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# Seasonal Assessment of Heavy Metal Pollution in Tropical Mangrove Sediments (Goa, India)

Kuldeep Attri and Savita Kerkar*

*Department of Biotechnology, Goa University, Taleigao, Plateau, Goa. 403 206. India*

## Article Info

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*Corresponding Author

*Tel : +91-8322451184*
*Fax : +91-8326519358*

*Email:*
*savitakerkar@gmail.com*



## Abstract

Mangrove swamps along the Mandovi estuary, Goa are exposed to an influx of metal effluents from the ferromanganese mining activities. The present study was carried out to assess the seasonal concentrations of metals in the sediments of Divar, an anthropogenically-influenced mangrove swamp in the Mandovi estuary, and compared to Tuvem along the Chapora River, a relatively pristine mangrove site. In both the sites, the average heavy metal concentration in sediments decreased in the order: Fe > Mn > Zn > Cu > Co > Pb > Cr and showed a marked seasonal variability ($p < 0.001$; df=2). However, the Pollution Load Index (PLI) for Divar sediments was far greater (1.65-2.19) than that of Tuvem (0.91-1.3) reflecting the intensity of anthropogenic inputs into the ecosystem. Further, Muller geochemical index values for Divar sediments indicated that during pre and post-monsoon season, the sediments were moderately contaminated with Fe whereas at Tuvem, the sediments were below contamination levels. The comparison with Screening Quick Reference Table (SQuiRT) also revealed the poor sediment quality for Divar. The transport of ferromanganese ore along the Mandovi River could be a major source of the entry of heavy metals in this riverine system. The Effect Range- Low (ER-L) values for these elements exceeded the reference values suggesting a potential eco-toxicological risk to the benthic organisms and a possible transfer to higher trophic levels.

Key Words: Metals, Pollution, Mangroves, Sediments, Mining

## Introduction

With increase in urbanization and industrialization, many coastal regions have been subjected to considerable environmental stress [1, 2]. Nearshore marine ecosystems are especially prone to anthropogenic inputs due to their proximity to the coast. Sediments are important carriers of trace metals in the hydrological cycle and because metals are partitioned with the surrounding waters, they reflect the quality of an aquatic system. In tropical zones, the most dominant intertidal areas comprise of the mangrove fringes [3]. Out of the ~20 million hectares, Asia harbors the largest area of mangrove vegetation which includes 3% of the global mangrove forest in India [4, 5]. Mangroves are often exposed to heavy metal pollution due to a variety of factors ranging from processing and post development of metal ores, shipping, sewage and storm-water discharge [6]. Marine suspended matter with an elevated metal load, gets actively trapped within mangrove sediments [7].

Goa is richly endowed with industrial minerals like iron ore, manganese ore, bauxite, lime stone and dolomite etc. The commonly used practice of 'open cast' mining creates up-to three tons of waste for each ton of ore produced. This waste pollutes rivers and lakes, many of which run red with ore. The estuarine channel of the Mandovi river is crucial for the economy of the state since it is used to transport large quantities of ore to the Marmagoa harbour. Lush mangrove vegetation fringes this estuarine system. The mining activity upstream in the watershed may influence the biological and geochemical conditions of these water bodies. Due to the bio-accumulation potential and metal toxicity the persistence and cycling of heavy metals is of a serious concern in mangrove environments [7, 8, 9, 10]. Currently, studies assessing the potential problems related to heavy metal accumulation from the Indian mangroves regions are limited [11, 12, 13, 14]. Although the impacts of iron-ore processing on the surface sediments of the Mandovi estuary have been documented [15], their influence on the surrounding mangrove ecosystem is sparsely addressed. In the present study, we compare the seasonal variation in the concentration of heavy metals viz., Fe, Co, Cu, Cr, Mn, Pb and Zn in surficial sediments of two mangrove ecosystems of Goa viz. the relatively pristine site "Tuvem" and the anthropogenically-influenced site of "Divar". We have also evaluated the intensity of heavy metal pollution in the sediments through various indices, and we hypothesize that the mining activity adjoining the Mandovi estuary is the main source and cause of heavy metal pollution in these mangrove swamps. The measurement of the seasonal variation in trace metal concentrations and distribution in the sediments would give us a better understanding of the inputs of the accumulated metals in the mangrove ecosystem and thus the quality of local coastal environment.

## Materials and Methods

### *Study area and sampling*

The study included two mangrove forests located at Tuvem and Divar along the Chapora and Mandovi rivers in Goa respectively, located on the west coast of India (Fig. 1).

The site at Tuvem (15º39'94" N and 73º47'65" E) is set amidst coconut (*Cocos nucifera* L.), cashew (*Anacardium occidentale* L.), and banana (*Musa* L.) plantations and is comparatively less influenced by anthropogenic activities. The Divar mangrove ecosystem (15°30'35" N and 73°52'63" E) is separated from the mainland by the river Mandovi. *Rhizophora* sp., *Sonneratia* sp., *Avicennia* sp.and *Excoecaria* sp. are some of the dominant mangrove genera found along the Mandovi and Chapora estuaries. Iron ore beneficiation plants situated on the riverbanks carries out treatment and up-gradation of low grade ore. These plants use river water to wash the iron ore and in-turn discharge metal effluents directly into the aquatic system. Sediment samples (n=5) were collected during the low tide using PVC hand-held corers in the month of April (pre-monsoon), July (monsoon) and December (post-monsoon) of 2008. Upon collection, the cores were sealed at both the ends with sterile core caps and transported to the lab in an ice box for further analysis.

### *Physico-chemical and particle size analysis*

Hydrogen ion concentration (pH) of the surface sediment was measured instantly upon sample arrival at the laboratory using a portable pH meter (Thermo Orion model 420A) following the manufacturer's instructions. Total organic carbon (TOC) was estimated using titrimetric wet oxidation method as described by Allen et al., [16]. The sediments used to estimate organic carbon and nitrogen content were dried at 60(±2)$^{o}$C for 48 h. The samples were de-carbonated with HCl fumes and analyzed using an Elemental Analyzer (Thermo Finningan, Flash EA1112) with L-Cystine as standard. The precision of analysis was checked against NIST 1941b.

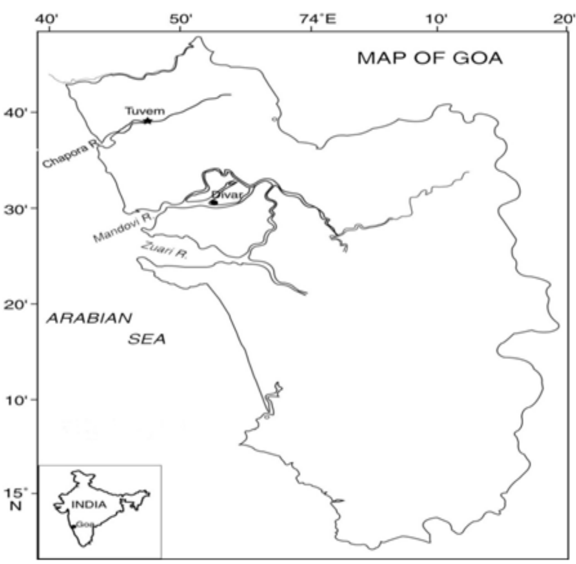


Fig. 1. Location of sampling sites along the Chapora and Mandovi rivers

Sub-samples for metal analysis were dried at 60(±2) $^{0}$C for 48 h and disaggregated in an agate mortar before chemical treatment for Fe, Cu, Co, Cr, Mn, Pb and Zn following sediment digestion methods as described by Balaram et al., [17]. Briefly, a known quantity (0.2 g) of sediment was digested in a Teflon vessel with a solution (10 ml) of concentrated HF, $HNO_3$, and $HClO_4$ (Merck,) in the ratio 7:3:1. The sediment was then dried on a hot plate in a fume hood chamber at 70$^{\circ}$C for 4-6 h. The procedure was repeated with 5 ml of acid mixture. Further 2 ml of concentrated HCl was added followed by 10 ml of $HNO_3$. The residue was warmed and transferred to a clean, dry standard flask to make a final volume of 50 ml with double distilled water. The concentration of the metals were analyzed with an atomic absorption spectrophotometer (AAS; GBC 932 AA model) equipped with deuterium background corrections. Blank corrections were applied wherever necessary and the accuracy was tested using standard reference material MAG-1 (United Geological Survey) and GR-1 (Green River sediment). The particle size analysis was carried out by the wet sieving method for sand and the pipette method for silt and clay as reported by Day [18] and Carver [19].

### *Sediment quality assessment*

To estimate the possible environmental consequences of metal pollution, our results were compared with Sediments Quality Values (SQV) using National Oceanic and Atmospheric Administration (NOAA) Screening Quick Reference Tables (SQuiRTs) [20]. Concentration factor and Pollution Load Index (PLI) was used as described by [21].

The geoaccumulation index ($I_{geo}$) of Muller, [22] was used to determine the intensity of metal pollution. The index can be expressed as:

$I_{geo} = \log_2 (C_n/1.5B_n)$

Where, $C_n$ = measured concentration of metal 'n' in the sediment

$B_n$ = the background values for the metal 'n'.

The Factor 1.5 is a value intended to offset potential oscillations in background data resulting from lithological variations.

### *Statistical analyses*

Significant variability in metal content was analyzed using two-factor analysis of variance (ANOVA) without replication in Analysis tool pack (*Microsoft Excel*). Pearson's correlation coefficients were used to assess inter-relationship between the abiotic parameters.

## Results and Discussion

### *Sediment characteristics*

The seasonal variation in environmental parameters at both the sampling locations has been presented in Table 1. The pH at both the sampling locations ranged between 6.82±0.08 to 6.98±0.13. Mangrove ecosystems have an active and continuous degradation of tree litter subsequently the hydrolysis of tannins release various acids [23] and/or the oxidation of sulfide pyrite which release the dissolved ferrous iron [24] is known to be responsible for a shift towards more acidic conditions. The present study reveals a high organic carbon content in the mangrove sediments. Thus, its degradation resulting in low pH is expected [23]. Grain size analysis in the mangrove sediments was clayey in nature during pre- and post-monsoon. However, there was a shift to sand dominated sediments during the monsoons which (up to 57.3±3.2% at Divar) could be attributed to the pre-dominance of terrestrial over tidal sediments [25].

Seasonal variation in heavy metal at Tuvem and Divar is depicted in Table 2. Seasonal fluctuation in concentration of metals was highly significant ($p< 0.001$; df=2) at both the sites. During the pre-monsoon, the maximum concentration of Fe at Tuvem was 7.1% while at Divar it was almost 5 times higher at 32.3%. The concentration of Fe observed at Divar was higher than the values reported by Nair et al., [26] in the Ashtamudi estuary (0.11 to 0.39%) and Thomas et al., [11]. along the Kerala coast (Table 3). A study by Alagarsamy [15] has shown that the concentration of Fe in the Mandovi estuary varies from 2.2 to 49.7%. An estuarine station in proximity to our study area (Divar) has reported maximum values of Fe to be approximately 12%. These high values of Fe in the mangrove sediment of Divar could be attributed to the precipitation of the respective metal sulfide compounds in anaerobic sediments [27]. These sulfides form a major sink for the heavy metals. Similarly, Mn concentrations at Divar were also higher as compared to Tuvem at maximum concentrations of 0.28%. These high concentrations of Mn and Fe at Divar could be explained by the the strong association of the geochemical matrix between the two elements. This association is not unusual and has been previously recognized by several authors [28, 29].

Concentration of Pb varied from 11.4 to 28.1 µg $g^{-1}$ at Tuvem and 7.9 to 50.5 µg $g^{-1}$ at Divar. As observed in Table 2, the present values were comparatively high at Divar during pre-monsoon and post-monsoon season which might be ascribed to river-borne sources [30], ore mining [15] and agriculture practices in the basin [31]. Lead(Pb) concentration in clean coastal sediments is around 25 µg $g^{-1}$ or less [32] and average Pb values in Indian River sediments is about 14 µg $g^{-1}$ [33]. However the present values are below the USEPA (1996) prescribed maximum values of 90 µg $g^{-1}$ for non-polluted sediments [34]. The values observed in the present study, are also lower in comparison to the values reported in Kerala mangroves [11] and Tamil Nadu mangrove sediments [12] (Table 3). While the concentration of Cu, Co, Cr and Zn were 49.5 µg $g^{-1}$, 32.45 µg $g^{-1}$, 28.25 µg $g^{-1}$ and 64.25 µg $g^{-1}$ respectively at Tuvem, and almost double these values were recorded at Divar. Our values are lower than those reported from Maharastra, where lethal concentration (LC50) have been assessed by Chourpagar and Kulkarni [35] for *Barytelphusa cunicularis*. Intensive anthropogenic activities such as mining in the upstream of Mandovi estuary, ferry services, sewage drainages from the mainland and other commercial activities are likely to be potential sources for the enrichment of these metals at Divar. Increased levels of metals like copper are known to accompany sewage sludge [36]. The enrichment of copper and cobalt in the mangrove sediments of Divar and Tuvem may be due to association with land-derived input of organic matter. During the monsoon season at Divar, most of the metal concentrations were lower, as compared to the non monsoon seasons, due to the restriction of ore transportation in the monsoon season.

Table 1: Seasonal variation in physico-chemical parameters at Tuvem and Divar sediments

| | Tuvem | | | Divar | | |
|---|---|---|---|---|---|---|
| | Pre-monsoon | Monsoon | Post-monsoon | Pre-monsoon | Monsoon | Post-monsoon |
| pH | 6.82±0.08 | 6.96±0.11 | 6.98±0.13 | 6.84±0.17 | 6.98±0.08 | 6.88±0.08 |
| TOC | 4.09±0.74 | 1.40±0.29 | 3.38±0.43 | 2.29±0.76 | 3.33±0.80 | 1.29±0.27 |
| C:N | 9.22±0.4 | 11.07±2.24 | 11.81±1.03 | 2.7±1.9 | 14.6±0.4 | 6.01±1.2 |
| Sand | 4.41±0.98 | 39.18±5.12 | 6.36±1.80 | 31.7±14.1 | 57.3±3.2 | 21.5±2.8 |
| Silt | 27.5±3.01 | 21.5±5.10 | 22.2±2.52 | 5.41±2.32 | 26.05±2.72 | 21.5±2.8 |
| Clay | 68.1±2.18 | 39.3±1.01 | 71.5±2.22 | 62.8±14.6 | 16.8±5.1 | 57±3.37 |

Total organic carbon (TOC), and grain size content have been expressed as %.

Table 2: Seasonal variation in concentrations of heavy metals (±SD) at Tuvem and Divar

| | Tuvem | | | Divar | | |
|---|---|---|---|---|---|---|
| | Pre-monsoon | Monsoon | Post-monsoon | Pre-monsoon | Monsoon | Post-monsoon |
| Fe | 6.93±0.34 | 6.93±0.22 | 4.41±0.42 | 29.85±2.51 | 8.10±1.43 | 16.90±1.69 |
| Mn | 0.11±0.007 | 0.18±0.003 | 0.097±0.01 | 0.25±0.03 | 0.15±0.04 | 0.16±0.009 |
| Cu | 32.75±3.84 | 39.54±4.65 | 46.35±2.23 | 34.95±3.93 | 78.30±10.15 | 40.15±5.98 |
| Zn | 43.65±5.35 | 49.44±10.38 | 36.93±6.21 | 91.25±3.61 | 101.2±17.12 | 114.65±8.65 |
| Cr | 24.43±14.10 | 18.85±4.21 | 5.1±2.10 | 27.65±6.0 | 17.55±2.30 | 10.35±2.75 |
| Co | 27.86±3.47 | 21.90±2.60 | 27.57±3.88 | 39.31±5.01 | 56.44±5.41 | 33.12±2.35 |
| Pb | 13.18±3.61 | 24.03±5.38 | 18.74±4.37 | 36.59±11.50 | 12.87±3.71 | 29.65±4.84 |

Except for Fe & Mn, values for total metal content have been expressed as µg $g^{-1}$ (n=5 at each sampling).

Table 3: A comparison of heavy metals (µg. $g^{-1}$) reported from mangrove ecosystems in India

| Location | Fe (%) | Mn (%) | Cu | Co | Cr | Pb | Zn | Reference |
|---|---|---|---|---|---|---|---|---|
| Kerala | 4.7-12.1 | 0.032-0.11 | 652-845 | 159-261 | | 1800-1950 | 1550-2372 | [11] |
| Tamil Nadu | 0.45-0.47 | 0.04-0.33 | 34-58 | 21-44 | 1.45-2.7 | 16-95 | | [12] |
| Bay of Bengal | 0.18-2.69 | 0.02-0.06 | 7-44 | 6-14 | 24-111 | 9-28 | 44-163 | [37] |
| Tuvem,Goa | 3.9-7.4 | 0.09-0.17 | 27.3-49.5 | 18.4-33.1 | 3-28.3 | 11.4-28.1 | 29.5-64.3 | Present study |
| Divar,Goa | 6.5-32.3 | 0.15-0.28 | 31.8-94.3 | 31-63.7 | 7.8-36.8 | 7.9-50.5 | 79.5-123.3 | Present study |

Fe and Mn have been expressed as %.

Table 4: Screening quick reference table (SQuiRT) for metals in marine sediments (Buchman, 1999).

| Elements | Background | Threshold effect level (TEL) | Effect range low (ERL) | Probable effect level (PEL) | Effect range medium (ERM) | Apparent effect threshold (AET) |
|---|---|---|---|---|---|---|
| Fe (%) | | - | - | - | - | 22 (Neanthes) |
| Mn | | - | - | - | - | 0.026 (Neanthes) |
| Cu | 10.0–25.0 | 18.7 | 34 | 108 | 270 | 390 (Microtox and oyster larvey) |
| Zn | 7.0–38.0 | 124 | 150 | 271 | 410 | 410 ( Infaunal community) |
| Cr | 7.0–13.0 | 52.3 | 81 | 160 | 370 | 62 (Neanthes) |
| Co | | - | - | - | - | 10 (Neanthes) |
| Pb | 4.0–17.0 | 30.2 | 46.7 | 112 | 218 | 400 |

Except for Fe and Mn which have been expressed as %, concentration of other metals is in μg $g^{-1}$. ; Threshold effect level (TEL) = Maximum concentration at which no toxic effects are observed; Effects range low (ERL) = 10th percentile values in effects or toxicity may begin to be observed in sensitive species; Probable effects level (PEL) = Lower limit of concentrations at which toxic effects are observed; Effects range median (ERM) = 50th percentile value in effects; Apparent effects threshold (AET) = Concentration above which adverse biological impacts are observed

### *Comparison with SQuiRT*

According to NOAA SQuiRT (Table 4), Mn and Co concentration were above the AET while Fe was below the AET at Tuvem for all three seasons. High Mn, Co and Fe indicate their possible toxicity which may impart an adverse effect on the biota [20]. Zinc and Cr were below TEL for all three season (Table 2) at this location. At Divar, though Cu was below ERL, the toxic effects due to high Fe, Mn and Co concentration were evident as they exceeded the AET throughout the study period.

### *Concentration factor (CF) and Pollution Load Index (PLI)*

At Tuvem, the concentration factor for elements such as Fe, Mn, Co and Cu were high (Table 5). The observed high values can be ascribed to the influence of external source (agricultural, sewage runoff, intense fishing or recreational boating activities). Based on an annual average, the CF values were found to fall in the following sequence:

Co > Mn > Cu > Fe > Pb > Zn > Cr

At Divar, except for Cr, CF values for most of elements analyzed were high (>1) for all the three seasons. However in Tuvem, Co showed higher CF values based on an annual average:

Co > Fe > Mn > Cu > Zn > Pb > Cr

According to the PLI, lower values imply no appreciable input from anthropogenic sources [38]. The present study showed that the values of PLI were 0.91 to 1.29 at Tuvem and 1.65 to 2.19 at Divar (Fig. 2) indicating that the anthropogenic input at Divar is far greater as compared to Tuvem.

Table 5: Seasonal variation in concentration factor of Fe, Mn, Co, Zn, Cu, Cr and Pb at Tuvem and Divar

| | Fe | Mn | Co | Zn | Cu | Cr | Pb |
|---|---|---|---|---|---|---|---|
| Tuvem (Chapora river) | | | | | | | |
| Pre-monsoon | 1.39 | 1.77 | 2.79 | 0.61 | 1.31 | 0.70 | 0.66 |
| Monsoon | 1.39 | 2.85 | 2.19 | 0.70 | 1.58 | 0.54 | 1.20 |
| Post-monsoon | 0.88 | 1.62 | 2.76 | 0.52 | 1.85 | 0.15 | 0.94 |
| Annual average | 1.22 | 2.08 | 2.58 | 0.61 | 1.58 | 0.46 | 0.93 |
| Divar (Mandovi estuary) | | | | | | | |
| Pre-monsoon | 5.97 | 4.01 | 3.93 | 1.29 | 1.40 | 0.79 | 1.83 |
| Monsoon | 1.62 | 2.56 | 5.64 | 1.43 | 3.13 | 0.50 | 0.64 |
| Post-monsoon | 3.38 | 2.69 | 3.30 | 1.61 | 1.61 | 0.30 | 1.48 |
| Annual average | 3.66 | 3.09 | 4.29 | 1.44 | 2.05 | 0.53 | 1.32 |

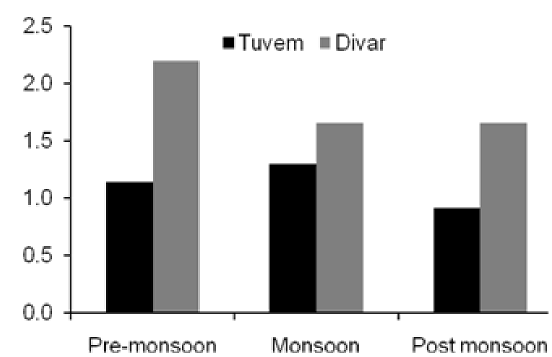


Fig. 2. Seasonal variation in Pollution Load Index at Tuvem and Divar.

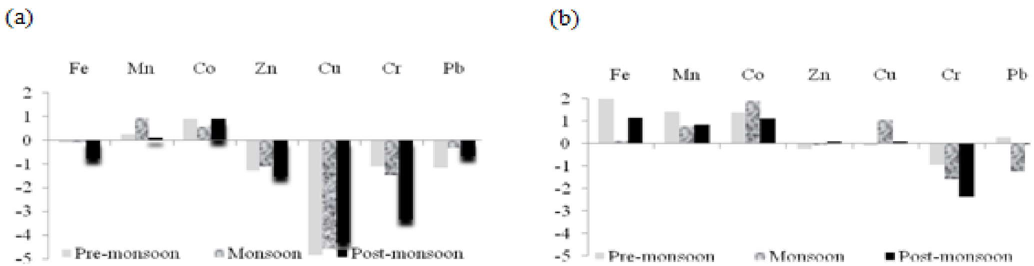


Fig. 3 . Geo-accumulation index for metals at Tuvem (a) and Divar (b).

*Geoaccumulation index*

The geoaccumulation index ($I_{geo}$) has been widely used as a measure of pollution in fresh water [39, 40] and marine sediments [32, 41]. Geo-accumulation index of different metals in Tuvem and Divar sediments is shown in Figs. 3a & b respectively. Crustal average values were taken as the baseline [42]. According to the $I_{geo}$ classification, it could be inferred that at Tuvem, Co and Mn were among "uncontaminated to moderately contaminated" category, while other metals fell in the uncontaminated group for all the seasons.

At Divar, the sediments were moderately contaminated by Fe, Mn and Co during pre-monsoon while Zn, Cu, Cr and Pb were below contamination levels. During monsoon, moderate contamination from Co and Cu was observed. Whereas in the post-monsoon, moderate contamination of Co was persistent along with Fe while, all the other metals showed no contamination to the benthic environment. As the concentration of metals increased, the eco-toxicological risk also increased for the benthic organism and there is a possible transfer to higher trophic levels [20]. Vidya and Chandrasekaran [43] have shown that heavy metal concentration increase through various levels of food chain.

*Inter-elemental and physico-chemical parameter relationship*

In order to study the inter-elemental associations, the correlation coefficient of the elements were analyzed for Tuvem and Divar. The analysis was carried out to understand the behavior of the metals during the transport to the mangrove ecosystem and to find out the source of origin of the metals. A positive correlation ($r=0.56$, $p<0.01$, $n=15$) was observed to exist between Fe and Mn at Tuvem (Table 6a), probably due to the strong association within the geochemical matrix of the two elements. The weak association of Mn with metals like Co, Zn and Cu suggest that Mn oxide may only be a minor host phase [15] for these elements in mangrove sediments of Divar. The variation in Fe was responsible for about 68% variation in the concentration of Mn ($r=0.82$, $p<0.001$, $n=15$; Table 6b). Fe-Mn mining upstream the Mandovi estuary, could be attributed to be a major source for the abundance of these elements in the Divar mangrove swamps. Fe also exhibited a positive correlation with Pb ($r=0.77$, $p<0.001$) and Cr ($r=0.53$, $p<0.001$) suggesting the adsorption of these elements by amorphous Fe-oxyhydroxide. Here, a significant correlation of C: N ratio with Cu ($r=0.93$, $p<0.001$), Co ($r=0.76$, $p<0.001$) and TOC ($r=0.60$, $p<0.01$) was also observed (Table 6b). In general, low C: N values of 5-7 are characteristic for marine organic matter [44] and values higher than 20 indicate a terrestrial source [45]. Except during the pre-monsoon season at Divar, C: N values recorded in the present study indicate considerable terrestrial influence at both the locations affirming the possible land-derived origin of these elements in the estuarine complex.

Table 6(a): Correlation matrix (r) for elements, organic carbon, sand, clay, silt, pH and C/N ratio at Tuvem (n=15). Significant r values have been highlighted in bold.

| | Fe | Mn | Co | Zn | Cu | Cr | Pb | TOC | Sand | Clay | Slit | pH | C/N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | 1 | | | | | | | | | | | | |
| Mn | 0.561 | | | | | | | | | | | | |
| Co | -0.246 | -0.683 | | | | | | | | | | | |
| Zn | 0.521 | 0.541 | -0.407 | | | | | | | | | | |
| Cu | -0.693 | -0.080 | -0.196 | -0.008 | | | | | | | | | |
| Cr | 0.674 | 0.200 | -0.048 | 0.070 | -0.774 | | | | | | | | |
| Pb | 0.091 | 0.559 | -0.386 | 0.162 | 0.276 | -0.052 | | | | | | | |
| TOC | -0.226 | -0.826 | 0.557 | -0.321 | -0.194 | -0.150 | -0.598 | | | | | | |
| Sand | 0.429 | 0.946 | -0.623 | 0.387 | -0.013 | 0.169 | 0.600 | -0.918 | | | | | |
| Clay | -0.554 | -0.988 | 0.672 | -0.567 | 0.066 | -0.190 | -0.568 | 0.856 | -0.967 | | | | |
| Slit | 0.258 | -0.224 | 0.074 | 0.459 | -0.174 | 0.006 | -0.342 | 0.568 | -0.502 | 0.265 | | | |
| pH | -0.343 | 0.164 | -0.119 | 0.279 | 0.521 | -0.458 | 0.227 | -0.214 | 0.215 | -0.182 | -0.197 | | |
| C/N | -0.268 | 0.326 | -0.288 | 0.461 | 0.711 | -0.501 | 0.588 | -0.387 | 0.289 | -0.326 | 0.014 | 0.710 | 1 |

Table 6(b): Correlation matrix (r) for elements, organic carbon, sand, clay, silt, pH and C/N ratio at Divar (n=15). Significant r values have been highlighted in bold.

| | Fe | Mn | Co | Zn | Cu | Cr | Pb | TOC | Sand | Clay | Silt | pH | C/N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | | | | | | | | | | | | | |
| Mn | 0.824 | | | | | | | | | | | | |
| Co | -0.540 | -0.251 | | | | | | | | | | | |
| Zn | -0.375 | -0.393 | -0.247 | | | | | | | | | | |
| Cu | -0.799 | -0.435 | 0.844 | 0.035 | | | | | | | | | |
| Cr | 0.539 | 0.563 | 0.110 | -0.614 | -0.161 | | | | | | | | |
| Pb | 0.779 | 0.545 | -0.720 | -0.169 | -0.831 | 0.207 | | | | | | | |
| TOC | -0.342 | 0.043 | 0.777 | -0.298 | 0.785 | 0.361 | -0.602 | | | | | | |
| Sand | -0.556 | -0.290 | 0.869 | -0.175 | 0.834 | 0.205 | -0.816 | 0.856 | | | | | |
| Clay | 0.812 | 0.564 | -0.841 | -0.053 | -0.921 | 0.109 | 0.892 | -0.729 | -0.925 | | | | |
| Silt | -0.938 | -0.828 | 0.438 | 0.438 | 0.690 | -0.639 | -0.651 | 0.186 | 0.391 | -0.712 | | | |
| pH | -0.377 | -0.017 | 0.355 | 0.029 | 0.524 | -0.322 | -0.116 | 0.385 | 0.199 | -0.319 | 0.406 | | |
| C/N | -0.920 | -0.677 | 0.768 | 0.153 | 0.936 | -0.279 | -0.843 | 0.605 | 0.783 | -0.930 | 0.806 | 0.428 | 1 |

## Conclusion

The impact and consequences of mining activities has caused extensive damage to the marine environment in Goa. The geo-accumulation index, contamination factor and PLI used to examine the intensity of metal pollution in the two tropical mangrove sediments in Goa, revealed high pollution in the anthropogenically-influenced site Divar as compared to the relatively pristine site of Tuvem. Mining activities in upstream locations of the adjoining Mandovi estuary, transportation of ferromanganese ore through the estuarine channel and sewage discharge are mostly accountable for the high pollution levels observed at Divar. Government and non-government organization including the local scientific communities need to be vigilant and initiate appropriate environmental pollution monitoring schemes to keep a check on the contamination of these indispensable mangrove ecosystems. These measures would help in minimizing heavy metal toxicity in these coastal estuarine ecosystems, especially the delicate and sensitive mangrove fringes.


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