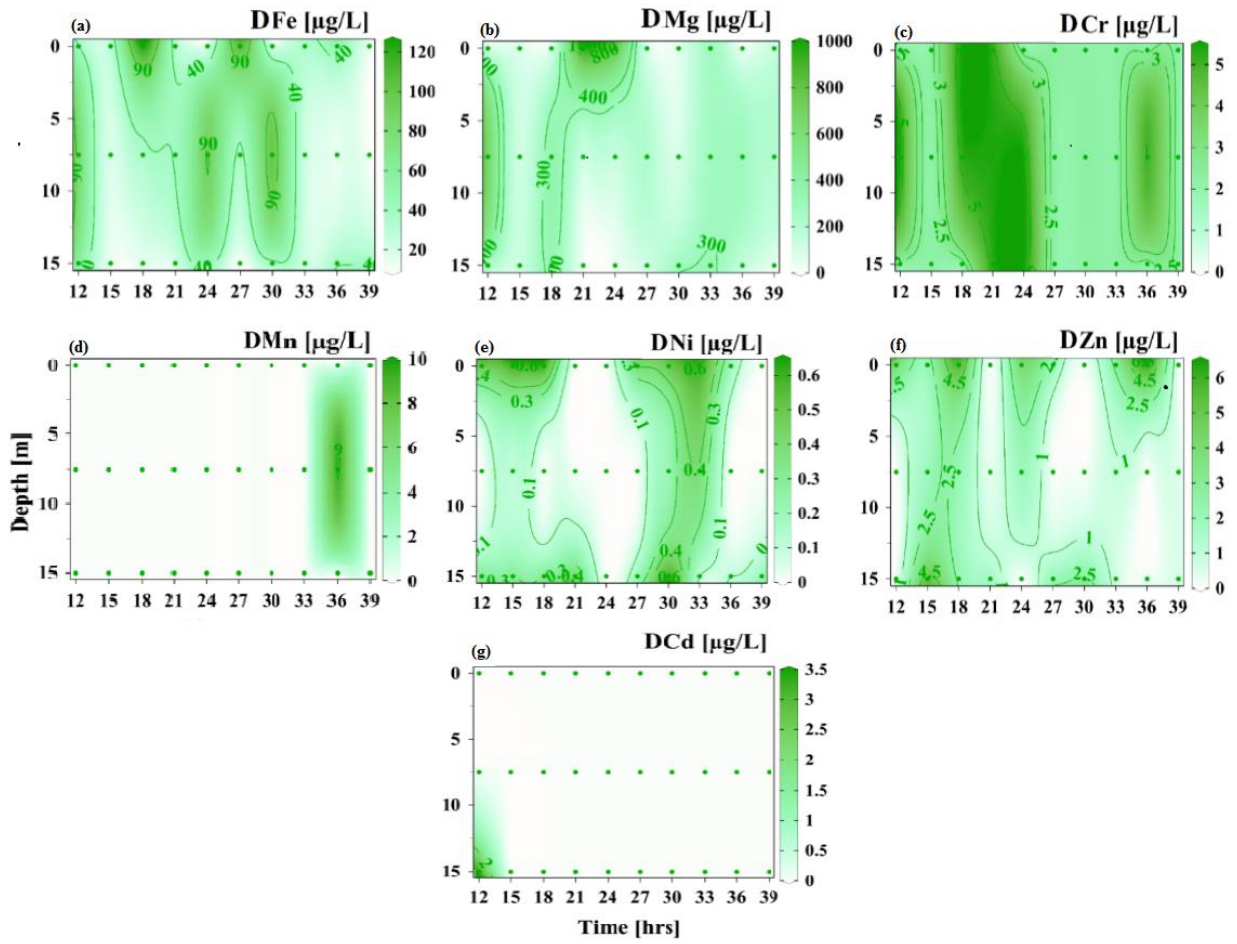


Figure 4 Variation in dissolved (a) Fe, (b) Mg, (c) Cr, (d) Mn, (e) Ni, (f) Zn and (g) Cd at Cochin inlet during 3-4 November 2015.

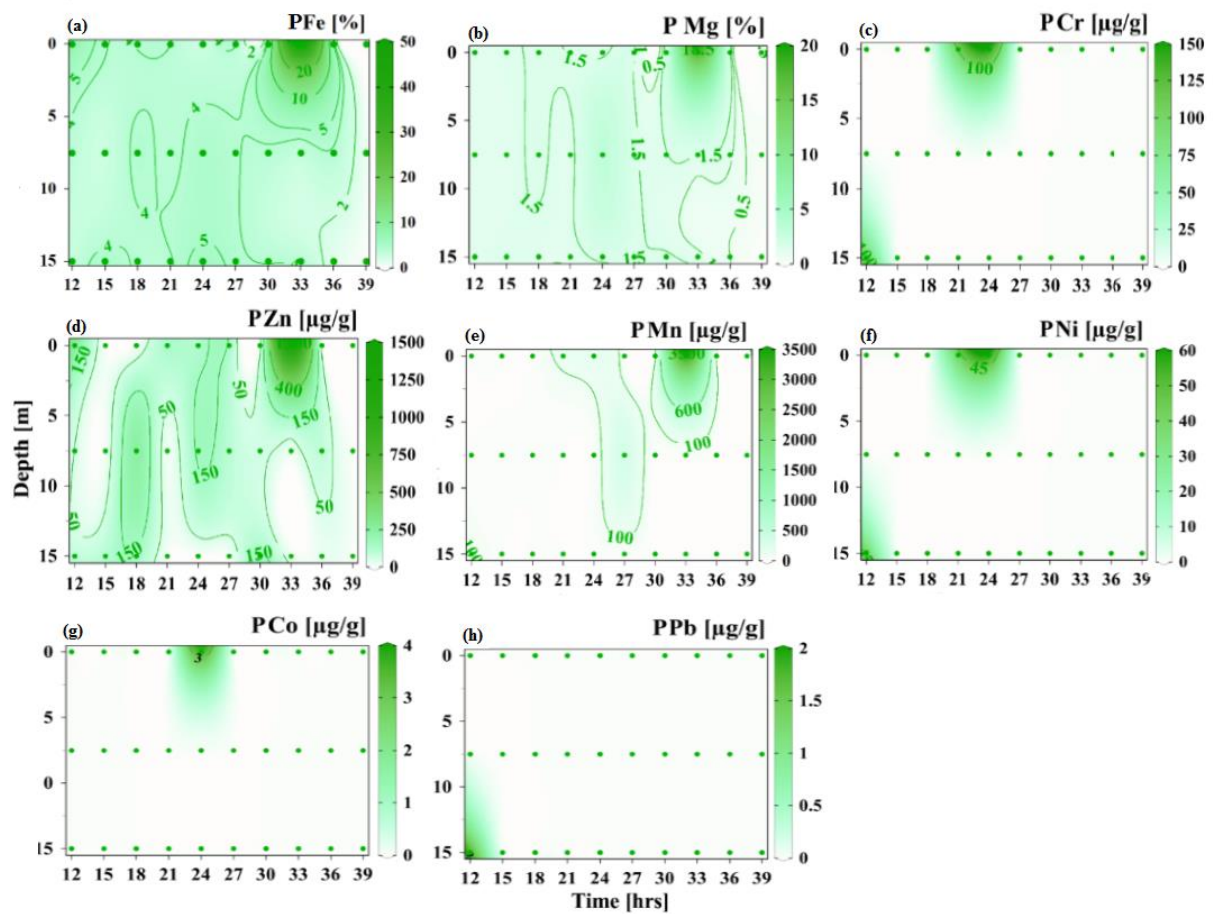


Figure 5 Variation in particulate (a) Fe, (b) Mg, (c) Cr, (d) Zn, (e) Mn, (f) Ni, (g) Co and (h) Pb at Cochin inlet during 3-4 November 2015.

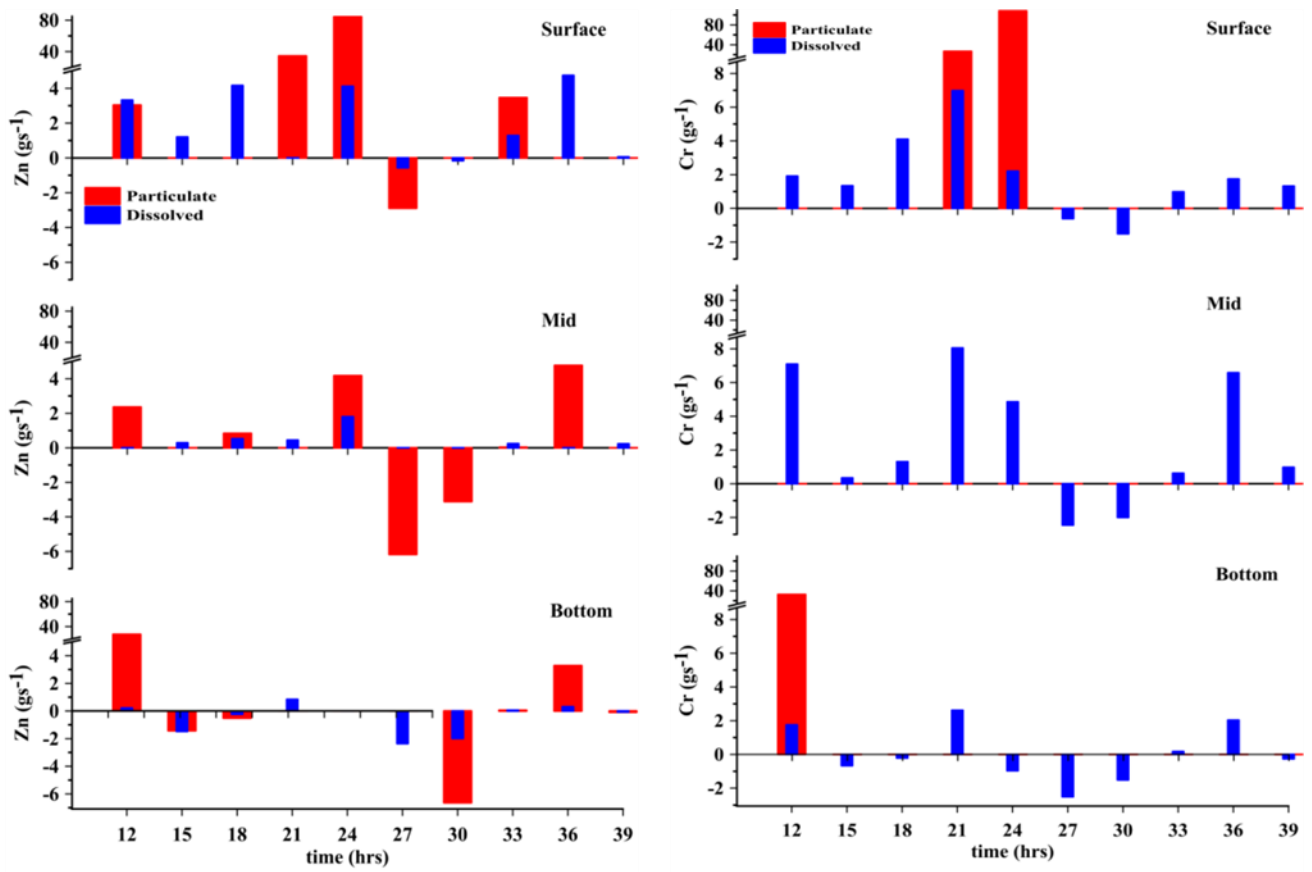
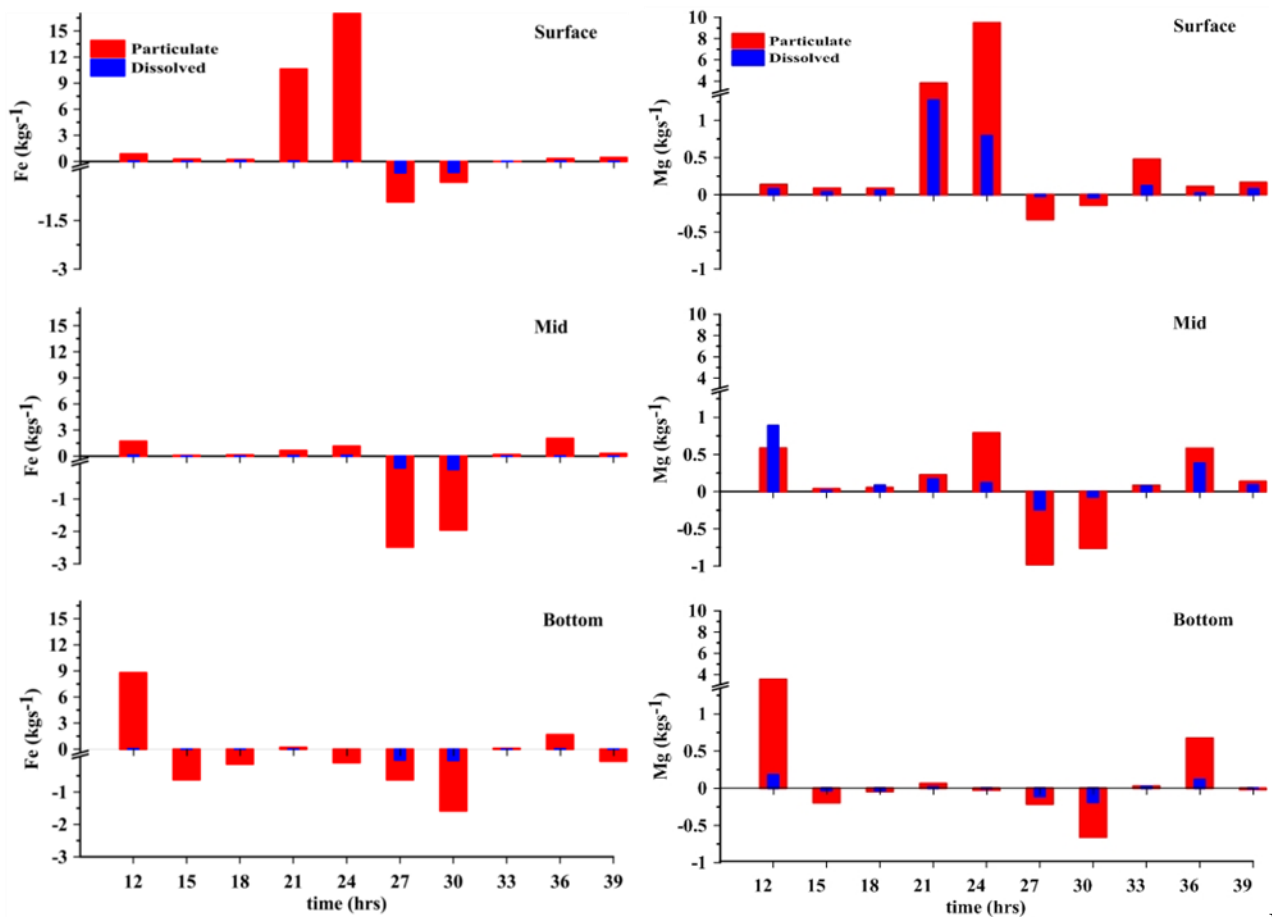


Figure 6 Variation in the fluxes (gs⁻¹) of particulate (red) and dissolved (blue) Zn and Cr in the surface, mid and bottom of Cochin inlet during 3-4 November 2015.



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Figure 7 Variation in the fluxes (gs^{-1}) of particulate (red) and dissolved (blue) Fe and Mn in the surface, mid and bottom of Cochin inlet during 3-4 November 2015.

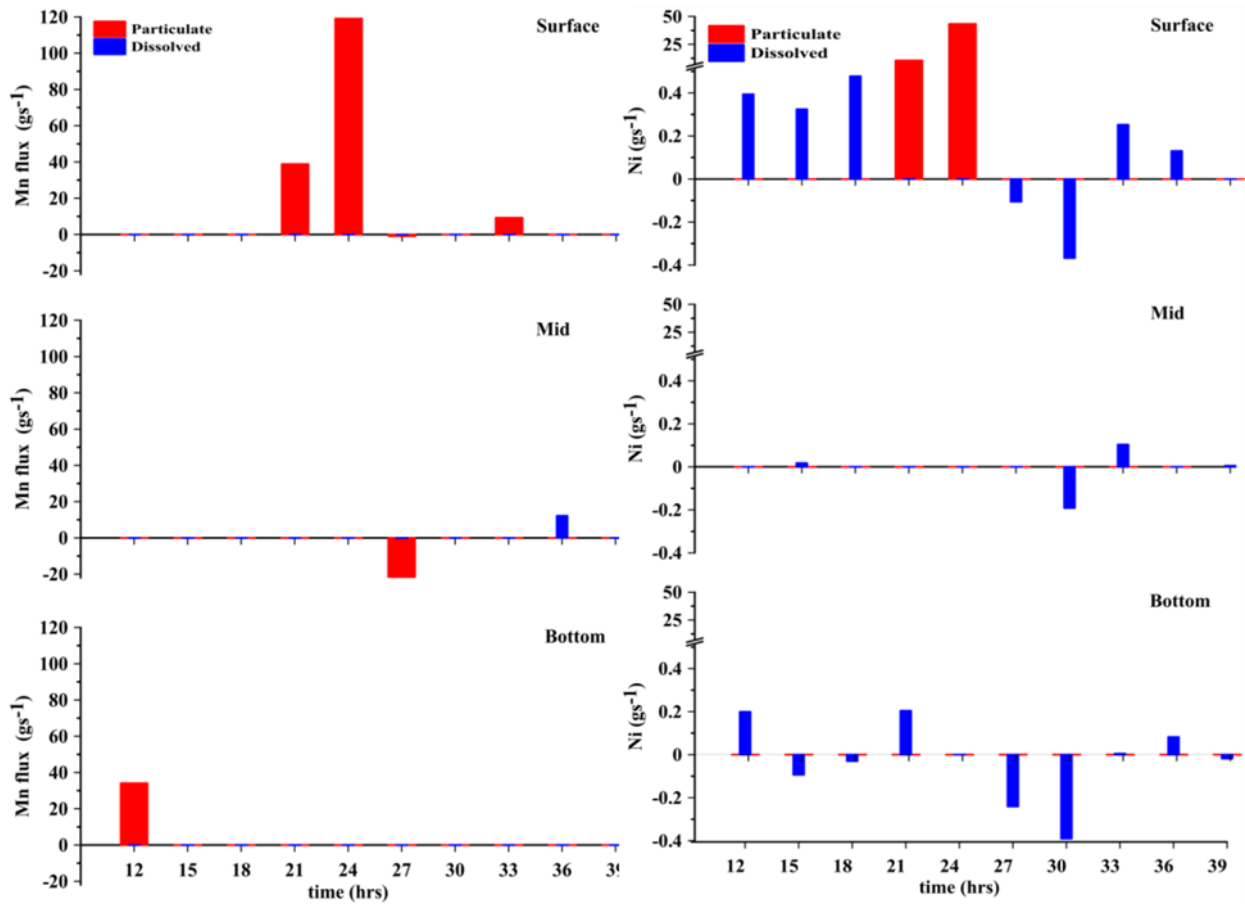


Figure 8 Variation in the fluxes (gs^{-1}) of particulate (red) and dissolved (blue) Mn and Ni in the surface, mid and bottom of Kochi inlet during 3-4 November 2015.

Table 1 Location of sampling stations in the Cochin estuary

SI No	Station name	Station code	Latitude	Longitude
1	Periyar	R1	10° 10' 22.3"N	76° 27' 38.1"E
2	Muvattupuzha	R2	9° 48'21.1"N	76° 27' 14"E
3	Meenachil	R3	9° 40' 34.6"N	76° 36' 33.9"E
4	Manimala	R4	9° 25' 55.9"N	76° 40' 3.4"E
5	Pamba	R5	9° 19' 43.6"N	76° 41' 6.2"E
6	Achankoil	R6	9° 14' 2.7"N	76° 38' 20.6"E
7	Purappillikkavu	S1	10° 8' 39.2"N	76° 16' 59.9"E
8	Moolampilly	S2	10° 2' 17.6"N	76° 16' 8.2"E
9	Cochin inlet	S3	9° 58' 15.3"N	76°14 ' 42.1"E
10	Murinjupuzha	S4	9° 49'17.3"N	76° 23' 31.8"E
11	Ithipuzha	S5	9° 46'50.6"N	76° 22' 29.6"E
12	Kariyar	S6	9° 42' 5.8"N	76° 24' 10.9"E
13	Kumarakom	S7	9° 35' 47.8"N	76° 25' 46.3"E
14	Pallathuruthy	S8	9° 27' 47.2"N	76° 21' 46.5"E

Table 2. Input (kg/d) and export (kg/tidal cycle) fluxes of heavy metals in the Cochin estuary

Metal	Input fluxes from 6 rivers (kg/d)	Export fluxes (kg/tidal cycle)
Dissolved Zn	334.8	150.2
Particulate Zn	111.9	1397.0
Dissolved Cr	82.9	514.8
Particulate Cr	236.9	1635.5
Dissolved Fe	2432.7	3271.3
Particulate Fe	86301.6	332122.4
Dissolved Mn	Nd	102.4
Particulate Mn	604.8	1747.5
Dissolved NI	259.3	4.6
Particulate Ni	Nd	586.3

'D' & 'P' represent dissolved and particulate fractions of heavy metals. Nd represents non-detectable