Bull Environ Contam Toxicol (2011) 87:662–668
DOI 10.1007/s00128-011-0402-0

Seasonal Dynamics of Dissolved Metals in Surface Coastal Waters of Southwest India

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Received: 3 May 2011 / Accepted: 2 September 2011 / Published online: 16 September 2011

Abstract Spatial and temporal variations in concentration of dissolved metals viz. Copper (Cu), Lead (Pb), Chromium (Cr), Nickel (Ni), Zinc (Zn), Cadmium (Cd) and Mercury (Hg) in surface waters of southwest coast of India were studied. Concentrations of metals showed an aberration both temporally and spatially. Seasonal average concentrations of the analyzed metals followed the order Zn > Ni > Cu > Pb > Cd > Cr > Hg. The degree of contamination due to metal was determined by comparison with coastal water quality criteria. It established enrichment of Cu, Zn, Ni and Hg due to anthropogenic influence along southwest coast of India.

Keywords Heavy metal · Enrichment factor · Coastal water · Southwest India

Coastal waters are highly affected by pollution because they are shallow water bodies, heavily used, close to pollution sources and not well circulated as the open ocean. A significant quantity of the environmental contaminant impinges into coastal waters mainly due to by-products of anthropogenic activities in the watershed, including urban, industrial effluents and agricultural runoff (Accornero et al. 2004). The ubiquitous presence of metals in the environment, toxicity, persistence, ability to bioaccumulate in the aquatic food web and occurrence of many catastrophic events of human health significance in the past has made its determination meaningful in marine pollution studies. Further, knowledge of the distribution and concentration of heavy metals in coastal water can assist in identifying the sources of pollution in the system. This is particularly true for southwest coast of India, where untreated domestic sewages and industrial effluents are disposed into the coastal waters routed through fresh water bodies. It is estimated that about 17,104 m^3/day of treated and untreated effluents from both medium as well as large scale industries are being discharged, thus impairing the quality of coastal waters drastically. There has been a dearth of information on the concentration of dissolved metals in the coastal waters of southwest India. The present study, therefore, was undertaken with a view to determine the spatial and temporal variability in the distribution of dissolved metals viz. Cu, Pb, Cr, Ni, Zn, Cd and Hg along the southwest coast of India.

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Materials and Methods

Five transects having six sampling points (0.5, 1.0, 3.0, 5.0, 7.5 and 10.0 km) each from bar mouth to offshore along southwest coast of India was selected for the present study (Fig. 1). The selection of locations was based on the inflow of pollutants from different sources. Cochin [major port, fishing harbors, densely populated zone, busy waterways, tourist destination, major industrial center], Chettuva [agricultural region, municipal wastes, river estuary, fishing village], Ponnani [fishing harbor, densely populated area, agricultural region, small scale industries], Calicut

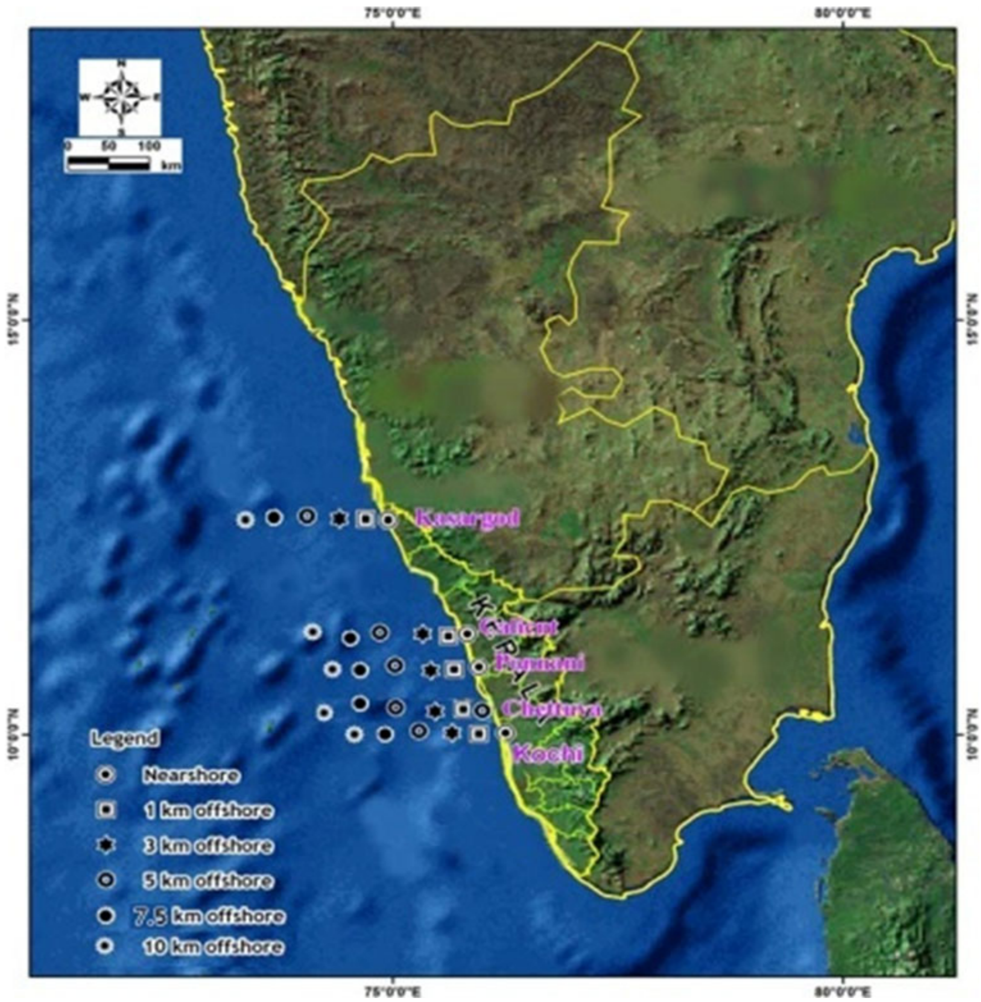

Fig. 1 Area of investigation along the southwest coast of India

[commercial port, fishing harbor, densely populated area, industrial city] and Kasargod [fishing harbor, small scale industries, agricultural region]. Marine surface water samples were pooled seasonally representing post monsoon, pre monsoon and monsoon in the year 2008 using PVC Niskin sampler (5L) operated onboard Coastal Research Vessels (CRV'S) *Sagar Purvi* and *Sagar Paschimi*. The pooled surface sea water sample was immediately filtered through 0.45-µm pore-size Millipore filters to polypropylene bottle, in a completely closed system to minimize contamination from the atmosphere of the ship's laboratory. Filters were previously acidified with 10% nitric acid solution. After filtration, each filtered 1 L sample was acidified with 1 ml Supra pure conc. HNO_3 to pH 2, kept in plastic bags to prevent contamination and stored at 4°C. In the laboratory, dissolved metals were determined after a preconcentration – complexation treatment (APDC/MIBK). Re-extraction of each sample with the addition of APDC and MIBK to each aliquot was treated as the blank. For the determination of mercury, the dissolved metal was extracted by dithizone/CCl_4, in which the organic layer was back extracted by means of sodium nitrite and hydroxyl amine hydrochloride (Grasshoff 1999). Extraction for each sample was done in triplicate and the concentration of heavy metals was determined by ICP-OES. The average value of triplicate analysis for each heavy metal is reported as its concentration. The recoveries >90% for each metal were observed from the spiked standards in metal free sea water employing the above extraction method. The limits of detection (LODs) for Cu, Pb, Cr, Ni, Zn, Cd and Hg were 0.0097, 0.0042, 0.0071, 0.0016, 0.0018, 0.0027 ppm and 1.0 ppb respectively.

Results and Discussion

Heavy metals such as Cu, Pb, Cr, Ni, Zn, Cd and Hg were found in the coastal waters in detectable levels and at varying concentrations among different seasons (Fig. 2). The sources of metals in water and its relation to higher population densities, urbanization and industrialization are well documented (Salomons and Fostner 1984; Furness and

Rainbow 1990). In the whole study area, the seasonal average concentrations of the analyzed heavy metals followed (in decreasing order) 3.93–35.58 ppb for Zn, 0.56–13.83 ppb for Ni, 3.88–13.06 ppb for Cu, 0.05–5.33 ppb for Pb, 0.10–4.60 ppb for Cd, BDL–0.47 for Cr and 0.05–0.26 ppb for Hg (Fig. 2). Concentrations of the dissolved metals measured in the coastal waters of southwest India were within the ranges reported for other areas of the world and the region is not as much polluted as the other coastal waters of India (Table 1).

Seasonal variation in the mean concentrations of metals showed a high trend for Cu (6.78–13.06 ppb) at all transects during monsoon and low (4.21–6.32 ppb) during post monsoon except at Ponnani (Fig. 2a). This may be due to the presence of major sources of metal pollution through agricultural runoff and sewage outlets. Phytoplankton activity might also facilitate the seasonal variation in Cu, as this metal is an essential element for their growth (Tada et al. 2001). High concentrations of Cu recorded during monsoon, can be attributed to land run-off carrying the

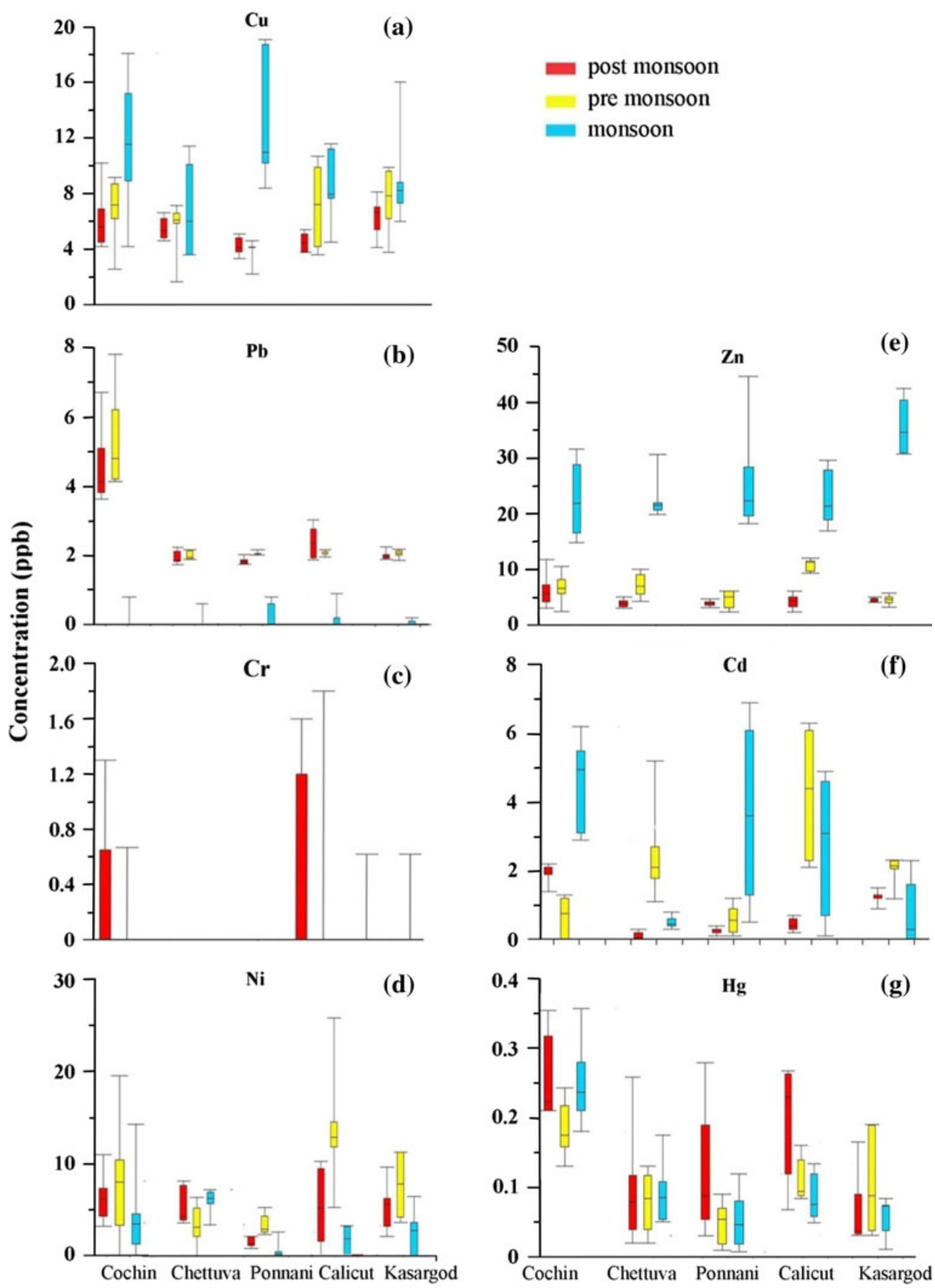

Fig. 2 Dissolved metal concentration (ppb) in coastal waters along the southwest coast of India shown through box whisker plot

Table 1 Average heavy metal concentration (ppb) found in coastal waters from various regions of the world

Location	Cu	Pb	Cr	Ni	Zn	Cd	Hg	References
Southwest coast, India	3.88–13.06	0.05–5.33	BDL–0.47	0.56–13.83	3.93–35.58	0.10–4.60	0.05–0.26	Present study
Bay of Bengal, India	1.20–17.50	–	–	0.80–30.30	1.90–174.0	0.30–2.90	0.05–0.30	Qasim and Sengupta (1983)
Pondicherry Coast, India	0.70–61.50	–	–	ND–14.80	16.70–135.70	3.20–69.00	ND–0.15	Govindasamy et al. (1997)
Coromandel coast, India	0.31–50.70	–	–	ND–14.60	9.00–130.60	0.30–66.80	ND–0.12	Govindasamy and Azariah (1999)
Greek coastal waters	0.03–20.7	0.03–12.2	–	0.06–41.9	0.02–120	0.002–2.3	–	Dassenakis et al. (1996)
Coastal Mediterranean Sea	0.01–50	0.016–20.5	–	–	0.20–210	0.002–0.9	–	UNEP (1996)
Southern Adriatic Sea (Apulia)	0.50–5.00	0.04–2.93	–	0.11–1.26	0.07–20.94	0.01–0.25	–	Accornero et al. (2004)
Basque coast	0.20–15.0	0.30–68.0	2.0–5.0	0.30–8.50	1.10–454	0.2–11.0	0.30–3.0	Maria et al. (2004)

BDL below detectable limit, *ND* not detectable

washing of polluted land surface area. In addition the extensive use of antifouling paint residues arising from boat maintenance and vessel repair would have released cuprous oxide which in turn enriches the Cu content in water. In unpolluted coastal waters Cu have levels in the range of 2–5 μg L^{-1}, while its concentration greater than 30 μg L^{-1} are categorized as contamination and a range of 80–160 μg L^{-1} can significantly reduce algal biomass (Hoare et al. 1995; Le jeune et al. 2007). In the present study the coastal region is moderately polluted with Cu and the increased concentration during monsoon cannot produce a direct effect on the primary producers.

Lead (Pb) is an extremely reactive element; it is removed from the water column through its association with particulates and subsequent sedimentation. It is classified as a scavenged element. Mainly dissolved Pb is derived from industrial discharges and a significant input of Pb originates from atmospheric contamination (Maria et al. 2004). Concentration of Pb showed a relatively restricted range of variability and an even distribution throughout the study area (Fig. 2b). However, the seasonal average value of Pb in surface water was found to be high at Cochin (0.13–5.33 ppb) and Calicut (0.18–2.37 ppb) due to intense boat trafficking and harbour activities. During monsoon Pb concentration was low (0.05–0.23 ppb) in studied transects where much of it may be removed from the surface water by organic matter through deposition brought by monsoonal flushing. In general, dissolved Pb is highly homogeneous, both spatially and vertically, over the whole southwest coast of India. Combined effects of atmospheric deposition, which prevents surface depletion, and active vertical mixing, which attenuates surface enrichment may be a plausible explanation. Anthropogenic input of lead into these coastal waters seems to be insignificant, as very high concentrations are not encountered at any transects except at Cochin, where its level is intensified by industrial discharges and port activities.

Chromium was not detectable in all transects, though low concentration was observed at Cochin and Calicut in the near shore region of 0.5 and 1.0 km from the coast (Fig. 2c). In aquatic environment Cr is found as Cr(III) and Cr(VI) as water soluble complex anions. Information on the geochemical behavior of Cr in seawater is limited. Chromium is known to have no major biochemical function, and it is therefore not surprising that many species of plankton do not concentrate Cr to any greater extent. Chromium is known to decrease rapidly during fresh water – sea water mixing either as particulate Cr or precipitation as chromium hydroxide (Mayer 1988). The meager presence of Cr in the southwest coastal waters does not mean that it is being absent or not being added to the environment. Enrichment of Cr in the southwest coastal sediments has been well documented (Balachandran et al. 2005). A plausible explanation in the present study can be the removal of Cr by precipitation and deposition in sediments.

The concentration of Ni did not show a seasonal trend, but much variation in its concentration (3.37–13.83 ppb) was observed during pre monsoon and relatively low concentration (0.56–5.92 ppb) during monsoon (Fig. 2d). The depletion and enrichment of Ni can be attributed to its involvement in the biogeochemical cycling resulting in its removal from surface waters by plankton or biologically produced particulate matter and subsequent regeneration either by oxidation and resolubilisation. The concentration was relatively high at Cochin (4.49–8.19 ppb) and Calicut (1.70–13.83 ppb) compared to other transects due to the inflow of untreated effluents from harbor activities, urban agglomeration and various industrial assortments situated along the coastal belt of this region. Nonetheless, laboratory data demonstrate that Ni is necessary for the assimilation of urea for phytoplankton proliferation and should exhibit a surface depletion characteristic of nutrients (Price and Morel 1991). However, the high surface concentration of Ni in the study area is perplexing. Despite marine phytoplankton need for Ni to assimilate urea, it may be unable to deplete the nickel concentration of surface seawater simply because of the kinetic inertness of the Ni^{2+} ion (Hudson et al. 1992).

Zinc showed a definite seasonal pattern with low concentration (3.93–6.25 ppb) during post monsoon and high concentration (22.57–35.58 ppb) during monsoon (Fig. 2e). Zinc could get strongly depleted from the surface waters as it has a nutrient type distribution in sea water (Govindasamy and Azariah 1999). The low concentration might have resulted due to the utilization by biota including phytoplankton. Diatoms playing an important role in the biogeochemical cycling of Zn have been documented (Bruland et al. 1978). The primary role of Zn acting as metal centre in the transport of $Si(OH)_4$ for silica frustule formation in diatoms is well studied (Hildebrand 2000). The very large local variations in the diatoms arising due to the increased concentration of silicate during monsoon and its significant contribution to the phytoplankton community throughout the season in the southwest coastal waters has been reported (Venkataraman and Wafar 2005). The major involvement of diatoms in phytoplankton production and their remineralization might have led to the increased concentration of Zn at all transects in the southwest coastal waters during monsoon besides land based discharges in the present study.

The concentration of Cd exhibited a wider variation (0.50–4.60 ppb) during monsoon, while its variation was low (0.10–1.90 ppb) in post monsoon (Fig. 2f). The mean value was high at Cochin during post monsoon (1.90 ppb) and monsoon (4.60 ppb). Cadmium is released into the atmosphere by fossil fuel and by the burning of agricultural and municipal wastes including dried sewage sludge and industrial wastes (Mart and Nurnberg 1986). These activities are relatively prominent at Cochin, facilitating high input of Cd into the coastal waters. In general, a higher value of Cd concentration during monsoon season at all transects appear to be related to monsoon flushing bringing agricultural runoff, urban wastes and industrial discharges.

Mercury did not show any seasonal pattern; its concentration being relatively identical at all transects except at Cochin where it was high (0.18–0.26 ppb) during all seasons due to industrial influence (Fig. 2g). An increase in the mean value of Hg (0.20 ppb) was noted at Calicut during post monsoon. This may be due to some point discharges.

As per the quality criteria (QC) for dissolved metals in coastal waters defined by EPA and values furnished by European directives, a concentration greater than 1 ppb for Cu, 2 ppb for Pb, 12 ppb for Cr, 2 ppb for Ni, 20 ppb for Zn, 0.5 ppb for Cd and 0.3 ppb for Hg represents contamination due to metals (Maria et al. 2004). The number of samples and the percentage of samples that exceed the QC for each variable analyzed using the above criteria in each transect are summarized in Table 2. It followed the order Cochin > Kasargod > Chettuva > Calicut > Ponnani. The high percentage 53.97%, observed at Cochin is probably due to industrial influence, urbanization and port activities. While, at other transects it mainly results from

Table 2 Number of samples (N) which exceed the quality criteria (QC), for each variable in each of the coastal transects, together with the total percentage of variables that exceed the QC in southwest coast of India

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	18	12	0	15	4	16	3	68	53.97
Chettuva	18	4	0	17	5	9	0	53	42.06
Ponnani	18	7	0	9	4	8	0	46	36.51
Calicut	18	9	0	13	4	13	0	57	45.24
Kasargod	18	8	0	16	6	15	0	63	50.00
N	90	40	0	70	23	61	3		
%	100	44.44	0	77.78	25.56	67.78	3.33		

Table 3 Number of samples (N) which exceed the minimal risk concentration (MRC) of metals, for each variable in each of the coastal transects, together with the total percentage of variables that exceed the MRC in southwest coast of India

Transect	Cu	Pb	Cr	Ni	Zn	Cd	Hg	N	%
Cochin	4	0	0	15	4	0	18	41	32.54
Chettuva	2	0	0	17	5	0	8	32	25.40
Ponnani	5	0	0	9	4	0	4	22	17.46
Calicut	3	0	0	13	4	0	10	30	23.81
Kasargod	1	0	0	16	6	0	3	26	20.63
N	15	0	0	70	23	0	43		
%	16.67	0	0	77.78	25.56	0	47.78		

the metal residue brought through agricultural runoff and contribution from small scale industries situated in the hinterland which impinges into the coastal water through freshwater bodies. In general, on the basis of the total number of water samples analyzed along the southwest coast of India, 100% samples exceed the established QC value for Cu; around 77.78% and 67.78% exceeded that for Ni and Cd respectively. A relatively good number of the samples (44.44%) reached the QC established for Pb; Zn and Hg registered low values, while Cr remained without any contribution.

In order to identify the relative importance of dissolved heavy metals in the study area, the concentrations of dissolved metals of each transect were compared with those considered for minimal risk concentration of metals reported for water quality criteria (WQC 1972). A concentration of 10 ppb for Cu, 10 ppb for Pb, 50 ppb for Cr, 2 ppb for Ni, 20 ppb for Zn, 10 ppb for Cd, 0.10 ppb for Hg represents minimal risk of deleterious effect. Enrichment factors (Ef) for each metal was determined by comparing the observed dissolved metal concentration over minimal risk concentration of heavy metals reported for water quality criteria. Ef values greater than 1 indicate the enrichment of the waters with metals, relative to the water quality criteria. Table 3 present the percentage of samples showing Ef values greater than one at each transect. Lead, Cd and Cr metals registered low Ef values, while Cu, Ni, Zn and Hg showed enrichment. The coastal waters in terms of enrichment of metals along the southwest India followed the order Cochin > Chettuva > Calicut > Kasargod > Ponnani. The high enrichment at Cochin (32.54%) can be attributed to various industrial assortments situated along the coastal belt. It is not surprising that the essential elements Cu (16.67%) and Zn (25.56%) showing enrichment, while the presence of Ni (77.78%) and Hg (47.78%) may possess some ecotoxicological risks for organism inhabiting these waters. A recent study has revealed increased bioaccumulation of Cu, Zn, and Ni in both demersal and pelagic fishes due to enhanced bioavailability of these metals along the southwest coast of India (Rejomon et al. 2010). The present study bears testimony to this recent finding.

Results clearly indicated that seasonal variability plays an important role in accentuating the distribution of dissolved metals in coastal waters. Increased anthropogenic activities along the coast at Cochin might certainly turn it as a hotspot location in terms of land based heavy metal pollution. Enrichment factor values used as a tool for quantification of contamination reveal Cu, Ni, Zn and Hg showing enrichment due to anthropogenic influence along southwest coast of India.

Acknowledgments The authors thank Dr. N. P. Kurian, Director, CESS for the facilities provided. The financial assistance from Ministry of Earth Science, New Delhi in the form of a sponsored project Coastal Ocean Monitoring and Prediction System (COMAPS) is gratefully acknowledged.

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