Environ Monit Assess (2021) 193: 220
https://doi.org/10.1007/s10661-021-09019-9

Fractionation and accumulation of selected metals in a tropical estuary, south-west coast of India

K. K. Jayasooryan · E. V. Ramasamy ·
P. K. Chandini · Mahesh Mohan✉

Received: 10 October 2020 / Accepted: 18 March 2021 / Published online: 24 March 2021

Abstract Estimating the fractional distribution of sediment-bound heavy metals is highly significant for its ecological risk assessment in contaminated aquatic systems, since environmental factors enhance the mobility of heavy metals and its accumulation in different ecological matrices. In this study, the fractional distribution of Zn, Cd, Pb and Cu in the sediments of the Cochin estuary, along the south-west coast of India, was estimated along with its accumulation in four edible crustaceans. The high mobility of heavy metals in the Cochin estuary was evident from the distribution in fractions other than residual fraction. The exchangeable fractions of Zn and Cd were high in the Cochin estuary, indicating its high bioavailability. Even though the exchangeable fraction is negligible, Pb poses the risk of bioaccumulation due to the presence of oxidisable and reducible fractions. The level of heavy metals varies in different species of edible prawns, and high accumulation of all metals was observed in *Metapenaeus dobsoni*. Various risk assessment indices show that Cd and Pb pose significant ecological and human health risks in the Cochin estuary.

Keywords Pollution · Sediment · Water · Speciation · Bioavailablity · Cochin estuary

Introduction

The contamination of aquatic ecosystems by heavy metals is a serious concern worldwide, including in the polar regions, because of their persistency and eco-toxicological effects (Chu et al., 2019; Vardhan et al., 2019). Heavy metals, which reach the aquatic ecosystems and settle in the sediment, accumulate in microorganisms, aquatic flora and fauna and finally reach human beings, causing serious health effects (Zhao et al., 2012; Cuong & Obbard, 2006). The insoluble and particulate metals reach the aquatic environment from various sources, such as atmospheric fallout, urban surface run-off, domestic waste dumps and other anthropogenic sources like industrial effluents, municipal sewage and solid waste (Bai et al., 2016; Kumar et al., 2019; Hader et al., 2020).

Estuaries, being an ecotone between the sea and freshwater, perform several important ecological functions, including biodiversity conservation. They

---

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10661-021-09019-9.

K. K. Jayasooryan
KSCSTE-Centre for Water Resources Development and Management, Kozhikode, Kerala, India

E. V. Ramasamy · P. K. Chandini · M. Mohan✉
School of Environmental Sciences, Mahatma Gandhi University, Kottayam, Kerala, India
e-mail: maheshmohan@mgu.ac.in

P. K. Chandini (✉)
School of Environmental Studies, Cochin University of Science and Technology, Cochin, Kerala, India

regulate the water regime, act as natural filters for contaminants and play an important role in the biogeochemical dynamics of nutrients, primary productivity and bacterial processes (Sobolewski, 1999). Sediments of estuarine systems act as the sink for heavy metal discharged into the ecosystem as well as a source to aquatic biota by mobilising it with respect to environmental conditions (Enya et al., 2019; Kurilov et al., 2009; Ghrefat et al., 2012). Thus, analysing the sediment-bound heavy metals is an unavoidable part of risk assessment of heavy metal contamination. The toxicity and bioavailability of heavy metals in sediments depend on the chemical association of different components of the ecosystem, such as organic matter, oxides of ferric and manganese, carbonates, and silicates, among others. (Alonso Castillo et al., 2011; Bai et al., 2019; Nakazato et al., 2006; Yuan et al., 2009). Mobilisation through solubility, oxidation and reduction processes in response to the prevailing environmental conditions help to evaluate the ecological or human health risks due to the contamination (Nael et al., 2009; Nemati et al., 2011). This approach is helpful for assessing the transport of metals into the sea from the estuarine system.

The quantitative estimation of metals in different tissues of aquatic organisms indicates the distribution pattern and retention potential of metals within the organism (Murugan et al., 2008). Benthic organisms occupy a key position within the metal biogeochemical cycles, which are closely linked to the structural and functional properties and the microhabitats (Ferraro et al., 2009; Reynoldson, 1987). Thus, benthic organisms are the most convenient species for biomonitoring and developing human health risk assessment indices (Amirah et al., 2013; Jiang et al., 2014; Passos et al., 2008). The direct and indirect relation between biotic communities and human impact on estuaries reinforces the choice of such communities as biological indicators.

The geochemistry of heavy metals in the estuary indicates that the contamination began during the 1940s after the industrialisation of the region and peaked during the 1990s (Shylesh Chandran et al., 2019). A number of studies have highlighted the heavy metal contamination in the Cochin estuary (George et al., 2016; Kumar et al., 2011; Salas et al., 2017; Sheeba et al., 2017, 2020). The complex nature and flow restrictions in the lake favoured the accumulation of pollutants in the sediments (Balachandran et al., 2005). Only a few attempts were made so far to study the biogeochemical dynamics of heavy metals in the estuary (Mohan et al., 2014; Sruthi et al., 2018; Shylesh Chandran et al., 2019), especially accumulation and transportation through biota. Even though heavy metal pollution was reported from various species of fishes (Mohan et al., 2012; Nair et al., 2006), its impact on other important biota, especially edible prawns, remains absent.

The Cochin estuary is one of the major prawn production/harvesting as well as exporting centres in India. Edible prawns are highly preferred by the local community due to its high nutritional value and affordable price (Ginson & Bindu, 2017). Since prawn harvesting is high in the contaminated estuarine region, proper risk assessment is necessary for the sustainable utilisation of these resources. Hence, it is crucial to study the metal fractions and bioavailability in this productive ecosystem. The major objectives of this study are to estimate the ecological risk associated with the various fractions of heavy metals in the estuarine environment, as well as to understand the metal bioaccumulation in benthic organisms, which plays a key role in the biogeochemistry of metals in the estuary.

Materials and methods

Study area

The Cochin estuary (Fig. 1) (9° 40′–10° 12′ N and 76° 10′–76° 30′ E), a tropical positive estuarine system through which six rivers in Kerala joins with Arabian Sea, supports the livelihood for thousands of people through its vast natural resources (Menon et al., 2000). The Cochin industrial area, the largest industrial belt in the Indian state of Kerala (Ramzi et al., 2017), discharges nearly 0.104 M m^3 untreated/partially treated effluents, which is the major source of heavy metals in the estuary.

Sample collection and preparation

The sediment samples were collected from five locations of the Cochin estuary using a grab sampler. The first sampling site (S1) was close to the regulator-cum-bridge near the industrial area, and the other

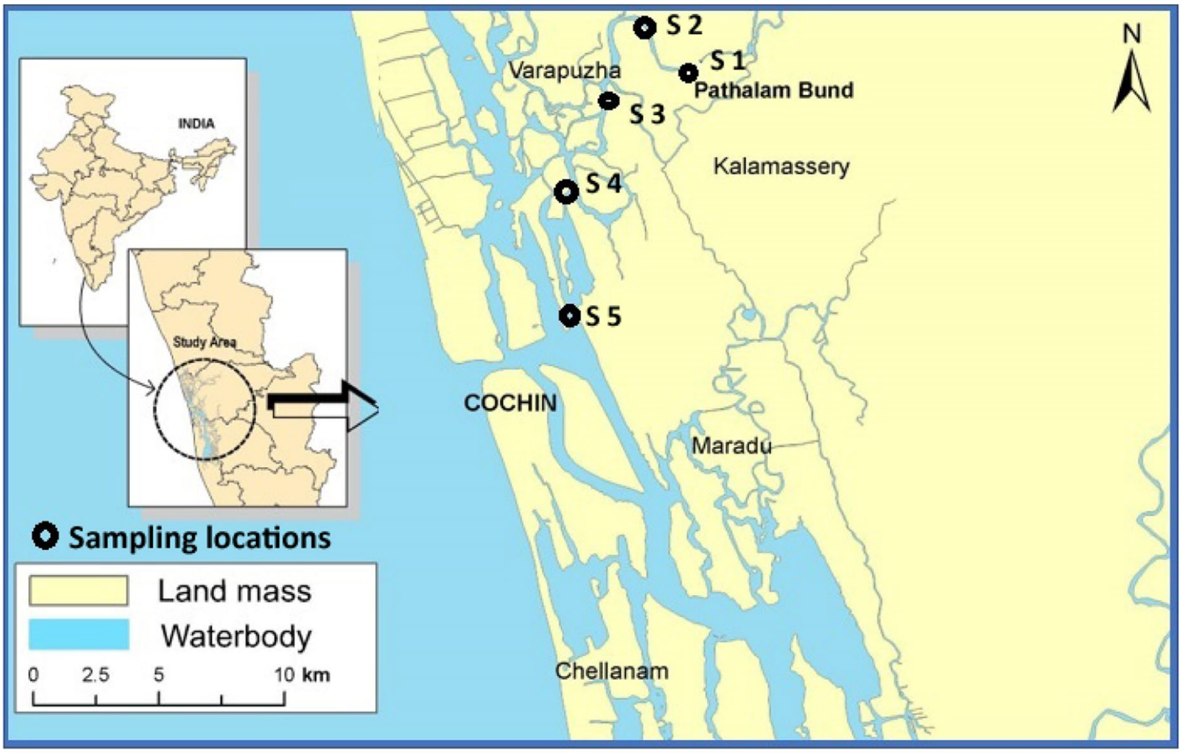


Fig. 1 Map showing the study area and sampling locations

sites (S2, S3, S4 and S5) were located towards downstream at 1–2 km apart. The samples were brought to the laboratory, air dried, powdered, sieved through 63 μ sieve and preserved for the metal analysis. Four species of prawns, *Metapenaeus dobsoni*, *Metapenaeus monoceros*, *Penaeus indicus* and *Macrobrachium rosenbergii* were collected with the help of fishermen using cast net or Chinese dip net from the estuary. The samples were immediately put in ice, transported to laboratory and frozen until analysis. Muscle tissues were separated, washed in deionised water and oven dried at 40 °C until constant weight.

For determining the total metal content, 0.25-g sediment sample was digested in a microwave-assisted digester (MARS X-Press, CEM) using a mixture of Suprapur HNO_3 (65%) and HCl (37%) (3:1) (USEPA, 2007). After digestion, the samples were filtered and made up to suitable volume with ultrapure water. The biological samples were digested with HNO_3–$HClO_4$ using the microwave-assisted digester and diluted to the desired volume with ultrapure water.

Fractionation of metals

The BCR procedure (Table 1) was used for the fractionation of the selected metals (Zn, Cd, Pb and Cu) (Arain et al., 2009; Fedotov et al., 2012; Golia et al., 2007; Rauret et al., 2000; Sutherland & Tack, 2003; Wang et al., 2002). One gram of the dried sediment sample was used for the extraction, to which the corresponding reagent or reagents were added and all the extractions were carried out at room temperature, where the samples along with reagents were mixed continuously for 16 h using a mechanical shaker. The extract was separated by centrifugation for 20 min, at 3000 rpm, and the resultant supernatant liquid was transferred into polyethylene bottles. The residue was washed by adding 20 mL of deionised water after each step, and shaken for 15 min to be centrifuged for 20 min at 3000 rpm. The supernatant was decanted, and the residue was subjected to further extraction in the subsequent step. The residual fraction was estimated

Table 1 Sequential extraction procedure for fractionation of metals in sediments

	Soil fraction	Extraction procedure
Step 1	F1—exchangeable and water-soluble fraction	40 ml of acetic acid (0.11 M) was added and shaken overnight (16 h) at room temperature.
Step 2	F2—Fe and Mn hydroxide-bound (reducible fraction)	To the residue of step 1, 40 ml of hydroxylammonium chloride (0.5 M, pH 1.5) was added and shaken overnight (16 h) at room temperature.
Step 3	F3—organically bound (oxidizable fraction)	To the residue of step 2, 10 ml hydrogen peroxide (8.8 M, pH 2) was added and kept for 1 h at room temperature and 1 h at 85 °C, and again, 10 ml hydrogen peroxide was added and kept 1 h at 85 °C, and then, 50 ml ammonium acetate (1 M, pH 2) was added, cooled and shaken overnight (16 h) at room temperature.
Step 4	F4—residual fraction	To the residue of step 3, 8 ml of 3:1 HCl-HNO_3 mixture was added and digested in a microwave-assisted digester.

by acid digestion of the residue of the samples using a microwave-assisted digester and made up to the desired volume with deionised water.

Estimation of heavy metals

Anodic stripping voltammetric method, using hanging mercury drop electrode of voltammetric trace metal analyser (797 VA Computrace, Metrohm, Switzerland) was used for the detection of total metal and fractions. The silver–silver chloride electrode in 3 M KCl was used as reference and platinum electrode as auxiliary (Bott, 1995; Locatelli et al., 1999).

Risk assessment

Various risk assessment indices were applied to estimate the extent of ecological and human health risks of heavy metal contamination in the Cochin estuary. The bioavailable fraction of metals was determined by summing up the first three fractions (F1 + F2 + F3) (Morales-Hern et al., 2004). A RAC was applied (Supplementary Table 1) for the fractions (Aydin & Kucuksezgin, 2012). Statistical tests, including the correlation between different fractions of heavy metals and fractional distribution as well as metal content in benthic organisms, were conducted with SPSS software.

Quality assurance

All the samples, chemical solutions and standards were prepared using ultrapure water. Working standards were prepared from 1000 ppm standard stock solution of metals (Merck, Germany). The acids used were of Suprapur quality. In order to check the validity of measurements, certified reference material PACS-3 was used, where Zn, Cd, Pb and Cu showed > 98% recovery for the same.

Results and discussions

Heavy metals in sediment

The total heavy metal content of the sediment samples was estimated directly by (1) acid digestion as well as (2) the sum of the different fractions, as shown in (Supplementary Table 2). Zn was found in the highest level ranging from 739.92 (S4) to 1509.71 (S3) (µg/g) with an average of 1082.11(µg/g) in the study area. Cd was found the highest in S3 (33.66 µg/g) and the lowest in S5 (15.44 µg/g) with an average of 21.36 µg/g. The distribution of Pb showed more variation among sites, ranging from 14.57 to 54.44 µg/g with an average of 27.93 µg/g. Cu was ranged between 49.45 (S2) and 76.24 (S4) with an average of 59.4 µg/g in the Cochin estuary. The comparison of the total metal with the sum of fractions showed that the difference was minimal, indicating the accuracy of the analytical estimation. Earlier studies have reported that a variation of ± 15% was acceptable for the fractionation analysis using the BCR method (Sutherland & Tack, 2002).

The average values of the total metal content obtained using both methods in this study were compared with the metal content reported previously from the same locations and other major wetlands of India (Table 2). It was

Table 2 Heavy metals (μg/g) reported from different estuarine systems from India and Kerala

Sl. No	Location	Author and Year	Zn	Cd	Pb	Cu
1	Thamraparni	Magesh et al. (2011)	198.6	11.13	26.16	40.19
2	Mandovi	Siraswar and Nayak (2011)	74–83		59–85	146–157
3	Mahanadi	Raj et al. (2013)		23.88	1.45	
4	Tirumalairajan river estuary	Venkataramanan et al. (2014)	23.40–56.32		1.73–6.74	13.68–28.06
5	Matla estuary	Mukherjee et al. (2009)	45		13	24
6	Saptamu	“	35		9	24
7	Hugli	“	44		14	32
8	Thamraparni	Jayaraju et al. (2011)	473–1200	0.42–0.92	0.3–170	62.8–115.35
9	Sunderbans	Saha et al. (2001)	197.22–347.63	2.84–5.78	36.81–61.38	43.61–79.87
10	Hugli	Chaterjee et al. (2006)	62.00–72.90		25.21–30.70	15.3–25.9
11	Vamleshwar (Narmada)	Nirmal kumar et al. (2011)	8.1	0.73	73.6	
12	Mullippallam	Sundararajan and Natesan (2010)	64.3		43.04	38.89
13	Veli	“	313		1346	125
14	Kottuli wetland	Harikumar and Jisha (2010)	384.25	0.02	6.9	76.76
15	Cochin estuary	Salas et al. (2017)	386.08 ± 636.85	5.07 ± 9.02	21.91 ± 15.54	26.74 ± 26.44
16	Zuary estuary, Goa	(Gaonkar & Matta, 2019)	47.83–166.41		0.08–90.82	35.80–90.5835
17	Valanthakkad Regions of Vembanad Lkae	(Joseph et al., 2019)	20.1 ± 5.04		4.1 ± 3.7	5.4 ± 0.9
18	Vellar estuary, India	(Venkatramanan et al., 2018)	102.7		7.9	47.6
19	Coleroon estuary, India	(Venkatramanan et al., 2018)	47.6		9.2	23
20	Tirumalairajan estuary, India	(Venkatramanan et al., 2018)	36		3.7	23.5
21	Cochin estuary	Present study	1062.496	26.684	37.33	63.82

observed that the heavy metal contamination of Cochin estuary was much higher than other wetlands systems, which established the study area as a chemical hot spot.

Fractional distribution of heavy metals in sediment

The natural range of Zn in the earth's crust varies from 10 to 300 mg/kg. It is an essential nutrient for animals and plants, necessary for several metabolic processes. At higher concentrations, Zn accumulates in the tissues of organisms and causes adverse effects and leads to deficiency of other metals such as Cu. In the present study, the fractional distribution of Zn in the sampling sites was in the order of F1 > F2 > F3 > F4 in site 1 and F1 > F2 < F3 > F4 in the other four locations. The total Zn (Fig. 2) was the

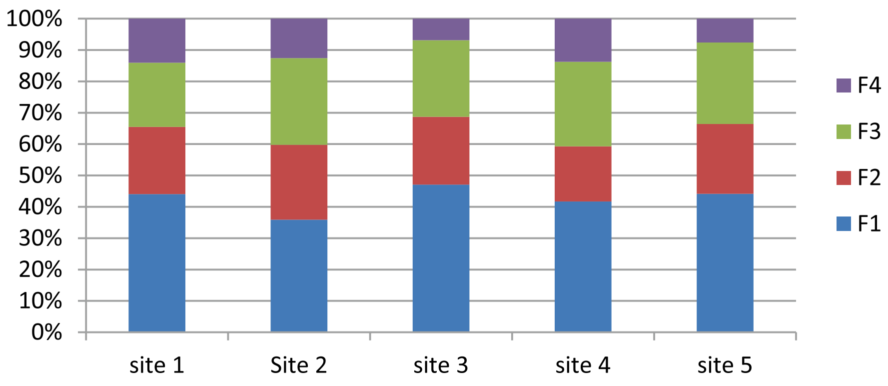
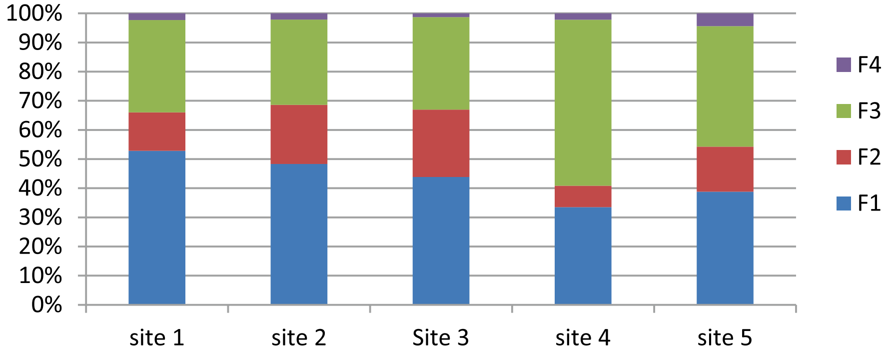


Fig. 2 Percentage distribution of Zn fractions in the sediments of Cochin estuary

Fig. 3 Percentage distribution of Cd fractions in the sediments of Cochin estuary

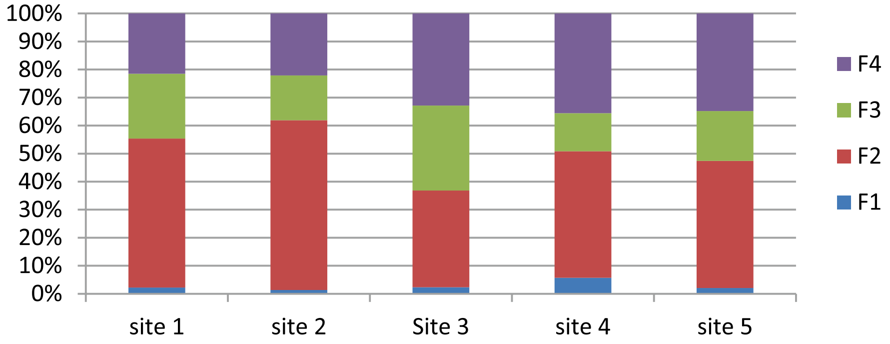


highest in location S3 (1760.55 µg/g) and the least in S5 (702.0516 µg/g). It was observed that more than 85% of the Zn present in the sediment samples is bioavailable with maximum of 93% at location S3. The exchangeable and water-soluble fraction varied between 36 and 47% in all the locations indicating high mobility of Zn in the study area. The oxidisable fraction ranging between 20 and 27% was the second highest fraction in S2, S3, S4 and S5 locations, followed by reducible fraction.

Cadmium is one of the metals strongly absorbed by living cells, especially by vegetation. Its toxicity in the environment and human beings was widely studied. Cd was found to be highly bioavailable to organisms since more than 96% was in the bioavailable fraction in all the sampling locations (Fig. 3). Cd distribution was in the order of F1 > F2 < F3 > F4 in all the five locations. The exchangeable and acid soluble fraction (F1) was found to be highest in S1, S2 and S3, followed by the oxidisable fraction (F3) and reducible fraction (F2). The S4 and S5 were dominated by oxidisable fraction, followed by exchangeable and acid soluble fraction and reducible fraction. The residual fraction of Cd was found the lowest in all the locations. The variation in percentage distribution may be due to the multiple sources of cadmium during the river's course. The observations based on the RAC shows that only Cd at the S2 comes under very high-risk criteria.

The bioavailability of Pb (Fig. 4) was high in all locations with maximum at S1 (79%) and minimum at S4 (64%). Pb was in the order as F1 < F2 > F3 > F4 in locations 1, 3 and F1 < F2 > F3 < F4 in locations 2, 4 and 5. The reducible fraction was dominating in all the locations, with a minimum of 35% (S3) to maximum 61% (S2) and residual fraction varied between 22% (S1) and 35% (S4), which was the second highest fraction in all locations except S1. Even though the exchangeable and acid soluble fractions were present at the least concentration (1–6%), the bioavailability of Pb in the study area remained high due to the elevated concentration of reducible and oxidisable fractions. The residual fraction was found the highest in S1 and S2 (43 and 39%), followed by oxidisable fraction (39 and 38%) and reducible fraction (20 and 18%). The oxidisable fraction was dominant in S3 and S4 (51 and 43%). The oxidisable and reducible fractions were found equally distributed and the

Fig. 4 Percentage distribution of Pb fractions in the sediments of Cochin estuary



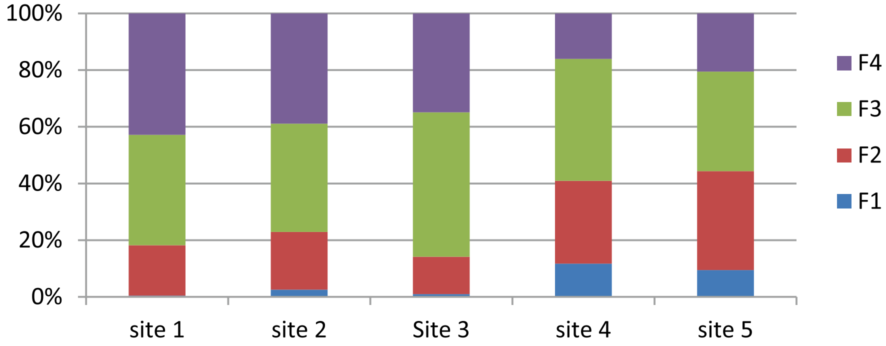


Fig. 5 Percentage distribution of Cu fractions in the sediments of Cochin estuary

bioavailable fraction was found highest among all the sites in S5. More than 50% of Cu was bioavailable in all the locations (Fig. 5), with maximum of 84% at S4 and minimum of 57% at S1.

Heavy metals in benthic organisms

Four species of edible arthropods, *Metapenaeus dobsoni*, *Metapenaeus monoceros*, *Penaeus indicus* and *Macrobrachium rosenbergii*, were collected for the analysis of heavy metals. Zn was detected in all the species and the highest concentration was found in *M. dobsoni*, and the least was in *P. indicus*. Cd was detected from *M. dobsoni*, *M. monoceros* and *M. rosenbergii*, but the concentration was low. Pb was found only in *M. dobsoni*, at a higher concentration. Cu was found in high concentration at *M. monoceros* and *P. indicus*. The results are given in Table 3.

Table 3 Heavy metal accumulation in benthic organisms collected from Cochin estuary

Species	Heavy metals				Biometric parameters		
	Zn	Cd	Pb	Cu	Length (cm)	Width (cm)	Weight (g)
Metapenaeus dobsoni	62.179	4.732	69.695	ND	10 ± 2	2 ± 0.3	10 ± 2.5
Metapenaeus monoceros	53.096	2.349	ND	72.227	8 ± 0.5	1.4 ± 0.3	14 ± o.5
Penaeus indicus	24.78681	ND	ND	45.554	10 ± 2	2 ± 0.3	10 ± 2.5
Macrobrachium rosenbergii	60.805	4.565	ND	ND	19.000	6.000	60.000

The biota concentration factor (BCF) for metals was calculated using the formula BCF = Cx/Cs (where, Cx is the mean concentration in organism, and Cs is the mean concentration in sediment as bioavailable fraction) (Table 4). The BCF values indicate the capacity to accumulate, regulate or eliminate the metal in the biota through metabolism (Morales-Hern et al., 2004). The highest BCF was observed in *M. dobsoni* (2.58) for Pb. Cu was present in two species, *M. monoceros* and *P. indicus*, and showed high BCF (1.63 and 1.13). Cd was present three species, except *P. indicus*, but showed low BCF and Zn present in all the species showed lowest BCF. However, the biota concentration factor of Pb in *M. dobsoni* is much higher than Cd in other species. Compared to the earlier reports of Kaladharan et al. (2005), the concentration of Zn and Cd showed a significant increase in *M. dobsoni* in the study area.

The macrobenthic community assemblages and their potential use of ecological risk assessment have remained primarily unexplored expect a few attempts. Among the metals studied, only Cd and Pb have the regulations of the European Union for hazardous metals (Sivaperumal et al., 2007) and is 0.5 mg/kg (EC, 2001)

Mobility and risk assessment of heavy metals

The mobility factor can be considered an index of mobility and bioavailability of metals in the soils (Lu et al., 2007), which was calculated as the ratio of water soluble, exchangeable and carbonate bound fractions to the total of all fractions (Table 5), since the

Table 4 Biota concentration factor for heavy metal accumulation in benthic organisms

	BCF BioFRac	BCF BioFRac	BCF BioFRac	BCF BioFRac
Metapenaeus dobsoni	0.065	0.181	2.580	
Metapenaeus monoceros	0.056	0.090		1.631
Penaeus indicus	0.026			1.132
Macrobrachium rosenbergii	0.064	0.175		

first three fractions are most bioavailable and mobile (Pueyo et al., 2003). The MF of heavy metals for each location was calculated, and the comparison of values did not show any location-specific variation, which indicates that similar ecological condition is prevailing throughout the study area. Mohan et al. (2012) found that Cd in Vembanad Lake is weakly bound with sediment and hence highly bioavailable than Pb and Cu. A similar condition was observed in the present study, but the mobility of Cu is slightly higher than Zn. Since the level of Zn in the sediments is extremely higher than other metals, the comparison of mobility is difficult. The metals distributed in different fractions have different behaviour in the environment, and thus, its remobilisation and bioaccumulation potential also vary (Fig. 6). As reported earlier, the bonding strength of metals with sediment is the major factor determining the reactivity; fractional distribution can be a risk assessment tool for the heavy metal contamination in the aquatic ecosystems (Jain et al., 2010). Based on this, the RAC was applied for the sediments of the study location (Aydin & Kucuksezgin, 2012).

The RAC indicates the sediment, which can release in the exchangeable and water-soluble fractions. If the release of F1 fraction of the metal concerned is < 1% of the total metal present in the sediment, then it will be considered safe for the environment. On the contrary, if the sediment is releasing F1 fraction constituting more than 50% of the total metal, then such sediment has to be considered highly dangerous, and the metal released can easily enter the food chain. Various RACs based on the fractional distribution had been effectively utilised for ecological risk assessment (ERA) of heavy metals in different ecosystems. The RAC based on the percentage of bioavailable fractions can qualitatively express the risk as high, medium and low, which was successfully applied to various wetlands, such as Hussainsagar Lake, Hyderabad (Jain et al., 2010), the Sunderbans, West Bengal (Mukherjee et al., 2009), the Ganga River (Purushothaman & Chakrapani, 2007) and the Achankovil river basin, Kerala (Prasad et al., 2006). Observations based on the above RAC show that only Cd at the S2 comes under very high-risk criteria, while Zn and Cd at all the locations are under the high-risk category, indicating the increased potential of Cd to enter into the food chain and cause threats to biota in the Cochin estuary (Fig. 7). Pb in all locations and Cu in four locations (except S4 where it is under medium risk) were under the low-risk criteria.

Table 5 Contribution of F1 (%) to the sum of all fractions of heavy metals

Location	% of F1 in the in all fractions			
	Zn	Cd	Pb	Cu
S 1	44.05	52.84	2.21	0.46
S 2	35.88	48.30	1.37	2.56
S 3	47.06	43.86	2.32	0.99
S 4	41.70	33.52	5.72	11.76
S 5	44.16	38.78	2.06	9.49

It was reported earlier that industrial pollution is the major source of heavy metals in the study area, and seasonal variation in distribution of heavy metals is negligible (Menon et al., 2000; Selvam et al., 2012). In the present study, sediment-bound heavy metals showed several fold increases over the early values reported by Kaladharan et al. (2005) indicating continuing discharge of industrial effluents in the estuary. The analysis of heavy metal status and geochemistry (Balachandran et al., 2005) concludes that the level of heavy metals has not reached to an extreme, but the enrichment factors of Zn and Cd are high to be included in the category of impacted estuary compared to other estuaries. Kaladharan et al. (2011) reported that cadmium has reached critical levels, and lead has attained levels of caution in the Cochin estuary, while copper and lead have attained levels of caution in Cochin inshore waters. Later, Shylesh Chandran et al. (2019) reported high level of ecological risk due to Cd deposits in the region. Significant

Table 6 Correlation between different fractions of heavy metals from Cochin estuary

		Zn				Cd				Pb				Cu			
		F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
Zn	F1	1															
	F2	.956*	1														
	F3	.937*	.938*	1													
	F4	.401	.403	.310	1												
Cd	F1	1.00**	.956*	.937*	.401	1											
	F2	.931*	.942*	.956*	.111	.931*	1										
	F3	.544	.314	.555	.098	.544	.454	1									
	F4	.004	−.174	−.152	−.666	.004	.058	.293	1								
Pb	F1	−.035	−.237	−.126	.570	−.035	−.341	.505	−.142	1							
	F2	−.080	−.033	−.254	.796	−.079	−.361	−.406	−.533	.432	1						
	F3	.517	.510	.276	.826	.517	.232	−.052	−.279	.298	.787	1					
	F4	.289	.127	.101	.818	.289	−.074	.403	−.204	.876	.665	.716	1				
Cu	F1	−.530	−.713	−.449	−.410	−.530	−.522	.419	.352	.484	−.393	−.658	.026	1			
	F2	−.764	−.899*	−.706	−.453	−.764	−.749	.118	.311	.398	−.242	−.651	−.054	.948*	1		
	F3	.530	.441	.643	.588	.530	.400	.728	−.441	.577	.019	.182	.541	.116	−.137	1	
	F4	.313	.510	.289	.714	.313	.221	−.468	−.757	−.140	.690	.703	.223	−.854	-.773	.122	1

positive correlation between the fractions of Zn and Cd indicates a common source of origin and potential of mobility in similar environmental conditions (Table 6). Most of the fractions of Pb and Cu were negatively correlated with fractions of Zn and Cd. This may be attributed to the continuous discharge of Zn and Cd in the sediments and active conversion in the prevalent environmental conditions. The positive correlation of F1 and F4 of Cu, along with negative correlation between F1 and F4, indicates that the reducing environment in the lake sediment helps it to convert into more bioavailable fractions.

The partitioning of Zn is influenced by depth of water columns, reduction potential of sediments and cycling of hydroxides, sulphates, carbonates, etc. The prominent ecological condition, persisting along the lower reaches of Periyar River, will enhance the bioavailability of Zn. Mobility and bioavailability of Cd remain highly influenced by the ionic species. Cd, in sediments of aquatic ecosystems, is present mainly in the exchangeable fraction, followed by the Fe–Mn oxides and then residual fractions (Bradl, 2004; Jain et al., 2010; Yao, 2008). Due to high affinity of Cd towards suspended organic matter, it may attain

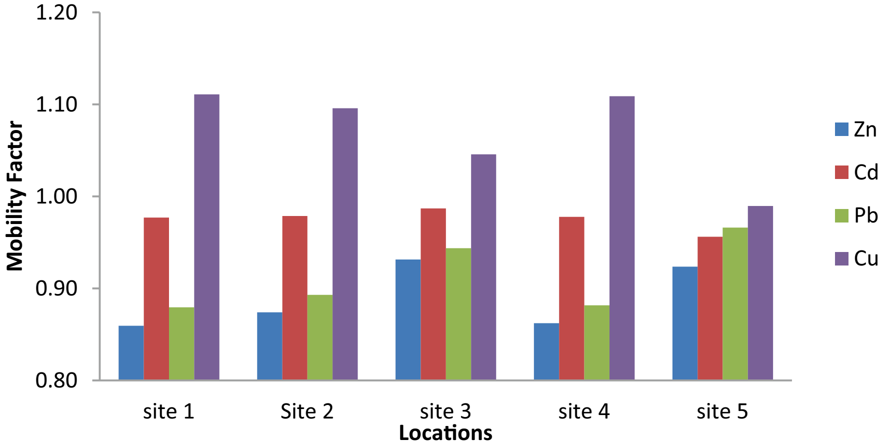


Fig. 6 Variation in mobility of heavy metals in different sampling locations

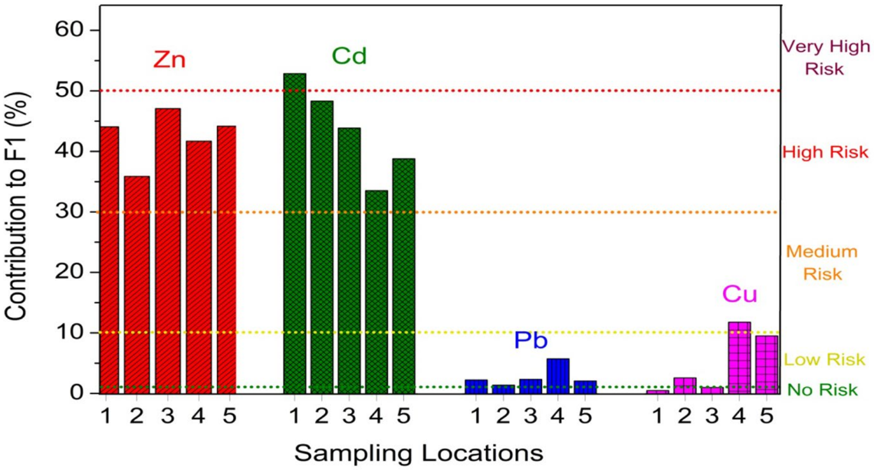


Fig. 7 Ecological risk posed by heavy metals in Cochin estuary based on risk assessment code

more mobility and be easily available to plants and other organisms (Ayodele et al., 2016). High disturbances in the water column owing to various natural and anthropogenic reasons affecting the organic carbon dynamics in the estuary have influential impact on the biogeochemistry of Cd. Pb is highly toxic in ecosystems, especially for aquatic plants and has no role in biological systems (Zulfiqar et al., 2019). The dominance of reducible fraction of Pb indicates the anthropogenic input, along with lithogenic and other natural sources. Due to high toxicity and carcinogenicity, Pb requires special attention in the Cochin estuary, since it is highly bioavailable in the region. Copper was found less bioavailable to organisms compared to other metals because of the dominance of residual fraction. The bioavailability of copper was found to be increasing towards the lower stretches of the river. This may due to the single point discharge of copper from the industrial area located near the Periyar River. High concentration of reducible fraction in all the locations shows its potential mobility and possible ecological risks. Sediment flux studies, based on the suspended sediment concentration (Vinita et al., 2017), shows that contaminants from the Cochin estuary can be easily transported to the coastal regions of the adjacent Arabian Sea, thus high potential to pollute the sediments. The particle residence time in Cochin estuary is 25 to 30 days, with a significant seasonal variation (John et al., 2020), which highlights that contamination of the Cochin estuary poses considerable ecological and human health risks along the coastal belt.

Monitoring and estimating ecological risk indices in an essential part of lake management, especially when the pollution continues and the prevailing ecological conditions, enhance the mobility of pollutants. Under the stress of urbanisation, over exploitation, reclamation and land use/land cover changes in the catchment, contaminants from polluted matrices pose more ecological and human health risks (Lu et al., 2016; Han et al., 2019). The estimation of fractional distributions of heavy metals can be an effective risk assessment tool, since fractionation is influenced by environmental changes and physical stress in the ecosystem (Xiao et al., 2015; Zhang et al., 2017). As an important estuarine system in terms of ecological and economical aspects of the region, the Cochin estuary requires immediate management interventions for its sustainability. Various indices derived from the present study can be effectively utilised for implementing strict pollution control measures and biota consumption regulations for the lake. Indices based on the bioaccumulation of heavy metals can be helpful to minimise the risk of consumption by the local community, thus ensuring better management of bioresources of the lake.

Conclusion

The study indicates that significant quantity of Zn, Cd, Pb and Cu is present in bio-available form, which poses a threat of bioaccumulation and associated ecological risk in the Cochin estuary. More studies and regular monitoring of Pb and Cd are required due to their high mobility and toxicity, despite their lower level of contamination compared to Zn. Even though the level of metals in the edible prawns remained within the limits of international standards, the species show significant capacity for bioaccumulation of metals. Since industries located along the banks of the river are the major source of heavy metal pollution, regular monitoring and risk assessment are suggested for the sustainability of the Cochin estuary.

Acknowledgements The first author acknowledges the University Grants Commission, Ministry of Human Resources Development, Govt. of India, for support through Junior Research Fellowship and Senior Research Fellowship. The authors acknowledge the KSCSTE-SARD, DST-FIST and DST-PURSE funding for the instrumental facility.

Author contribution All the authors have contributed to the manuscript in various ways such as problem identification, sampling and analysis, interpretation, writing, editing and proof reading.

Funding The funding is from MoES, DST-FIST and PURSE programme.

Availability of data and material All data and materials are available with the authors.

Declarations

Ethics approval Authors declare that there is no experiment included in the manuscript which require ethics approval.

Consent to participate All the authors give consent for participation in the work.

Consent for publication All the authors give consent for publication, and no data of any individual person have been included in the manuscript.

Conflict of interest The authors declare no competing interests.

References

Alonso Castillo, M. L., Vereda Alonso, E., Siles Cordero, M. T., Cano Pavón, J. M., & García de Torres, A. (2011). Fractionation of heavy metals in sediment by using microwave assisted sequential extraction procedure and determination by inductively coupled plasma mass spectrometry. *Microchemical Journal, 98*(2), 234–239. https://doi.org/10.1016/j.microc.2011.02.004

Amirah, M. N., Afiza, A S., Faizal, W. I. W., Nurliyana, M. H., & Laili, S. (2013). Human health risk assessment of metal contamination through consumption of fish. Journal of Environment Pollution and Human Health (1), 1–5. https://doi.org/10.12691/jephh-1-1-1

Arain, M. B., Kazi, T. G., Jamali, M. K., Baig, J. A., Afridi, H. I., Jalbani, N., & Sarfraz, R. A. (2009). Comparison of different extraction approaches for heavy metal partitioning in sediment samples. *Pedosphere, 19*(4), 476–485. https://doi.org/10.1016/S1002-0160(09)60140-5

Aydin, S., & Kucuksezgin, F. (2012). Distribution and chemical speciation of heavy metals in the surficial sediments of the Bakırçay and Gediz Rivers. *Eastern Aegean. Environmental Earth Sciences., 65*, 789–803. https://doi.org/10.1007/s12665-011-1124-7

Ayodele, O. A., Gabriel, A. O., Celinah, A., Kayode, S. A., & Olateju, D. A. (2016). Distributions of cadmium and lead in peri-urban wetlands as influenced by soil organic matter, clay fraction, and moisture content. *Cogent Food & Agriculture, 2*(1), 1159406. https://doi.org/10.1080/23311932.2016.1159406

Bai, J., Jia, J., Zhang, G., Zhao, Q., Lu, Q., Cui, B., & Liu, X. (2016). Spatial and temporal dynamics of heavy metal pollution and source identification in sediment cores from the short-term flooding riparian wetlands in a Chinese delta. *Environmental Pollution, 219*, 379–388. https://doi.org/10.1016/j.envpol.2016.05.016

Bai, J., Zhao, Q., Wang, W., Wang, X., Jia, J., Cui, B., & Liu, X. (2019). Arsenic and heavy metals pollution along a salinity gradient in drained coastal wetland soils: Depth distributions, sources and toxic risks. *Ecological Indicators*, 96 (August 2018), 91–98. https://doi.org/10.1016/j.ecolind.2018.08.026

Balachandran, K.K., Raj, C.M.L., Nair, M., Joseph, T., Sheeba, P., Venugopal, P. (2005) Heavy metal accumulation in a flow restricted, tropical estuary Estuarine, Coastal and Shelf Science. 65 https://doi.org/10.1016/j.ecss.2005.06.013

Bott, A. W. (1995). Voltammetric determination of trace concentrations of metals in the environment. *Current Separation., 14*(1), 24–30.

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloidal and Interface Sciences., 27*, 1–18. https://doi.org/10.1146/annurev.arplant.55.031903.141701

Chatterjee, M., Filho, E. V. S., Sarkar, S. K., Sella, S. M., Bhattacharya, A., Satpathy, K. K., & Bhattacharya, B. D. (2006). Distribution and possible source of trace elements in the sediment cores of a tropical macrotidal estuary and their ecotoxicological significance. *Environment International., 33*, 346–356.

Chu, W. L., Dang, N. L., Kok, Y. Y., Ivan Yap, K. S., Phang, S. M., & Convey, P. (2019). Heavy metal pollution in Antarctica and its potential impacts on algae. *Polar Science, 20*, 75–83. https://doi.org/10.1016/j.polar.2018.10.004

Coung, D. T., & Obbard, O. J. (2006). Metal speciation in coastal marine sediments from Singapore using a modified BCR sequential extraction procedure. *Applied*

Geochemistry, 21, 1335–1346. https://doi.org/10.1016/j.apgeochem.2006.05.001

EC. (2001). Commission regulations as regards heavy metals, Directive, European Union, 2001/22/EC, No: 466.

Enya, O., Lin, C., & Qin, J. (2019). Heavy metal contamination status in soil-plant system in the Upper Mersey Estuarine Floodplain, Northwest England. *Marine Pollution Bulletin, 146*, 292–304. https://doi.org/10.1016/j.marpolbul.2019.06.026

Fedotov, P. S., Kördel, W., Miró, M., Peijnenburg, W. J. G. M., Wennrich, R., & Huang, P. M. (2012). Extraction and fractionation methods for exposure assessment of trace metals, metalloids, and hazardous organic compounds in terrestrial environments. *Critical Reviews in Environmental Science and Technology, 42*(11), 1117–1171. https://doi.org/10.1080/10643389.2011.556544

Ferraro, L., Sammartino, S., Feo, M. L., Rumolo, P., Manta, D. S., Marsella, E., & Sprovieri, M. (2009). Utility of benthic foraminifera for biomonitoring of contamination in marine sediments: A case study from the Naples harbour (Southern Italy). *Journal of Environmental Monitoring, 11*(6), 1226–1235. https://doi.org/10.1039/b819975b

Gaonkar, C., & Matta, V. M. (2019). Assessment of metal contamination in a tropical estuary, West Coast of India. *Environmental Earth Sciences, 79*, 2. https://doi.org/10.1007/s12665-019-8745-7

George, R., Martin, G. D., Nair, S. M., Thomas, S. P., & Jacob, S. (2016). Geochemical assessment of trace metal pollution in sediments of the Cochin backwaters. *Environmental Forensics, 17*(2), 156–171. https://doi.org/10.1080/15275922.2016.1163623

Ghrefat, H. A., Yusuf, N., Jamarh, A., & Nazzal, J. (2012). Fractionation and risk assessment of heavy metals in soil samples collected along Zerqa River. *Jordan. Environmental Earth Sciences, 66*(1), 199–208. https://doi.org/10.1007/s12665-011-1222-6

Ginson, J., & Bindu, J. (2017). Review on biochemical composition and microflora of prawns. *Fishery Technology, 54*(2), 75–85.

Golia, E. E., Tsiropoulos, N. G., Dimirkou, A., & Mitsios, I. (2007). Distribution of heavy metals of agricultural soils of central Greece using the modified BCR sequential extraction method. *International Journal of Environmental Analytical Chemistry, 87*(13–14), 1053–1063. https://doi.org/10.1080/03067310701451012

Häder, D. P., Banaszak, A. T., Villafañe, V. E., Narvarte, M. A., González, R. A., & Helbling, E. W. (2020). Anthropogenic pollution of aquatic ecosystems: Emerging problems with global implications. *Science of the Total Environment, 713*, 136586. https://doi.org/10.1016/j.scitotenv.2020.136586

Han, L., Bai, J., Gao, Z., Wang, W., Wang, D., Cui, B., & Liu, X. (2019). Polycyclic aromatic hydrocarbons (PAHs) in surface soils from reclaimed and ditch wetlands along a 100-year chronosequence of reclamation in a Chinese estuary: Occurrence, sources, and risk assessment. *Agriculture, Ecosystems and Environment, 286*(February), 106648. https://doi.org/10.1016/j.agee.2019.106648

Harikumar, P. S., & Jisha, T. S. (2010). Distribution pattern of trace metal pollutants in the sediments of an urban wetland in the southwest coast of India. *International Journal of Engineering Science and Technology, 2*(5), 840–850.

Jain, C. K., Rao, V. V. S. G., Prakash, B. A., Kumar, K. M., & Yoshida, M. (2010). Metal fractionation study on bed sediments of Hussainsagar Lake, Hyderabad. *India. Environmental Monitoring and Assessment, 166*(1–4), 57–67. https://doi.org/10.1007/s10661-009-0984-8

Jayaraju, N., Reddy, B. C. S. R., & Reddy, K. R. (2011). Anthropogenic metal pollution in surface sediments of the Tambaraparni River Estuary. *Chemistry and Ecology, 27*, 37–41. https://doi.org/10.1080/02757540.2011.570752

Jiang, D., Hu, Z., Liu, F., Zhang, R., Duo, B., Fu, J., & Li, M. (2014). Heavy metals levels in fish from aquaculture farms and risk assessment in Lhasa, Tibetan Autonomous Region of China. *Ecotoxicology, 23*, 577–583. https://doi.org/10.1007/s10646-014-1229-3

John, S., Muraleedharan, K. R., Revichandran, C., Azeez, S. A., Seena, G., & Cazenave, P. W. (2020). What controls the flushing efficiency and particle transport pathways in a tropical Estuary? Cochin Estuary. *Southwest coast of India. Water, 12*(3), 908. https://doi.org/10.3390/w12030908

Joseph, P., Nandan, B. S., Adarsh, K. J., et al. (2019). Heavy metal contamination in representative surface sediments of mangrove habitats of Cochin. *Southern India. Environmental Earth Sciences, 78*, 490. https://doi.org/10.1007/s12665-019-8499-2

Kaladharan, P., Krishnakumar, P. K., Prema, D., Nandakumar, A., Khambadkar, L. R., & Valsala, K. K. (2011). Assimilative capacity of Cochin inshore waters with reference to contaminants received from the backwaters and the upstream areas. *Indian Journal of Fisheries, 2*, 75–83.

Kaladharan, P., Prema, D., Valsala, K. K., & Leelabhai, K. S. (2005). Trends in heavy metal concentrations in sediment, finfishes and shellfishes in inshore waters of Cochin, southwest coast of India. *Journal of Marine Biological Association India, 47*(1), 1–7.

Kumar, I. J. N., Sajish, P. R., Nirmal, R., Basil, G., & Shailendra, V. (2011). An assessment of the accumulation potential of Pb, Zn and Cd by *Avicennia marina (Forssk) Vierh*. in Vamleshwar Mangroves , Gujarat , India. *Journal of Water and Land Development*, 3(1), 36–40.

Kumar, V., Parihar, R. D., Sharma, A., Bakshi, P., Singh Sidhu, G. P., Bali, A. S., & Rodrigo-Comino, J. (2019). Global evaluation of heavy metal content in surface water bodies: A meta-analysis using heavy metal pollution indices and multivariate statistical analyses. *Chemosphere, 236*, 124364. https://doi.org/10.1016/j.chemosphere.2019.124364

Kurilov, P. I., Kruglyakova, R. P., Savitskaya, N. I., & Fedotov, P. S. (2009). Fractionation and speciation analysis of heavy metals in the Azov Sea bottom sediments. *Journal of Analytical Chemistry, 64*(7), 738–745. https://doi.org/10.1134/S1061934809070144

Locatelli, C., Astara, A., Vasca, E., & Campanella, V. (1999). Voltammetric and spectroscopic determination of toxic metals in sediments and sea water of Salerno Gulf. *Environmenatl Monitoring and Assessment, 58*, 23–37. https://doi.org/10.1023/A:1006078927576

Lu, Q., Bai, J., Gao, Z., Zhao, Q., & Wang, J. (2016). Spatial and Seasonal Distribution and Risk Assessments for

Metals in a TamarixChinensis Wetland, China. *Wetlands, 36*, 125–136. https://doi.org/10.1007/s13157-014-0598-y

Lu, Y., Zhu, F., Chen, J., Gan, H., & Guo, Y. (2007). Chemical fractionation of heavy metals in urban soils of Guangzhou. *China. Environmental Monitoring and Assessment, 134*(1–3), 429–439. https://doi.org/10.1007/s10661-007-9634-1

Magesh, N. S., Chandrasekar, N., & Roy, D. V. (2011). Spatial analysis of trace element contamination in sediments of Tamiraparani estuary, southeast coast of India. *Estuarine, Coastal and Shelf Science, 92*(4), 618–628. https://doi.org/10.1016/j.ecss.2011.03.001

Menon, N. N., Balchand, A. N., & Menon, N. R. (2000). Hydrobiology of the Cochin backwater system – a review. *Hydrobiologia, 430*, 149–183.

Mohan, M., Augustine, T., Jayasooryan, K. K., ShyleshChandran, M. S., & Ramasamy, E. V. (2012). Fractionation of selected metals in the sediments of Cochin estuary and Periyar River, southwest coast of India. *The Environmentalist, 32*(4), 383–393. https://doi.org/10.1007/s10669-012-9399-0

Mohan, M., Shylesh Chandran, M. S., Jayasooryan, K. K., & Ramasamy, E. V. (2014). Mercury in the sediments of Vembanad Lake, western coast of India. *Environmental Monitoring and Assessment, 186*(6), 3321–3336. https://doi.org/10.1007/s10661-014-3620-1

Morales-Hernndez, F., Soto-Jimnez, M. F., & Pez-Osuna, F. (2004). Heavy Metals in sediments and lobster (*Panulirus gracilis*) from the discharge area of the submarine sewage outfall in Mazatln Bay (SE Gulf of California). *Archives of Environmental Contamination and Toxicology, 46*(4), 485–491. https://doi.org/10.1007/s00244-003-3064-z

Mukherjee, D., Mukherjee, A., & Kumar, B. (2009). Chemical fractionation of metals in freshly deposited marine estuarine sediments of Sundarban ecosystem. *India. Environmental Geology, 58*(8), 1757–1767. https://doi.org/10.1007/s00254-008-1675-4

Murugan, S. S., Karuppasamy, R., Poongodi, K., & Puvaneswari, S. (2008). Bioaccumulation pattern of zinc in freshwater fish *Channa punctatus (Bloch)* after chronic exposure. 59, 55–59.

Nael, M., Khademi, H., Jalalian, A., Schulin, R., Kalbasi, M., & Sotohian, F. (2009). Effect of geo-pedological conditions on the distribution and chemical speciation of selected trace elements in forest soils of western Alborz. *Iran. Geoderma, 152*(1–2), 157–170. https://doi.org/10.1016/j.geoderma.2009.06.001

Nair, M., Jayalakshmy, K. V., Balachandran, K. K., & Joseph, T. (2006). Bioaccumulation of toxic metals by fish in a semi-enclosed tropical ecosystem. *Environmental Forensics, 7*(3), 197–206. https://doi.org/10.1080/15275920600840438

Nakazato, T., Akasaka, M., & Tao, H. (2006). A rapid fractionation method for heavy metals in soil by continuous-flow sequential extraction assisted by focused microwaves. *Analytical and Bioanalytical Chemistry, 386*(5), 1515–1523. https://doi.org/10.1007/s00216-006-0700-2

Nemati, K., Abu Bakar, N. K., Bin Abas, M. R., Sobhanzadeh, E., & Low, K. H. (2011). Comparison of unmodified and modified BCR sequential extraction schemes for the fractionation of heavy metals in shrimp aquaculture sludge from Selangor. *Malaysia. Environmental Monitoring and Assessment, 176*(1–4), 313–320. https://doi.org/10.1007/s10661-010-1584-3

Passos, C. J. S., Da Silva, D. S., Lemire, M., Fillion, M., Guimarães, J. R. D., Lucotte, M., & Mergler, D. (2008). Daily mercury intake in fish-eating populations in the Brazilian Amazon. *Journal of Exposure Science & Environmental Epidemiology, 18*, 76–87. https://doi.org/10.1038/sj.jes.7500599

Prasad, M., Ramanathan, A. L., Shrivastav, S. K., & Anshumali. & Saxena, R. . (2006). Metal fractionation studies in surfacial and core sediments in the Achankovil River Basin in India. *Environmental Monitoring and Assessment, 121*(1–3), 77–102. https://doi.org/10.1007/s10661-005-9108-2

Pueyo, M., Sastre, J., Hernández, E., Vidal, M., López-Sánchez, J. F., & Rauret, G. (2003). Prediction of trace element mobility in contaminated soils by sequential extraction. *Journal of Environmental Quality, 32*, 2054–2066. https://doi.org/10.2134/jeq2003.2054

Purushothaman, P., & Chakrapani, G. J. (2007). Heavy metals fractionation in Ganga River sediments. *India. Environmental Monitoring and Assessment, 132*(1–3), 475–489. https://doi.org/10.1007/s10661-006-9550-9

Raj, S., Jee, P. K., & Panda, C. R. (2013). Textural and heavy metal distribution in sediments of Mahanadi estuary, East coast of India. *Indian Journal of Geo-Marine Sciences, 42*, 370–374.

Ramzi, A., Habeeb Rahman, K., Gireeshkumar, T. R., Balachandran, K. K., Jacob, C., & Chandramohanakumar, N. (2017). Dynamics of polycyclic aromatic hydrocarbons (PAHs) in surface sediments of Cochin estuary. *India. Marine Pollution Bulletin, 114*(2), 1081–1087. https://doi.org/10.1016/j.marpolbul.2016.10.015

Rauret, G., López-Sánchez, J. F., & Sahuquillo, a, Barahona, E., Lachica, M., Ure, a M., & Quevauviller, P. (2000). Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid. *Journal of Environmental Monitoring, 2*(3), 228–233. https://doi.org/10.1039/b001496f

Reynoldson, T. B. (1987). Interactions between sediment contaminants and benthic organisms. *Hydrobiologia, 149*(1), 53–66. https://doi.org/10.1007/BF00048646

Saha, S. B., Mitra, A., & Bhattacharyya, S. B. (2001). Status of sediment with special reference to heavy metal pollution of a brackish water tidal ecosystem in northern Sundarbans of West Bengal. *Tropical Ecology, 42*(1), 127–132.

Salas, P. M., Sujatha, C. H., Ratheesh Kumar, C. S., & Cheriyan, E. (2017). Heavy metal distribution and contamination status in the sedimentary environment of Cochin estuary. *Marine Pollution Bulletin, 119*(2), 191–203. https://doi.org/10.1016/j.marpolbul.2017.04.018

Selvam, A. P., Priya, S. L., Banerjee, K., Hariharan, G., Purvaja, R., & Ramesh, R. (2012). Heavy metal assessment using geochemical and statistical tools in the surface sediments of Vembanad Lake, Southwest Coast of India. *Environmental Monitoring and Assessment., 184*, 5899–5915. https://doi.org/10.1007/s10661-011-2389-8

Sheeba, V. A., Abdulaziz, A., Gireeshkumar, T. R., Ram, A., Rakesh, P. S., Jasmin, C., & Parameswaran, P. S. (2017). Role of heavy metals in structuring the microbial community associated with particulate matter in a tropical estuary. *Environmental Pollution, 231*, 589–600. https://doi.org/10.1016/j.envpol.2017.08.053

Sheeba, V. A., Anas, A., Jasmin, C., Vincent, M., & Parameswaran, P. S. (2020). Response of particle-associated bacteria to long-term heavy metal contamination in a tropical estuary. *World Journal of Microbiology and Biotechnology, 36*(5), 1–10. https://doi.org/10.1007/s11274-020-02842-1

Shylesh Chandran, M. S., Ramasamy, E. V., Mohan, M., Shruthi, N. S., Jayasooryan, K. K., Augustine, T., & Mohan, K. (2019). Distribution and risk assessment of trace metals in multifarious matrices of Vembanad Lake system, Peninsular India. Marine Pollution Bulletin, 145, 490–498. https://doi.org/10.1016/j.marpolbul.2019.06.034

Siraswar, R., & Nayak, G. N. (2011). Mudflats in lower middle estuary as a favourable location for concentration of metals, west coast of India. *Indian Journal of Geo-Marine Science, 40*, 372–385.

Sivaperumal, P., Sankar, T. V., & Nair, P. G. V. (2007). Heavy metal concentrations in fish, shellfish and fish products from internal markets of India vis-a-vis international standards. *Food Chemistry, 102*, 612–620. https://doi.org/10.1016/j.foodchem.2006.05.041

Sobolewski, A. (1999). A review of processes responsible for metal removal in wetlands treating contaminated mine drainage. *International Journal of Phytoremediation, 1*(1), 19–51. https://doi.org/10.1080/15226519908500003

Sruthi, S. N., & M S, S., Mohan, M., & Ramasamy, E. V. (2018). Distribution of priority pollutants in the sediment of Vembanad Estuary. *Peninsular India. Marine Pollution Bulletin, 133*(March), 294–303. https://doi.org/10.1016/j.marpolbul.2018.05.033

Sundararajan, M., & Natesan, U. (2010). Geochemistry of core sediments from Mullipallam Creek, South East coast of India. *Environment and Earth Sciences, 61*(5), 947–961.

Sutherland, R. A., & Tack, F. M. G. (2002). Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure. *Analytica Chimica Acta, 454*(2), 249–257. https://doi.org/10.1016/S0003-2670(01)01553-7

Sutherland, R. A., & Tack, F. M. G. (2003). Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Advances in Environmental Research, 8*(1), 37–50. https://doi.org/10.1016/S1093-0191(02)00144-2

USEPA. (2007). Microwave assisted acid digestion of sediments, sludges, soils, and oils. USEPA -METHOD 3051A.

Vardhan, K. H., Kumar, P. S., & Panda, R. C. (2019). A review on heavy metal pollution, toxicity and remedial measures: Current trends and future perspectives. *Journal of Molecular Liquids, 290*, 111197. https://doi.org/10.1016/j.molliq.2019.111197

Venkatramanan, S., Chung, S. Y., Ramkumar, T., & Vasudevan, S. (2014). A study on seasonal accumulation of metals in Tirumalairajan river estuary and adjacent coastal track, Tamil Nadu, east coast of India. *Indian Journal of Geo-Marine Sciences, 43*, 841–847.

Venkatramanan, S., Chung, S. Y., Ramkumar, T., & Selvam, S. (2018). Ecological risk assessment of selected heavy metals in the surface sediments of three estuaries in the south-eastern coast of India. *Environmental Earth Sciences, 77*, 116. https://doi.org/10.1007/s12665-018-7294-9

Vinita, J., Revichandran, C., & Manoj, N. T. (2017). Suspended sediment dynamics in Cochin estuary, West Coast. *India. Journal of Coastal Conservation, 21*(1), 233–244. https://doi.org/10.1007/s11852-017-0494-8

Wang, Z., Shan, X. Q., & Zhang, S. (2002). Comparison between fractionation and bioavailability of trace elements in rhizosphere and bulk soils. *Chemosphere, 46*(8), 1163–1171. https://doi.org/10.1016/S0045-6535(01)00206-5

Xiao, R., Bai, J., Lu, Q., Zhao, Q., Gao, Z., Wen, X., & Liu, X. (2015). Fractionation, transfer, and ecological risks of heavy metals in riparian and ditch wetlands across a 100-year chronosequence of reclamation in an estuary of China. *Science of the Total Environment, 517*, 66–75. https://doi.org/10.1016/j.scitotenv.2015.02.052

Yao, D., Mei, S., Fu-gui, Y., Heng-yi, J., Gong-sheng, L., & Chun-xiao, D. (2008). Environmental geochemistry of heavy metals in urban soils of Qingdao City. *Geology China, 35*, 539–550.

Yuan, X., Chen, Y., Li, B., & Siegel, D. I. (2009). Source of sediments and metal fractionation in two Chinese estuarine marshes. *Environmental Earth Sciences, 60*(7), 1535–1544. https://doi.org/10.1007/s12665-009-0288-x

Zhang, G., Bai, J., Xiao, R., Zhao, Q., Jia, J., Cui, B., & Liu, X. (2017). Heavy metal fractions and ecological risk assessment in sediments from urban, rural and reclamation-affected rivers of the Pearl River Estuary, China. *Chemosphere, 184*, 278–288. https://doi.org/10.1016/j.chemosphere.2017.05.155

Zhao, Q., Liu, S., & Deng, L. (2012). Spatio-temporal variation of heavy metals in fresh water after dam construction: A case study of the Manwan Reservoir. *Lancang River., 184*(7), 4253–4266. https://doi.org/10.1007/s10661-011-2260-y

Zulfiqar, U., Farooq, M., Hussain, S., Maqsood, M., Hussain, M., Ishfaq, M., & Anjum, M. Z. (2019). Lead toxicity in plants: Impacts and remediation. *Journal of Environmental Management, 250*, 109557. https://doi.org/10.1016/j.jenvman.2019.109557

Terms and Conditions

Springer Nature journal content, brought to you courtesy of Springer Nature Customer Service Center GmbH (“Springer Nature”).

Springer Nature supports a reasonable amount of sharing of research papers by authors, subscribers and authorised users (“Users”), for small-scale personal, non-commercial use provided that all copyright, trade and service marks and other proprietary notices are maintained. By accessing, sharing, receiving or otherwise using the Springer Nature journal content you agree to these terms of use (“Terms”). For these purposes, Springer Nature considers academic use (by researchers and students) to be non-commercial.

These Terms are supplementary and will apply in addition to any applicable website terms and conditions, a relevant site licence or a personal subscription. These Terms will prevail over any conflict or ambiguity with regards to the relevant terms, a site licence or a personal subscription (to the extent of the conflict or ambiguity only). For Creative Commons-licensed articles, the terms of the Creative Commons license used will apply.

We collect and use personal data to provide access to the Springer Nature journal content. We may also use these personal data internally within ResearchGate and Springer Nature and as agreed share it, in an anonymised way, for purposes of tracking, analysis and reporting. We will not otherwise disclose your personal data outside the ResearchGate or the Springer Nature group of companies unless we have your permission as detailed in the Privacy Policy.

While Users may use the Springer Nature journal content for small scale, personal non-commercial use, it is important to note that Users may not:

1. use such content for the purpose of providing other users with access on a regular or large scale basis or as a means to circumvent access control;
2. use such content where to do so would be considered a criminal or statutory offence in any jurisdiction, or gives rise to civil liability, or is otherwise unlawful;
3. falsely or misleadingly imply or suggest endorsement, approval , sponsorship, or association unless explicitly agreed to by Springer Nature in writing;
4. use bots or other automated methods to access the content or redirect messages
5. override any security feature or exclusionary protocol; or
6. share the content in order to create substitute for Springer Nature products or services or a systematic database of Springer Nature journal content.

In line with the restriction against commercial use, Springer Nature does not permit the creation of a product or service that creates revenue, royalties, rent or income from our content or its inclusion as part of a paid for service or for other commercial gain. Springer Nature journal content cannot be used for inter-library loans and librarians may not upload Springer Nature journal content on a large scale into their, or any other, institutional repository.

These terms of use are reviewed regularly and may be amended at any time. Springer Nature is not obligated to publish any information or content on this website and may remove it or features or functionality at our sole discretion, at any time with or without notice. Springer Nature may revoke this licence to you at any time and remove access to any copies of the Springer Nature journal content which have been saved.

To the fullest extent permitted by law, Springer Nature makes no warranties, representations or guarantees to Users, either express or implied with respect to the Springer nature journal content and all parties disclaim and waive any implied warranties or warranties imposed by law, including merchantability or fitness for any particular purpose.

Please note that these rights do not automatically extend to content, data or other material published by Springer Nature that may be licensed from third parties.

If you would like to use or distribute our Springer Nature journal content to a wider audience or on a regular basis or in any other manner not expressly permitted by these Terms, please contact Springer Nature at

onlineservice@springernature.com