



## Geochemistry of metals in grain size fractionated sediments from estuarine and coastal regions along Mumbai: A baseline information

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Differential metal accumulation in fractionated sediments within highly urbanized land-sea ecosystems is significant, often due to an imbalance between sluggish hydrodynamics and over dumping of contaminants. Here, an initial constraint on differential metal enrichment in fractionated sediments is highlighted along the estuary, creek, and nearshore regions of one of India's highly urbanized regions, Mumbai. Sediments were segregated into four fractions (A: < 25  $\mu\text{m}$ ; fine, B: 25 – 63  $\mu\text{m}$ ; moderate, C > 63  $\mu\text{m}$ ; coarse, and D: bulk) using the wet-sieving technique and were analysed for 23 metals. The results indicated that bulk sediment (D) constituted a moderate enrichment of transition metals Cr, Co, Ni, Cu, Hg, and Tl. The Distribution Factor (DF) indicated that metals such as Cr, Co, Ni, Cu, and Zn frequently showed  $DF > 1$  in fraction C. The reason for higher concentration of these metals in fraction C is indicative to weak tidal influence, that resist the flow of the higher density fraction and increases its residence time in the anthropogenically stressed region. Grain size showed a notable dominance of silt (> 80 %), mainly transported from the mudflats. Turbulence caused by activities such as periodic deepening, high-frequency vessel movement, and other modernization activities provoked the transport of fine particles. Considering that weak dynamic sediment transportation is mainly conducive to man-made changes, the association-dissociation of metals in size-specific sediment particles will significantly impact their further transport and cycling.

[**Keywords:** Anthropogenic activity, Aquatic pollution, Geological indices, Metal enrichment, Mumbai]

### Introduction

The transport and accumulation of metals have distinctive relationships with sediment textural characteristics in estuarine and coastal environments. In general, the finer fraction of sediment with a greater surface area has a higher potential for metal association than the coarser fraction<sup>1,2</sup>. The association of metals with sediment particles is predominantly due to sorption, complex formation, surface coating and coprecipitation<sup>3</sup>. Therefore, these mechanisms often gauge the impact of anthropogenic activities that cause metal enrichment in estuarine and coastal sediments. The metals associated with coarse (> 63  $\mu\text{m}$ ) fraction of sediment are often indicative of accumulation due to anthropogenic activities, which are due to the effects of prolonged particle residence time, weak transportation capacity, and poor hydrodynamic sorting in estuarine and coastal environment<sup>4</sup>. However, the higher concentration of metal adsorbed on the coarser fractions may be a consequence of agglomerate formation by finer particles<sup>5</sup>. Assessing the contents of metals associated with fractionated sediments in the estuarine and coastal environments will help to delineate the information on their further transport and

potential role in the aquatic ecosystem. This is because metals can be remobilised into the water column due to organic chelators or changes in physicochemical characteristics such as pH, temperature, nutrient load, turbidity, dissolved organic matter, and redox potential<sup>6</sup>. In addition to textural properties, the organic matter content also plays an essential role in the variation of metal enrichment in the sediment. In the present study, a preliminary attempt is made to understand the concentration of metals associated with different grain size fractions of sediments in anthropogenically affected tropical aquatic environment of west coast India.

With a coastline of more than 7,500 km, tropical peninsular India houses numerous coastal megacities, which have experienced rapid growth in population, industries, and urbanization. These together strain the aquatic bodies in and around the megacities. Coastal regions, creeks, and estuarine ecosystems located near these cities are often regarded as dumping sites for waste generated through various anthropogenic activities and are ultimately carried to the sea. One such hotspot on the central west coast of India is Mumbai, the country's financial capital, with a

population of 17 million (Census data). With numerous creeks and estuaries, the island city extends along a sizable coastal stretch of the Arabian Sea that covers 600 km<sup>2</sup>. The city of Mumbai has a tremendous strain of air pollutants, land-based runoff, domestic and industrial waste discharged into the aquatic ecosystems located in the vicinity<sup>7</sup>. Pollutants resulting from maritime traffic and ship-based discharge of two largest ports (JNPT and MbPT) also add to the list of pollutants. The city and suburban areas account for nearly 60 % of India's entire industry relative to fertilizer, pharmaceutical, chemical, and petrochemical production. These industries are closely connected to the Arabian Sea through the Thane Creek and Amba Estuary<sup>8</sup>.

The waters off Mumbai receive an average of 5.47 tons/day of metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd) through inland wastewaters<sup>9</sup>. The domestic discharge of wastewater accounts for up to  $2.2 \times 10^6$  m<sup>3</sup>/day in the region<sup>7</sup>. Most of the pollutants discharged through particulate and dissolved phases of the river and land runoff disproportionately sink into the sediments of estuaries and creeks in this region, which are later transported to the coastal region during the monsoon season. Pollutants released in the particulate phase are unlikely to have been deposited in the same area of discharge. However, the deposition pattern tends to vary according to the wave action, circulation, or turbulence of the water in the aquatic ecosystem<sup>10</sup>. Owing to a substantial residence period (almost during entire non-monsoon seasons) in the estuary and creek, the sediments in these regions hold robust control of the associated metals and other pollutants, which nonetheless affect the estuarine and creek ecosystems, as well as the surrounding region, during lateral and/or tidal advection<sup>11-12</sup>.

Information on the association between sediment texture and adsorption control of associated metals in estuarine and creek sediments has been sparsely addressed in previous studies<sup>13-14</sup>. In this study, an attempt is being made to analyze the relationship between the adsorbed metal content and grain size of the sediments. The concentration of metals associated with four grain size fractions *viz.* A (< 25 µm), B (25 – 63 µm), C (> 63 µm), and D (bulk sediment) were studied in sediments from three different environments (estuary, creek, and nearshore regions) with the objectives of (i) identifying their compositional pattern, (ii) assessing the metal contamination for bulk sediment through geological

index, (iii) identifying the adsorption potential, and (iv) assessing the level of pollution in bulk sediment.

## Materials and Methods

### Study area description

The Thane Creek adjoining the metropolitan city of Mumbai in the state of Maharashtra constitutes a nearshore region. The coastal region around Mumbai is biologically productive, with a fishery production of approximately 2,500 tons/yr<sup>15</sup>. In addition, the region is densely populated and houses approximately 25 large, 300 medium-, and small-scale industries that utilize hazardous chemicals<sup>11</sup>. The effluent discharge (treated and untreated) amounts to 28,750 m<sup>3</sup>/day, accounting for 64 % of the total industrial effluents generated in the Thane Creek area<sup>16</sup>. Apart from industrial waste, a considerable quantity ( $1.26 \times 10^3$  m<sup>3</sup>/day) of partially treated domestic sewage is discharged into the Thane Creek and Mumbai harbor system. Adjoining the creek is the Amba and Patalganga Estuaries, contributing an anthropogenic load of 6500 m<sup>3</sup>/day and 10,000 m<sup>3</sup>/day, respectively<sup>17</sup>. These drainages, along with harbor activities, domestic land runoff, and industrial waste, debouche the Eastern Arabian Sea due to diurnal tides with a speed range of 0.05 – 0.35 m/s<sup>(refs. 17, 48)</sup>.

### Sampling and pre-treatment

Spatially distributed sediments were collected along the estuary (E1, E2, and E3), creek (C1 and C2), and nearshore regions (M1 and M2) (Fig. 1). Sediment samples were collected during the pre-monsoon (March, 2019) using a Van-veen grab operated by a mechanized boat. The top 0 – 10 cm of the surficial sediment was collected immediately, avoiding contamination, and stored in acid-cleaned polythene container at 4 °C until further analysis. The sediments were oven-dried at 45 °C in the laboratory. To determine the bulk content (D) of the metals, sediments were homogeneously powdered and stored separately. Segregation of fractions A, B, and C was carried out with 25 g of dried-ungrounded sediment and 200 ml of Milli-Q water in a Perfluoro Alkoxy (PFA) beaker. The stirred sediment slurry was then passed through a 63 µm stainless steel sieve to collect fraction C. The residue was then passed through a 25 µm stainless steel sieve to collect fractions B and A. The fractions collected with Milli-Q water were centrifuged at 5000 rpm for 15 min, dried, and homogenized before chemical analysis. All apparatus

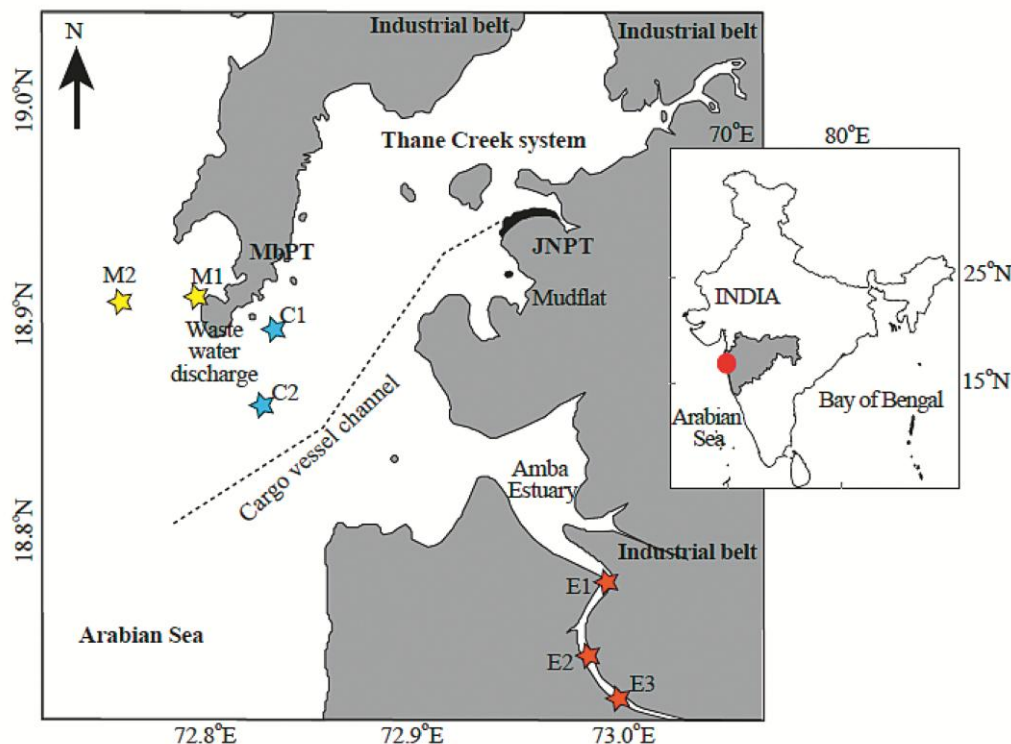


Fig. 1 — Map indicates spatial view of study areas selected for study along Mumbai, western coast of India, the hydrodynamic study in creek region pointed current speed towards 0 – 1.4 m/s. While in estuary, current speed was noted from 0 – 1.4 m/s (Velamala *et al.*<sup>17</sup>); both indicating tidal influence

used during the treatment were carefully handled and pre-cleaned using 1N supra-pure Nitric Acid (HNO<sub>3</sub>; Merck, Germany) and dried to avoid contamination.

#### Grain size analysis

The grain size of sediment was measured using the wet-sieving method described in Konert & Vandenberghe<sup>18</sup>. Briefly, 25 g of dried sediment was added to the 100 mL of 5 % solution of sodium hexametaphosphate Na<sub>6</sub>[(PO<sub>3</sub>)<sub>6</sub>]. The resulting slurry was stirred and passed through a 63 μm sieve. The slurry, containing a mixture of silt and clay was then transferred to a 1000 mL measuring cylinder. Silt (25 – 63 μm) was collected immediately from the upper 20 cm level, whereas clay (0 – 4 μm) was collected from the upper 10 cm layer of the measuring cylinder according to Stokes' law of density separation. Later, the isolated fractions were dried, weighed, and grain size distribution (%) was calculated using the formula described in Ramaswamy & Rao<sup>19</sup>.

#### Metal analysis

For the analysis of metals, powdered sediments (0.1 g) were digested using a mixture of acids

(3 mL HNO<sub>3</sub> + 2 mL HCl + 1 mL HF) using microwave digestion (Make: CEM, MARS) at 120 °C. The residue was then dissolved in 5 mL of HNO<sub>3</sub>, evaporated and diluted to 25 mL using 0.5 % HNO<sub>3</sub><sup>(ref. 20)</sup>. Reagent and equipment blanks were considered during digestion to monitor any cross-contamination by metal impurities. MESS-3 and PACS-3 were digested as Certified Reference Material (CRM) obtained from the National Research Council of Canada (NRCC). The ICP-MS (Make: Thermo Fisher, iCAP RQ) was employed in Kinetic Energy Discrimination (KED) mode to nullify polyatomic interferences for the determination of metals such as Be, V, Cr, Mn, Co, Ni, Zn, Sr, Y, Ba, Dy, Yb, Tl and, Pb. ICP-OES (Make: Perkin Elmer, Optima 3700 DV) was employed to determine metals such as Na, Mg, Al, K, Ca and, Fe. Mercury (Hg) analysis was performed in a concentration range of parts per billion (ppb) using the wet-digestion method<sup>47</sup> on a flow injection mercury system (Make: Perkin Elmer, FIMS-400). Phosphorous (P) was measured by an acid-molybdate method using a dual-beam spectrophotometer at 882 nm (Make: Lab India, UV 3200) method prescribed in Grasshoff *et al.*<sup>21</sup>. The

CRM values, as per the literature, are given in (Table 1).

**Geological indices**

The data generated were used to calculate the Distribution Factor (DF), Index of Geoaccumulation ( $I_{geo}$ ), and Pollution Load Index (PLI). The DF was calculated as follows: the  $DF > 1$  for any metal resembled enrichment in the respective fraction<sup>22</sup>.

$$DF_{metal} = \frac{\text{Concentration of metal in fraction A,B and C}}{\text{Concentration of metal in fraction D}}$$

The index of geo-accumulation was calculated following Muller<sup>23</sup> and Barbieri *et al.*<sup>24</sup>, with metal background value, as in the Upper Continental Crust (UCC)<sup>25</sup> with standard correction factor of 1.5 for lithogenic effects.

$$I_{geo} = \text{Log}_2 \frac{\text{Concentration of metals in fraction D}}{(1.5 \times \text{background value})}$$

Based on Contamination Factor (CF), which is the ratio of the concentration of individual metals in sediment and concentration in upper continental crust, the PLI was calculated as follows, where  $PLI > 1$  indicates load of pollution owing to anthropogenic activity<sup>23</sup>.

$$PLI = (CF_1 \times CF_2 \times \dots \times CF_n)^{1/n}$$

**Results and Discussion**

The characteristics of the geochemical constituents, such as grain size and metals in fraction D exhibited a small range of variation among the estuary, creek, and nearshore samples (Figs. 2 & 3). However, the limits of these constituents in fractions A, B, C and, D showed significant variations reflecting their differences in abundance (Tables 2) and grain size distribution (Table 3).

**Distribution of sediment grain size**

On average, the sedimentary grain size composition during this study was Silt > Clay > Sand, ranging between 50 – 92 %, 5 – 38 % and 0.7 – 11 %, respectively. The silt content was > 80 %, except at E3 station, whereas the composition of silt and clay was 50 % and 38 %, respectively. The percentage of sand in the sediment varied between 1 – 11 % (Fig. 2; Table 3). The water retention capacity varied from 41 to 52 %, calculated using the dry and wet weights of the sediment. Higher water retention resembles lower sand content, for example, at M2 station, while the

Table 1 — The Certified Reference Material (CRM) MESS-3 and PACS-3 procured from National Research Council of Canada, NRCC (Canada) was analyzed to verify % recovery between certificate of analysis and concentrations those observed by instruments used during the present analysis (ICP-MS, Thermo scientific, iCAP RQ) and ICP-OES (PerkinElmer, Optima 3700DV). Upper Continental Crust (UCC) values are given in the table. Representation - Metal concentration (µg/g), \* for (%), and " for (ng/g)

Metals	MESS-3 CRM	MESS-3 Observed	MESS-3* Recovery	PACS-3 CRM	PACS-3 Observed	PACS-3* Recovery	UCC <sup>(ref. 25)</sup>
Be	2.3	2.3	98.7	1.1	1.2	109.3	3.0
Na*	1.6	1.4	87.3	3.5	3.3	94.7	2.9
Mg*	1.6	1.7	106.3	1.5	1.4	95.2	1.3
Al*	8.6	8.2	95.5	6.6	6.4	97.1	8.0
P	1200	1298	108.2	...	...	...	700.0
K*	2.6	2.4	90.4	1.2	1.1	91.9	2.8
Ca*	1.5	1.3	88.4	1.9	1.8	96.3	3.0
V	243	214	88.1	129	122	94.6	60.0
Cr	105	102	96.7	92	82	89.1	35.0
Mn	324	311	96	425	410	96.4	600.0
Fe*	4.3	4.3	99.1	4.1	4.2	102.2	3.5
Co	14.4	14.6	101.2	12.1	12.9	106.7	10.0
Ni	46.9	41.8	89.1	39.9	35.8	89.7	20.0
Cu	33.9	31.8	93.8	327	306.9	93.9	25.0
Zn	129	138.8	107.6	379	363.2	95.8	71.0
Sr	159	143.6	90.3	268	258.6	96.5	350.0
Y	...	21.5	...	...	13.7	...	22.0
Ba	...	750.3	...	...	608.6	...	550.0
Dy	...	3.9	...	...	2.8	...	3.5
Yb	...	2.1	...	...	1.4	...	2.2
Hg"	...	...	...	...	...	...	50.0
Tl	...	2.7	...	...	2.6	...	0.7
Pb	21.1	22.3	105.7	188	161.8	86.1	17.0

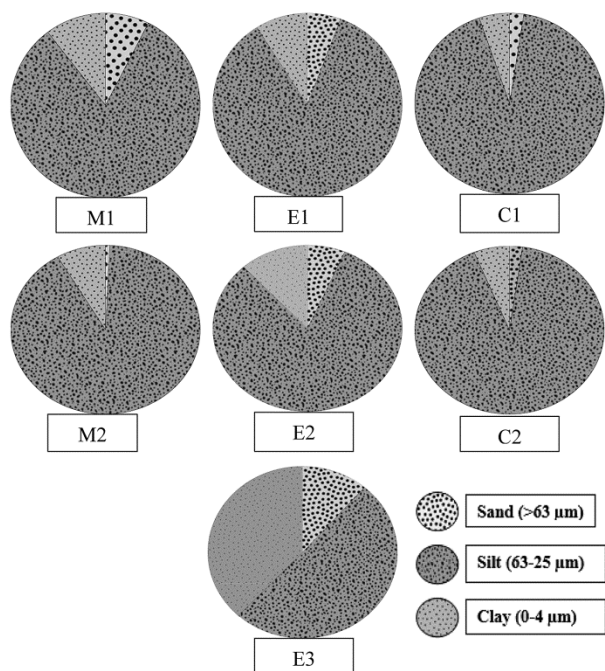


Fig. 2 — Pie chart explaining grain-size (%) of coarse, silt and clay present in sediments across different regions

opposite was observed at E3, where lower water retention resulted from higher sand content. The dominance of silt and clay has been attributed to fine sediment transportation from nearby mudflats<sup>26</sup>. Furthermore, weak hydrodynamic conditions increased the retention time of the sediment and favoured silt and clay transport by restricting sand transportation during the pre-monsoon period.

#### Geochemistry of metals

The metal concentration and respective DF in fractions A, B, C, and D in this study are presented in (Table 2 and Figs. 3 & 4). Previous studies have highlighted that the metal adsorption will be higher in the finer grain size, as they tend to have greater surface area<sup>2,27</sup>. The same phenomenon on the deposition of metals in finer fractions compared to coarser fractions has been observed in regions affected by weak dynamics, such as arid deserts<sup>28</sup>. However, the extent to which this information holds true in aquatic ecosystems cannot be ignored. The binding capacity of metals with different fractions was categorized using DF to sort the individual metal affinities to the respective fractions (Fig. 4). The DF values in fraction C for metals such as Ca and Sr at M1 station were 8.9 and 6.2, respectively. At M1, higher concentrations of other metals were observed

in fractions A and B, as the sediment had minimal exposure to tidal influences owing to the semi-enclosed bay. Higher enrichment for Ca and Sr found at M1 is indicative of higher assimilation of calciferous constituents<sup>29</sup>. At station M2, the highest DF was observed in fraction C for Ca, Cr, Co, Ni, Cu, Zn, Sr, which indicated substantial enrichment of metals in coarser sediment. Creek samples (C1 and C2) showed a similar phenomenon in the case of some metals (Mg, P, Ca, V, Cr, Mn, Co, Ni, Sr, Ba, Hg), indicating higher DF (> 1) in fraction C, while the rest of the metals (Be, Na, Al, K, V, Cu, Zn, Y, Dy, Yb, Tl, Pb) showed higher or equivalent DF in fractions A and B, as evident from the previous studies<sup>2,30</sup>. Lesser assimilation of metals in the finer fractions was the consequence of periodic deepening activities (e.g., dredging carried out to deepen the channel for transportation of cargo vessels along the commercial port, JNPT and MbPT) in the channel of creek, which generally enhances turbidity in water column resulting in mobilization of bed sediment and thereby transporting them towards the coastal region. The estuarine samples E1 and E2 showed enrichment of Mg, Ca, V, Cr, Co, Ni, and Hg in fraction C, and enrichment of Be, Al, P, K, Sr, Y, Ba, Dy, Yb, Tl, and Pb in fractions A and B (Fig. 4). E3 showed a nearly consistent distribution of metals in all three fractions, it could be due to the weak tidal influence in the upper estuary, where the bed sediment generally remains less disturbed. The distribution of Pb at all stations was notable, indicating strong adsorption towards finer grain sizes. Enrichment of Pb showed a similar trend in the entire study with considerable higher concentration in fraction A for all the respective stations. This highlights that Pb has consistent binding ability to finer grain sizes than the coarser fraction of sediment in the studied region<sup>31</sup>.

The higher DF for some metals in fraction C is influenced by anthropogenic processes such as sewage, land runoff, and effluents discharged in the water column<sup>32,33</sup>. These anthropogenic discharges enriched with metals further settle on the sediment bed. The metals adsorbed on finer grain fractions (A and B) are mobilized easily; however, the concentration of metals in coarser fraction C continues to accumulate due to restricted movement, thus prolonging its residence time in a particular region. A previous study also indicated the role of metal enrichment on coarser grain size, which results from land-based runoff and industrial effluents



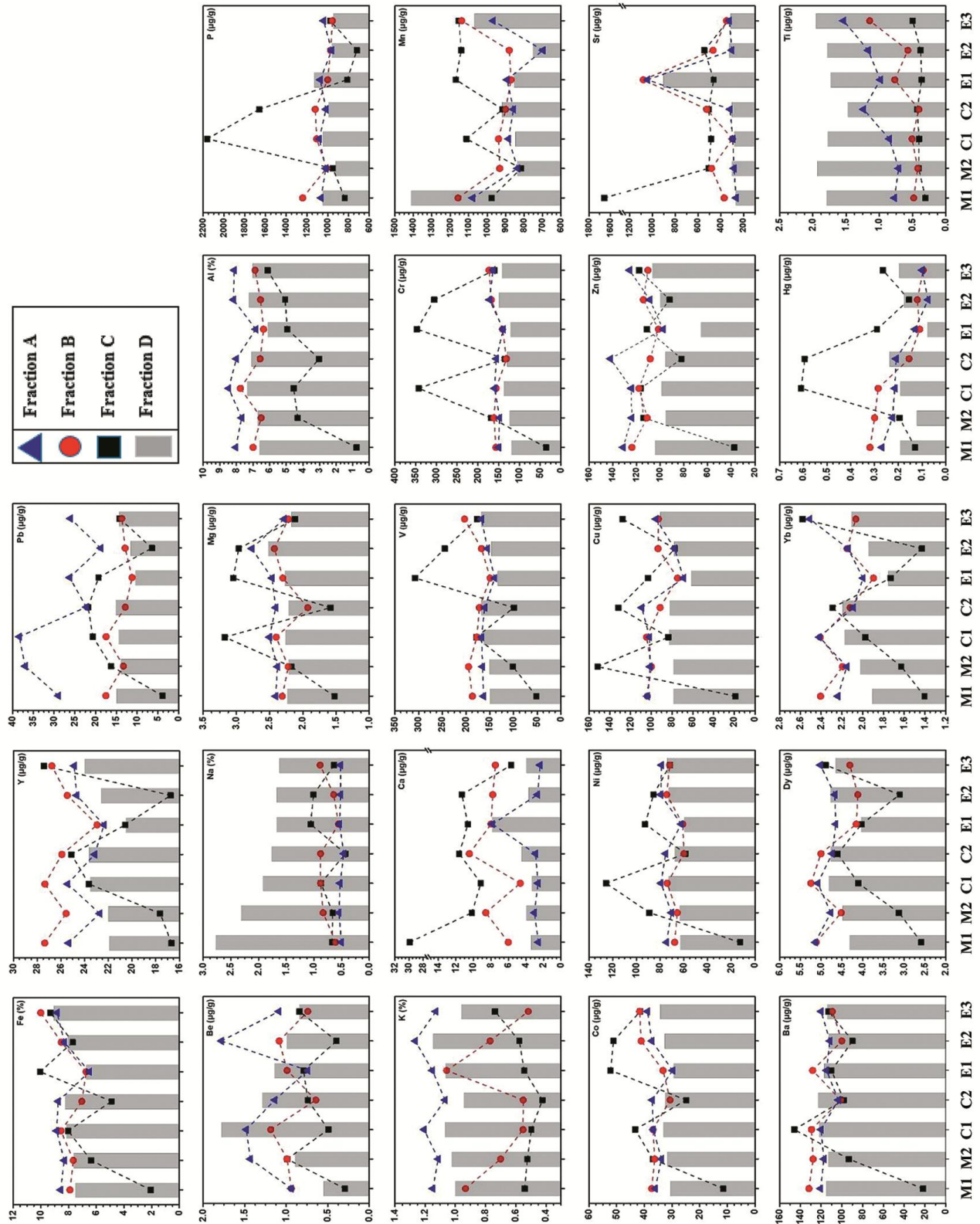


Fig. 3 — Scattered plot shows concentration of metal in individual grain size fraction (A, B and C) along with its comparison in bulk sediment (fraction D) and how the texture of sediment amounts to alteration of metal concentration in bulk sediment

Table 2 — Illustration of elemental concentration along different fractions indicating A (&lt; 25 µm), B (&gt; 25 – 63 µm), C (&gt; 63 µm) and D (bulk sediment) along aquatic ecosystem in Mumbai and its suburb, west coast of India

Id.	Type	Be µg/g	Na %	Mg %	Al %	P µg/g	K %	Ca %	V µg/g	Cr µg/g	Mn µg/g	Fe %	Co µg/g	Ni µg/g	Cu µg/g	Zn µg/g	Sr µg/g	Y µg/g	Ba µg/g	Dy µg/g	Yb µg/g	Hg* ng/g	Tl µg/g	Pb µg/g
M1	A	0.3	0.7	1.5	0.8	838	0.5	29.9	52.1	36.0	976.9	2.1	11.5	12.5	19.0	37.4	1657.0	16.7	21.9	2.6	1.4	129.7	0.3	3.9
	B	0.9	0.6	2.3	7.0	1242	0.9	6.0	186.7	156.6	1158.0	7.9	37.3	67.8	103.8	123.8	369.0	27.4	131.7	5.1	2.4	319.4	0.5	17.5
	C	0.9	0.5	2.4	8.0	1065	1.1	2.6	163.3	150.4	1079.0	8.6	36.1	74.6	103.7	131.3	265.0	25.4	120.6	5.1	2.2	269.4	0.8	29.0
	D	0.5	2.8	2.2	6.6	1046	1.0	3.4	150	118	1411	7.5	30.5	62.7	78.2	103.9	264.8	21.9	114.9	4.3	1.9	189.8	1.8	14.9
M2	A	1.0	0.7	2.2	4.3	952	0.5	10.2	101.3	168.3	817.0	6.4	37.0	89.0	151.7	114.0	507.0	17.6	93.4	3.1	1.6	195.3	0.4	16.3
	B	1.0	0.8	2.2	6.5	1013	0.7	8.6	194.8	161.5	932.2	7.7	36.2	65.5	99.9	110.9	481.0	25.6	127.7	4.5	2.2	299.9	0.4	13.3
	C	1.4	0.5	2.4	7.7	1010	1.1	3.0	165.4	147.9	835.6	8.3	33.8	70.4	101.2	123.9	284.0	22.7	117.4	4.8	2.2	224.8	0.7	37.0
	D	0.9	2.3	2.2	6.7	922	1.0	3.9	150	122	834	7.6	31.6	63.2	78.3	95.0	300.0	22.0	113.0	4.5	2.0	119.9	1.9	13.8
C1	A	0.5	0.9	3.2	4.6	2161	0.5	9.2	178.5	342.7	1112.0	8.0	43.3	125	83.5	116.3	485.0	23.6	145.8	4.1	2.0	609.3	0.4	20.7
	B	1.2	0.9	2.4	7.8	1107	0.6	4.7	177.5	156.3	938.1	8.6	36.9	74.1	104.4	117.9	297.0	27.3	129.2	5.2	2.4	284.7	0.5	17.5
	C	1.5	0.5	2.5	8.5	1082	1.2	2.6	167.3	160.1	884.2	8.9	36.8	79.3	101.6	124.3	295.0	25.4	120.2	5.1	2.4	214.9	0.8	38.4
	D	1.8	1.9	2.3	7.3	1044	1.1	3.3	162	137	845	8.1	32.9	72.5	82.4	98.4	279.1	23.5	121.7	4.8	2.2	190	1.8	14.3
C2	A	0.7	0.4	1.6	3.0	1661	0.4	11.6	99.6	135.4	916.5	4.9	24.8	58.6	131.5	82.0	507.0	25.1	98.3	4.6	2.3	594.0	0.4	21.8
	B	0.6	0.9	1.9	6.6	1122	0.6	10.5	171.9	131.3	900.5	7.0	30.7	59.9	91.5	108.3	524.0	25.9	101.3	5.0	2.1	154.9	0.4	12.9
	C	1.1	0.5	2.4	8.0	1018	1.1	2.9	161.1	155.7	857.8	8.8	37.1	75.4	109.1	141.9	318.0	23.2	103.4	4.7	2.1	209.7	1.2	22.3
	D	1.3	1.8	2.2	7.1	991	0.9	4.5	167	129	917	8.2	32.4	67.6	81.7	95.3	298.7	23.6	122.6	4.8	2.2	234.7	1.5	15.1
E1	A	0.8	1.1	3.0	4.9	813	0.5	10.6	307.5	347.3	1170.0	10.1	52.2	92.6	103.3	111.1	462.0	20.6	110.1	4.0	1.7	289.6	0.4	19.3
	B	1.0	0.6	2.3	6.4	1002	1.1	8.0	149.2	140.8	870.4	6.7	33.2	60.9	74.6	101.4	1080.0	22.9	128.2	4.2	1.9	109.9	0.8	11.2
	C	0.7	0.5	2.5	6.8	1073	1.2	7.8	139.6	139.2	892.7	6.5	29.8	62.2	68.9	97.5	1043.0	22.4	114.9	4.6	2.0	129.9	1.0	26.3
	D	1.1	1.7	2.3	6.1	1126	1.1	7.8	132	120	853	6.7	29.2	59.1	61.3	65.2	900.9	20.5	116.8	4.0	1.8	75.0	1.7	10.3
E2	A	0.4	1.0	3.0	5.1	720	0.6	11.3	244.7	305.0	1141.0	7.7	51.1	85.6	77.1	91.9	544.0	16.7	89.8	3.1	1.4	154.9	0.4	6.5
	B	1.1	0.6	2.4	6.6	974	0.8	7.8	167.5	167.8	880.4	8.5	41.1	74.5	93.5	114.1	468.0	25.5	100.0	4.1	2.2	120.0	0.6	12.9
	C	1.8	0.5	2.8	8.2	963	1.3	2.7	155.0	172.1	698.6	8.3	37.3	79.5	77.6	108.8	303.0	24.7	111.6	4.7	2.1	74.9	1.2	18.8
	D	1	1.7	2.5	7.2	956	1.1	3.6	146	149	750	8	32.5	72.6	77.4	99.5	321.4	22.6	112.4	4.8	1.9	174.8	1.8	11.5
E3	A	0.8	0.6	2.1	6.1	978	0.7	5.7	177.1	160.7	1154.0	9.3	41.6	71.7	127.7	117.7	335.0	27.4	112.8	4.9	2.6	264.9	0.5	14.2
	B	0.7	0.9	2.2	6.9	955	0.5	7.5	203.3	173.1	1138.0	10.0	41.7	71.9	93.1	110.3	350.0	26.8	109.1	4.3	2.1	94.9	1.1	13.7
	C	1.1	0.5	2.3	8.1	1041	1.1	2.4	167.4	163.8	967.6	8.8	38.8	78.9	95.3	125.8	325.0	24.9	120.1	5.0	2.5	100.0	1.5	26.1
	D	0.8	1.6	2.2	7	943	1.0	3.9	168	141	1068	9.1	34.1	73.9	91.0	106.2	309.5	24	114	4.7	2.1	194.9	2.0	14.3

accumulated in the sediment<sup>34</sup>. Therefore, it is partially true that only the finer-sized fractions have a higher affinity for metals. In the present study of urbanized aquatic systems, the coarser fraction (C) significantly contributed to higher metal accumulation, mainly conducive to weak tidal influence, which limits the transport of coarser sediment as compared to easy mobilization of finer fractions (silt and clay)<sup>35</sup>. Although, variation was observed in the distribution of metals in different grain sizes, the association-dissociation phenomenon of metal enrichments in fractions (A, B, and C) may alter due to change in physiochemical characteristics<sup>36</sup>, which happens temporally<sup>37,48</sup>. In addition, the relative decline of certain metals towards

finer fractions also corresponds to inadequate freshwater input during the pre-monsoon season, owing to high salinity resulting in further flocculation and transportation<sup>38,39</sup>. When the individual fraction was discussed with respect to metal concentration, it was worth considering the contribution of fractions to pollution load in the study region. Hence, compared with the UCC values<sup>25</sup>, fraction A of M1 showed the lowest value (< 1) for PLI, which is indicative of negligible pollution (Fig. 5). However, for the rest of the fractions along different locations, the PLI value ranged from 1.18-1.47 indicating anthropogenic metal pollution. Figure 5 reveals that PLI in bulk and fractionated sediments is > 1 highlighting metal pollution in the aquatic ecosystems. If the resulting

trend in PLI continues, the enrichment of non-essential and toxic metals (Pb and Hg) in species will greatly influence the biological food web and affect humans due to their dependency on aquatic diet<sup>40</sup>. Hence, it is important to understand the

disproportionate enrichment of metals in different fractions due to their bioavailability to the aquatic biota.

**Assessment of metal pollution**

The assessment of metal enrichment in bulk sediment (fraction D) across the studied ecosystems is a necessary parameter, considering the release of industrial and domestic land-runoff. Results obtained from Igeo calculated with respect to UCC indicated, alkali metals (Na, K) were  $\leq 0$  (uncontaminated) (Tables S1 & S2). Similarly, the concentrations of post-transition metals (Al and Pb) were in range of 6.1 – 7.2 % and 10.3 – 15.1  $\mu\text{g/g}$ , respectively, indicating  $I_{\text{geo}} \leq 0$ . However, the concentration of Tl was 1.5 – 1.9  $\mu\text{g/g}$  which is indicative of class 1

Table 3 — Average values (%) of grain size in bulk sediment along the study region

Id.	Sand	Silt	Clay	W. R
M1	7.5	82.1	10.4	44.5
M2	0.7	90.8	8.4	52.5
C1	2.4	92.4	5.2	49.6
C2	2.2	91.7	6.1	50.0
E1	5.7	85.4	9.0	48.6
E2	6.4	81.8	11.8	49.3
E3	11.3	50.5	38.2	40.9

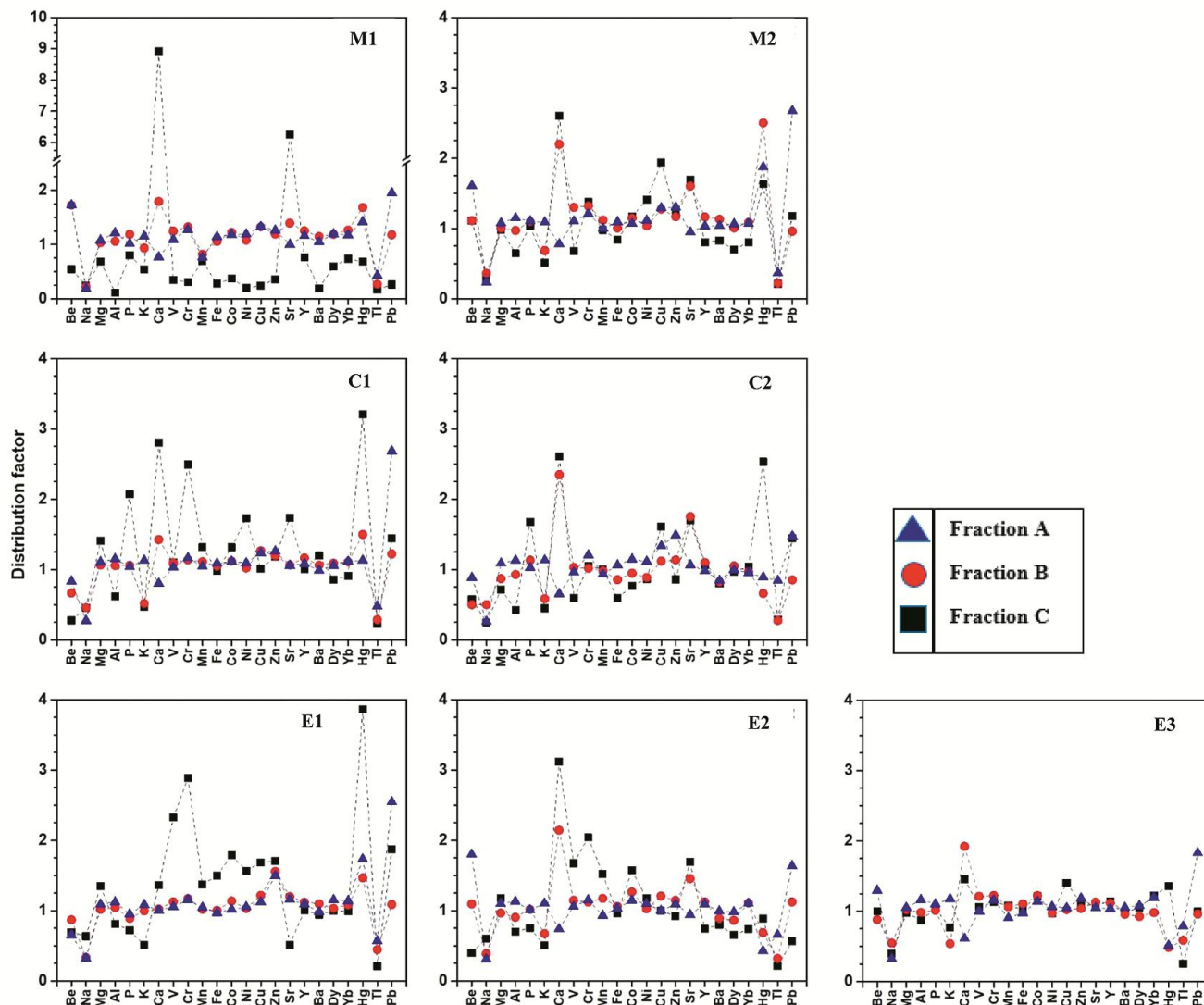


Fig. 4 — Scattered plot which shows enrichment of metals in different segregated fractions relative to distribution factor (DF); where,  $DF > 1$  signifies enrichment of certain element in respective grain size



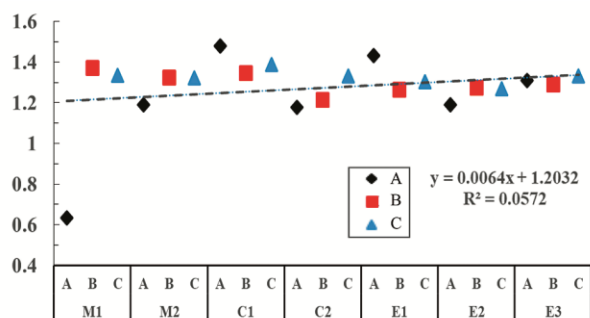


Fig. 5 — Variation in PLI across different fractions (A, B and C) of sediment along the study region

( $0 < I_{geo} < 1$ ) posing the risk of moderate contamination along the assessed locations. Although it is a non-essential element for metabolism in marine organisms, Tl is plausibly a high-risk toxic element when compared with other metals<sup>41</sup>, sourced from land runoff due to its use in sludge and fertilizer<sup>42</sup>. The presence of Tl in the study region can be attributed to industrial discharges and atmospheric deposition through fuel and coal combustion<sup>41</sup>, which is prominent in the region.

The risk of geo-accumulation in total sediment from alkaline earth metals (Be, Mg, Ca, Sr, Ba) was  $\leq 0$ , indicating uncontaminated sediment, with the respective concentration range of 0.5 – 1.8  $\mu\text{g/g}$ , 2.2 – 2.5 %, 3.4 – 7.8 %, 264.8 – 900.9  $\mu\text{g/g}$ , and 114 – 122  $\mu\text{g/g}$ , respectively. Knowing the significance of these metals for assimilation in marine species<sup>29</sup>, anthropogenic levels of alkaline earth metals were negligible. Whereas, the accumulation of studied transition metals was divided into three categories, for example, category-I (V, Mn, Fe) indicating class ( $0 < I_{geo} < 1$ ) metals indicating uncontaminated to moderately contaminated with concentrations differing from 132 – 168  $\mu\text{g/g}$ , 750 – 1411  $\mu\text{g/g}$ , and 6.7 – 9.1 %, respectively. Category-II (Zn, Y), which indicated zero accumulation in sediments than UCC ( $I_{geo} \leq 0$ ), showing the negligible potential of accumulation with concentrations varying from 63.2 – 106.2, and 20.5 – 24.0  $\mu\text{g/g}$ , respectively. Category-III (Cr, Co, Ni, Cu, Hg) were moderately contaminated ( $1 < I_{geo} < 2$ ), with the concentration ranging from 118 – 149  $\mu\text{g/g}$ , 29.2 – 39.9  $\mu\text{g/g}$ , 59.1 – 73.9  $\mu\text{g/g}$ , 61.3 – 82.4  $\mu\text{g/g}$ , and 75.0 – 234.7 ng/g, respectively. The PLI indicated a range of (1.27 – 1.38) for all the fractions, which is considered polluted. However, comparing the present study and other studies conducted in the Manori Creek, the PLI was in the range of 1.64 – 2.54<sup>(ref. 43)</sup>, higher than PLI

obtained during the present study. Anthropogenic land runoff, harbour activities, and domestic and industrial discharges act as a source of these metal pollutants<sup>44</sup>. Also, the atmospheric pollutants that precipitate and bind to suspended particulates of aquatic bodies are retained on sediment bed because of their accumulative behaviour<sup>45</sup>. Owing to heavy industrial and domestic discharges, weak tides, and turbulence, the creek and estuary must have enhanced sedimentary metal deposition. However, the moderate deposition observed in the study may likely be impacted by activities such as periodic deepening, which frequently resuspend the bed sediments and promote the transportation of metals predominantly associated with finer grain sizes into the sea<sup>44</sup>. Moderate deposition of pollutants may also be observed from weak hydrodynamic conditions in the study region, which enhances the ability to balance between pollutants released and their adequate dispersion and dilution during the tidal impact<sup>46</sup>.

A significant relationship between fractions (A, B, and C) reveals that any individual fraction may have differential metal accumulation. However, percentage of respective fraction is responsible for governing the concentration of metal concentration in the bulk sediment (fraction D). The grain size composition of bulk sediment in this study had a dominant fraction of silt ( $< 63 - 25 \mu\text{m}$ ) at all stations; therefore concentration of bulk sediment will be governed by silt. Although, the fraction C contributes to a higher concentration of some metals, its role in determining the metal concentration in bulk sediment is insignificant due to lower percentage of coarser fraction (0.7 – 11.3 %). As the concentration of metals in the bulk sediment is always reflective of the relative abundance of a specific grain size, which in present study are fractions A and B.

## Conclusion

The Distribution Factor revealed that the coarser fraction (C) is also enriched with metals. This enrichment of metals is often due to their adsorption capacity, owing to the higher residence time and lower transport rate in urbanized land-sea ecosystems. However, the lower proportion (%) of the coarser fraction in the bulk sediment plays an insignificant role in determining the fate of pollution because finer grain sizes, mainly silt, dominate this region. Moderate contamination ( $I_{geo}$ ) of metals such as Tl, Cr, Co, Ni, Cu, and Hg exists in the bulk sediment

across the study region, which may cause a potential threat to the aquatic life upon uptake.

Based on snapshot observations, natural sediment transport, weak fluvial dynamics, and anthropogenic sedimentary disturbances together cause the displacement of sediment with disproportionately varying grain sizes. Hence, metal concentrations among fractions can be unequally distributed and have a significant impact on the status of the aquatic environment.

### Supplementary Data

Supplementary data associated with this article is available in the electronic form at [https://nopr.niscpr.res.in/jinfo/ijms/IJMS\\_51\(12\)961-972\\_SupplData.pdf](https://nopr.niscpr.res.in/jinfo/ijms/IJMS_51(12)961-972_SupplData.pdf)

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### Conflicts of Interest

Authors assures no conflicts of interest.

### Ethical Statement

This is to certify that the reported work in the manuscript entitled "Geochemistry of metals in grain size fractionated sediments from estuarine and coastal regions along Mumbai: a baseline information" submitted for publication is an original one and has not been submitted for publication elsewhere. We further certify that proper citations to the previously reported work have been given and no data/table/figure has been quoted verbatim from other publications without giving due acknowledgement and without the permission of the authors. The consent of all the authors of this paper has been obtained for submitting the paper to the "Indian Journal of Geo-Marine Sciences".

### Author Contributions

UKP & SL: Method development and validation, field execution, laboratory analysis and preparing draft original manuscript. AR: Editing, reviewing, and mentoring. SL, PBU & BS: Reviewing, sampling, modifying figures and apparatus acquisition. The

respective authors have read, reviewed the final manuscript.

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