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Research Article

Spatial distribution and enrichment of heavy metals in nearshore surface sediments off Netravati–Uppala, southwestern India

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Offshore surface sediments were collected along the south Karnataka coast of India, from the Netravati River mouth to Manjeshwar, to investigate the spatial distribution of metals. Average concentration of the metals in the 90 km^2 area followed the order Cd < Pb < Co < Cu < Ni < Zn < Cr < Sr < Mn < Mg < Ti < Ca < Fe < Al. Trace metal contamination levels were assessed using various pollution indices, indicating that Mn, Ni, Cu, and Zn do not show significant contamination, whereas Cr exhibits moderate contamination in the study area. Areas around the mouth of the Netravati River and distant from the shore are considered polluted, as indicated by the Pollution Load Index (PLI), which is greater than 1. A close relationship between Cr and river-laden sediments indicates that the Netravati River is bringing Cr, an enriched element, to the study area.

[**Keywords**: Degree of contamination, Heavy metals, Marine pollution, Netravati River, Sediment geochemistry, Trace metals]

Introduction

It has been established that marine sediments are an important sink for persistent hazardous chemicals discharged into the aquatic environment from a variety of sources[1]. These harmful materials might contain heavy metals, which quickly dissipate into the bottom sediments after being released into the ocean[2]. In addition to their toxicity, heavy metals are significant pollutants due to their long persistence and bioaccumulation[3-5]. Although several heavy metals are essential at low concentrations for biological processes, they become toxic at elevated levels and in extreme cases, can pose serious risks to human health and other organisms[6]. Elevated concentrations of heavy metals in estuarine environments can result from both natural processes and human activities[2], even while the majority of heavy metals are naturally occurring byproducts of biogeochemical cycles such as rock weathering[7]. Power plants, nuclear weapons, dredging and reclamation, and municipal effluents can be the main anthropogenic sources of heavy metals in coastal environments[8,9]. Coastal locations must have their heavy metal pollution status evaluated because a significant portion of the heavy metal load eventually builds up in estuarine and continental shelf regions[9].

Mangalore is a port city on the southwest coast of India with several major industrial plants. Industrial effluents from these plants may lead to heavy metal enrichment in the coastal sediments off Mangalore. Sukumaran *et al*.[2] previously reported enrichment of Cr in the inner shelf sediments off Mangalore-Mulki, Karnataka coast, India, located on the northern side of the Netravati River mouth. This study aims to investigate the spatial distribution of metals in the south of the Netravati River mouth, with a special emphasis on heavy metal enrichment and pollution.

Materials and Methods

Study area

Mangalore city is encircled by the Netravati River flows to the south of the city, whereas the Gurupura River flows to the north. The rivers converge to form an estuary in the southern part of the city and eventually discharge into the Arabian Sea. The city hosts several major industries, including BASF, MRPL, MCF, KIOCL, HPCL, BPCL, JBF Petrochemicals, and Total Oil India Limited. Wood processing and plywood factories like Canara Wood and Plywood Industries are also located on the banks of the Netravati River. Of these, Mangalore Refinery and Petrochemicals Ltd. (MRPL) and the tanning and dying plant of BASF (India), have been discharging their effluents directly into the sea[2]. In addition to this, the Gurupura and Netravati rivers may carry industrial and other municipal waste from plants located on their banks to offshore sediments off Mangalore. The survey area extends from the Netravati River mouth in the north to Manjeshwar in the south, over a distance of 20 km (Fig. 1), at water depths of 3.16 m to 11.3 m.

Sampling

Surface sediment samples were collected from an area of 90 km^2 off the Netravati-Manjeshwar sector using mechanised boats. Forty samples were collected in a 1 km x 1 km grid (Fig.1), using a Van Veen grab sampler from different bathymetric zones. The samples were dried, homogenised by coning and quartering, and powdered in an agate mortar before analysis.

Laboratory procedures

Atomic Absorption Spectroscopy (AAS) (VARIAN make, AA240FS, Agilent Technologies, USA) was used to analyse the total major and trace metal contents after the marine sediments were completely decomposed using Loring and Rantala's

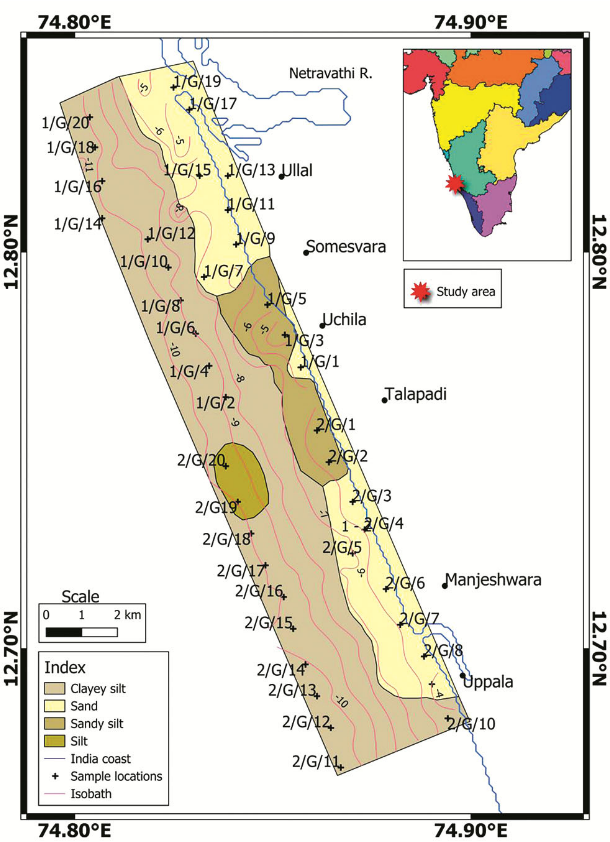

Fig. 1 — Study area showing distribution of surface sediments and location of samples

mixed acid (HF+HNO3+HCL) method[10]. Standard reference materials, including JMn-1 and BHVO-2, were analysed along with the samples to assess method accuracy. Duplicate samples were used to evaluate analytical precision, and method blanks were processed to monitor contamination. The measured concentrations of the reference materials were within ±2 standard deviations of the certified values, and the analytical precision, expressed as %RSD, was better than 3% for major elements and 10% for trace elements. 0.1 g of the sample was transferred to a dry polypropylene bottle, and 5 ml of aqua regia was added very slowly, followed by 5 ml of hydrofluoric acid. The bottle was immediately closed firmly, swirled intermittently and kept overnight. 50 ml of saturated boric acid solution was then added, and the solution was kept for an hour. It was then transferred into a 100 ml volumetric flask (plastic) and made up with distilled water. Solutions of standard samples and sample blank were prepared in the same way. For heavy metal analysis, 0.2 g of the sample was transferred into a dry PTFE beaker, and 10 ml of aqua regia was added very slowly, followed by the addition of 5 ml of hydrofluoric acid. The beaker was heated gently to dryness on a hot plate. After cooling, an additional 5 ml of hydrofluoric acid was added, and the mixture was heated to dryness again. It was followed by an addition of perchloric acid (2 ml) and heating again to dryness. 5 ml of nitric acid (1:1 V/V) was then added and warmed; the solution was then transferred to a graduated tube and made up to 20 ml. AAS was calibrated for the individual elements by using standard solutions. Absorbance was measured for a known concentration of the element. The sample solution was then aspirated into the AAS to measure the absorbance. From the absorbance, the concentration of the element was calculated. The analytical accuracy fell within ±2 standard deviations of the certified reference values. Precision, expressed as %RSD, was better than 3% for major elements and below 10% for trace elements.

Results and Discussion

Sediment distribution

Most of the area lying between the lowest low water line and 6 to 7 m isobaths is carpeted by sand except in an area of approximately 6 km stretch in the middle portion adjoining the coast where the sediment is mainly sandy silt (Fig. 1). Beyond 6 m water depth, the dominant sediment is clayey-silt with silt-rich patches within. Silt occupies the western portion of the central area.

Spatial distribution of metals

The average concentrations of metals decrease in the following order: Cd < Pb < Co < Cu < Ni < Zn < Cr < Sr < Mn < Mg < Ti < Ca < Fe < Al. Al is the most prevalent metal in the sediments, as indicated in Tables 1 and 2, as it is the main chemical component of the clay minerals that make up the local sediments. The weathering and hydrolysis of aluminium silicates in upland country rocks are the sources of clay minerals. The spatial distribution of Mg, Fe, Cu, Zn, Cr, and Ni reveals higher concentrations in areas away from the coast and close to the Netravati River mouth (Fig. 2a, b). The average zinc concentration (116 ppm) is on the higher end of the range for the west coast shelf sediments, according to Paropakari[11]. Since the concentration of Cr in the area is somewhat elevated, one sample near Someswara has a concentration below the average shale value, while all other samples have values above the average shale value. This is consistent with the results of Sukumaran *et al.*[2] for the area immediately north of the Netravati River mouth. Zinc, copper, nickel, chromium, iron, and magnesium concentrations vary from 20 to 245, 5 to 60, 15 to 110, 60 to 375, 13499.06 to 76937.63, and 519.10 to 10093.65 ppm, respectively, in the area. Distribution pattern of Ti and Mn is inverse to that of Ni, Zn and Cr, in which the higher concentrations are found near the coast and away from the river mouth. Higher concentrations of these elements are noticed in the coarser sediments. Calcium shows extremely high concentrations in two samples near Someswara and Talapadi, with concentrations of 60746.75 and 90659.62 ppm, respectively. The mean Ti concentration in the study area exceeds that of average shale, ranging from 1678.62 to 13189.18 ppm.

Evaluation of pollution by heavy metals

Several approaches have been developed to evaluate heavy metal contamination in sediments, including the Geoaccumulation Index (I_{geo}), Pollution Load Index (PLI), Enrichment Factor (EF), and Contamination Factor (CF). These methods are based on background concentrations derived from relatively uncontaminated sediments, against which the measured concentrations in the study samples are compared to assess contamination levels[12]. However,

Table 1 — Concentration of major elements in the samples. The values in parenthesis indicate the world average shale value

Sample No	Major elements (%)					Sample No	Major elements (%)				
	Al (8)	Mg (15)	Ca (22.1)	Fe (4.72)	Ti (0.46)		Al	Mg	Ca	Fe	Ti
1/G/1	3.78	0.16	1.36	3.86	0.94	2/G/1	2.61	0.12	6.07	2.79	0.66
1/G/2	6.75	0.53	2.54	5.45	0.64	2/G/2	7.12	0.57	2.02	5.53	0.63
1/G/3	6.97	0.57	2	5.6	0.7	2/G/3	4.29	0.22	2.57	3.15	0.51
1/G/4	9.52	1.01	1.78	7.46	0.54	2/G/4	4.46	0.22	0.8	3.04	0.32
1/G/5	4.48	0.31	2.08	4.96	1.3	2/G/5	7.21	0.54	2.01	4.86	0.46
1/G/6	9.59	0.91	1.92	7.66	0.53	2/G/6	3.8	0.22	1.73	3.33	0.68
1/G/7	3.98	0.24	1	5	1.32	2/G/7	4.41	0.31	2.14	3.81	0.82
1/G/8	9.72	0.84	2.05	7.5	0.56	2/G/8	4.04	0.17	2.7	3.02	0.46
1/G/9	1.95	0.05	9.07	1.35	0.17	2/G/9	4.85	0.23	1.91	4.6	1.17
1/G/10	7.55	0.67	4.66	6.34	0.67	2/G/10	9.63	0.96	2.33	6.94	0.49
1/G/11	3.82	0.15	0.64	3.87	0.81	2/G/11	9.51	0.82	2.25	6.92	0.49
1/G/12	9.66	0.94	1.73	7.51	0.56	2/G/12	9.68	0.84	2.32	6.97	0.57
1/G/13	3.9	0.13	0.69	3.99	0.79	2/G/13	8.8	0.87	3.1	6.62	0.62
1/G/14	8.95	0.65	2.21	7.03	0.62	2/G/14	7.72	0.73	2.78	5.88	0.56
1/G/15	4.18	0.15	0.96	3.18	0.49	2/G/15	8.82	0.84	2.92	6.65	0.5
1/G/16	10.5	0.66	1.6	7.69	0.53	2/G/16	9.21	0.93	1.71	7.04	0.53
1/G/17	4.36	0.21	0.34	3.18	0.45	2/G/17	8.44	0.74	2.44	6.26	0.51
1/G/18	10.75	0.83	0.69	7.68	0.51	2/G/18	9.4	0.97	1.85	7.14	0.5
1/G/19	10.07	0.77	0.86	7.38	0.5	2/G/19	9.49	0.98	2.16	7.18	0.51
1/G/20	3.57	0.06	0.75	3.22	0.44	2/G/20	9.27	0.96	2	7.02	0.49
Mean	*6.92*	*0.55*	*2.17*	*5.47*	*0.61*						

Table 2 — Concentration of heavy metals in the samples. The values in parenthesis indicate the world average shale value

Sample No	Heavy metals (ppm)							Sample No	Heavy metals (ppm)						
	Cu (45)	Pb (20)	Zn (95)	Ni (68)	Co (19)	Cr (90)	Mn (850)		Cu	Pb	Zn	Ni	Co	Cr	Mn
1/G/1	40	5	95	40	5	170	570	2/G/1	10	5	20	25	10	125	435
1/G/2	30	10	115	60	10	185	480	2/G/2	35	5	95	65	10	195	400
1/G/3	30	5	145	60	10	185	465	2/G/3	15	5	50	40	10	145	385
1/G/4	50	15	145	90	15	260	350	2/G/4	15	5	20	40	10	140	305
1/G/5	25	5	145	45	10	190	800	2/G/5	35	5	70	75	10	210	340
1/G/6	50	15	205	90	15	265	305	2/G/6	15	5	35	35	5	125	470
1/G/7	20	10	120	45	10	185	720	2/G/7	20	5	35	40	10	150	530
1/G/8	60	10	245	110	15	375	345	2/G/8	20	5	35	35	5	120	365
1/G/9	5	5	70	15	5	60	145	2/G/9	20	5	40	45	10	170	660
1/G/10	40	10	165	80	15	225	390	2/G/10	45	5	85	90	10	245	270
1/G/11	15	5	120	45	5	175	495	2/G/11	55	5	70	80	10	310	360
1/G/12	50	15	240	100	15	270	360	2/G/12	50	5	95	90	10	250	315
1/G/13	15	5	160	40	10	175	510	2/G/13	45	5	110	85	10	235	340
1/G/14	50	10	195	85	15	235	370	2/G/14	40	5	75	85	10	195	375
1/G/15	20	5	115	40	5	175	375	2/G/15	45	5	70	80	10	225	295
1/G/16	60	15	190	100	20	270	370	2/G/16	55	5	160	95	15	275	295
1/G/17	20	5	200	40	10	145	325	2/G/17	45	5	100	80	15	225	325
1/G/18	60	15	170	100	20	180	300	2/G/18	50	5	140	90	15	260	245
1/G/19	55	10	145	95	20	265	315	2/G/19	50	5	130	95	15	240	260
1/G/20	20	5	120	40	10	155	375	2/G/20	55	5	115	95	15	250	255
Mean	*35.9*	*7*	*116*	*67.13*	*11.4*	*206*	*389.8*								

no single index can fully characterize sediment pollution due to the inherent limitations of each approach. Therefore, the integrated use of multiple indices offers a more comprehensive assessment of heavy metal contamination. Similarly, in the successful interpretation of geochemical data, the choice of background values plays an important role. In the present study, the average shale values of elements published by Turekian & Wedepohl[13] are used as the background values.

Geoaccumulation index (I_{geo})

Possible metal enrichments in the area were evaluated using I_{geo} as given in Eq. (1)[14].

$$I_{geo} = \log_2 (C_n/(1.5B_n)) \quad \ldots (1)$$

Where, C_n is the concentration of metal n in the sediments, and B_n is the background concentration value for metal n[ref. 12], and the factor 1.5 is used because of possible variations in the background data due to lithological variations. I_{geo} was successfully calculated using the world average shale values[13]. Muller[14], classified the sediments based on the I_{geo} values as:

1. $I_{geo} > 5$ — Extremely contaminated
2. $> 4 \leq 5$ — Strongly to extremely contaminated
3. $> 3 \leq 4$ — Strongly contaminated
4. $> 2 \leq 3$ — Moderately to strongly contaminated
5. $> 1 \leq 2$ — Moderately contaminated
6. $> 0 \leq 1$ — Uncontaminated to moderately contaminated
7. $I_{geo} = 0$ — Uncontaminated

The computed average I_{geo} values for Cu, Zn, Ni, and Mn are ≤ 0 (Table 3), indicating that these heavy metals are not anthropogenically present in the sediments of the Netravati to Someshwar coastal area in Dakshin Kannada, Karnataka. Nonetheless, I_{geo} values > 0 are found in 14 Zn samples from Uchila in the south to the mouth of the Netravati River in the north (ranging from 0.03 to 0.78), as well as in one sample of Ni, east of Someswara. This suggests that the area northward from Uchila to the mouth of the Netravati River is non-contaminated to moderately contaminated with zinc (Table 3).

The region's average I_{geo} value for Cr is 0.54, indicating that it is either uncontaminated or moderately contaminated with Cr. Every sample in

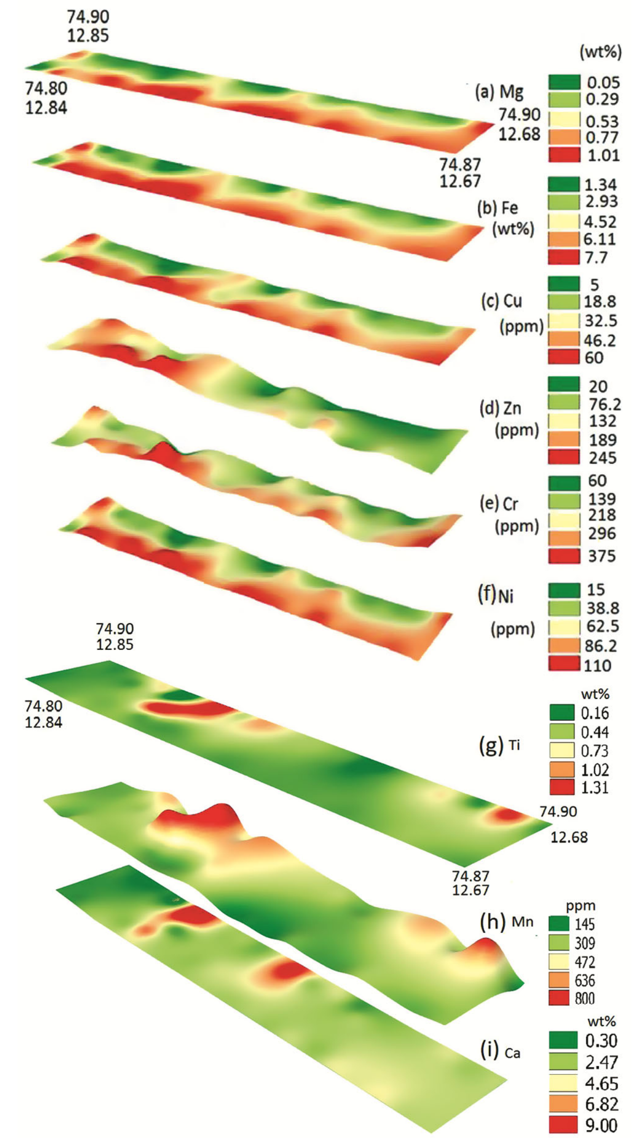

Fig. 2 — Surface distribution pattern of (a) Mg, (b) Fe, (c) Cu, (d) Zn, (e) Cr, (f) Ni, (g) Ti, (h) Mn, and (i) Ca, in the coastal sector from Netravati to Manjeshwara

the region had an I_{geo} value of Cr greater than zero, except for four samples close to the coast at Someswara, Talapadi, Manjeshwara, and Uppala. I_{geo} values for Cr in five samples taken at Ullal, Someswara, Manjeshwara, and south of Uppala, which are away from the coast, range from 1 to 1.47, indicating that these locations are moderately contaminated (Fig. 3).

Enrichment Factor (EF)

EF is one of the most commonly used geochemical parameters, in which the element concentration and the reference element in the sample are compared to the Clarke or world average shale values, as per the following formula:

$$EF = (A_e \cdot B_c)/(A_c \cdot B_e) \quad \ldots (2)$$

Where, A_e – element concentration in environmental sample; B_e – reference element concentration in environmental sample; A_c – Clarke value or average shale value of the element; and B_c – Clarke value or average shale value of the reference element.

Reference elements are either those that are inactive in biogeochemical cycles or those whose concentrations are so high in the earth's crust that human activity does not significantly alter them. The elements Si, Al, Fe, Sc, Cs, and Ti are the most often used reference elements[15]. In this study, Fe is taken as the reference element. This procedure, also known as normalisation, can be used to differentiate between the crustal and non-crustal origins of a given element.

Bam *et al.*[15] categorised the EF values into six categories as follows:

1. < 1 — background concentration
2. 1–2 — depletion to minimal enrichment
3. 2–5 — moderate enrichment
4. 5–20 — significant enrichment
5. 20–40 — very high enrichment
6. > 40 — extremely high enrichment

As presented in Table 4, the mean EF values of Zn is 1.3, indicating depletion to minimal enrichment. In contrast, those of Cu, Ni, and Mn are less than 1, indicating that these metals remain in the sediments due to background concentrations. Regardless of sediment type, the EF of zinc for samples from Uchila northward to the mouth of the Netravati River is depleted to minimally enriched. The region's average EF of Cr is 2.03, with a range of 1.22 to 2.88 (Fig. 4). Near the mouth of the Netravati and Gurupura Rivers, there is a moderate enrichment of Cr in the sand, sandy-silt, and clayey-silt sediments.

Contamination Factor (CF)

To assess the quality of the samples, the contamination factor is calculated using equation (3), in which the mean concentration of the element across all samples is divided by the Clarke value of the element.

$$CF = C_1/C_n \quad \ldots (3)$$

Where, C_i – mean content of element in all samples; and C_n – average shale value of the element.

Table 3 — I_{geo} values of heavy metals

Sample No	I_{geo} values					Sample No	I_{geo} values				
	Cu	Zn	Ni	Cr	Mn		Cu	Zn	Ni	Cr	Mn
1/G/1	-0.75	-0.58	-1.35	0.33	-1.16	2/G/1	-2.75	-2.83	-2.03	-0.11	-1.55
1/G/2	-1.17	-0.31	-0.77	0.45	-1.41	2/G/2	-0.95	-0.58	-0.65	0.53	-1.67
1/G/3	-1.17	0.03	-0.77	0.45	-1.46	2/G/3	-2.17	-1.51	-1.35	0.10	-1.73
1/G/4	-0.43	0.03	-0.18	0.95	-1.87	2/G/4	-2.17	-2.83	-1.35	0.05	-2.06
1/G/5	-1.43	0.03	-1.18	0.49	-0.67	2/G/5	-0.95	-1.03	-0.44	0.64	-1.91
1/G/6	-0.43	0.52	-0.18	0.97	-2.06	2/G/6	-2.17	-2.03	-1.54	-0.11	-1.44
1/G/7	-1.75	-0.25	-1.18	0.45	-0.82	2/G/7	-1.75	-2.03	-1.35	0.15	-1.27
1/G/8	-0.17	0.78	0.11	1.47	-1.89	2/G/8	-1.75	-2.03	-1.54	-0.17	-1.80
1/G/9	-3.75	-1.03	-2.77	-1.17	-3.14	2/G/9	-1.75	-1.83	-1.18	0.33	-0.95
1/G/10	-0.75	0.21	-0.35	0.74	-1.71	2/G/10	-0.58	-0.75	-0.18	0.86	-2.24
1/G/11	-2.17	-0.25	-1.18	0.37	-1.36	2/G/11	-0.30	-1.03	-0.35	1.20	-1.82
1/G/12	-0.43	0.75	-0.03	1.00	-1.82	2/G/12	-0.43	-0.58	-0.18	0.89	-2.02
1/G/13	-2.17	0.17	-1.35	0.37	-1.32	2/G/13	-0.58	-0.37	-0.26	0.80	-1.91
1/G/14	-0.43	0.45	-0.26	0.80	-1.78	2/G/14	-0.75	-0.93	-0.26	0.53	-1.77
1/G/15	-1.75	-0.31	-1.35	0.37	-1.77	2/G/15	-0.58	-1.03	-0.35	0.74	-2.11
1/G/16	-0.17	0.42	-0.03	1.00	-1.78	2/G/16	-0.30	0.17	-0.10	1.03	-2.11
1/G/17	-1.75	0.49	-1.35	0.10	-1.97	2/G/17	-0.58	-0.51	-0.35	0.74	-1.97
1/G/18	-0.17	0.25	-0.03	0.42	-2.09	2/G/18	-0.43	-0.03	-0.18	0.95	-2.38
1/G/19	-0.30	0.03	-0.10	0.97	-2.02	2/G/19	-0.43	-0.13	-0.10	0.83	-2.29
1/G/20	-1.75	-0.25	-1.35	0.20	-1.77	2/G/20	-0.30	-0.31	-0.10	0.89	-2.32
Average	*-1.12*	*-0.53*	*-0.74*	*0.54*	*-1.78*						

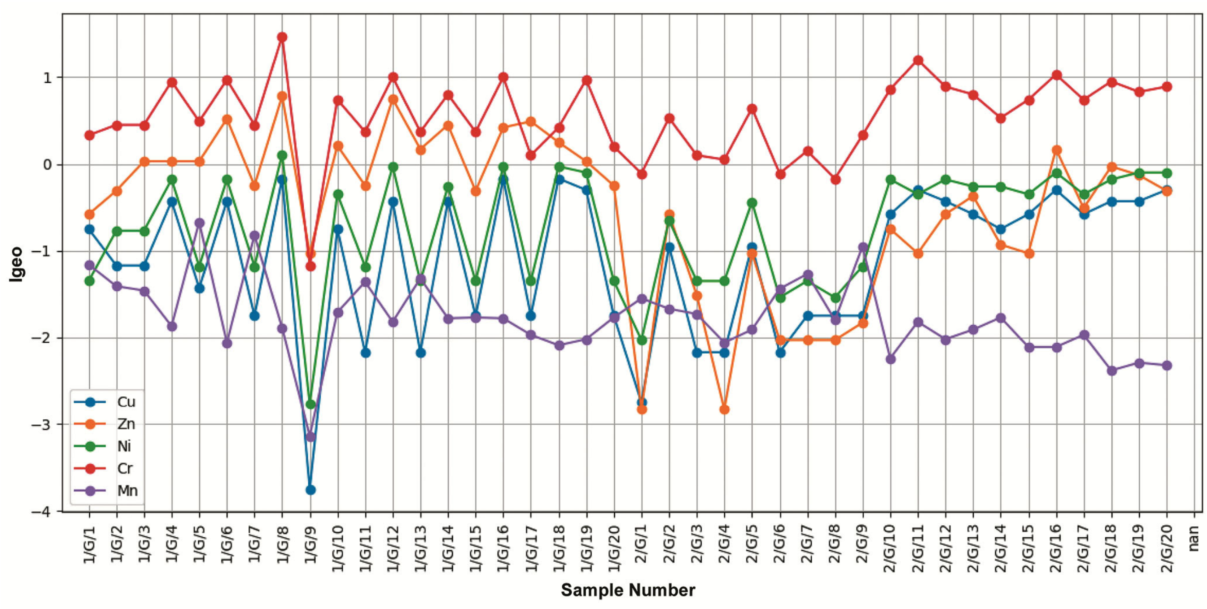

Fig. 3 — Variation in the I_{geo} values of heavy metals in the area

According to Hakanson[16], there are four CF classes as given below:

1. CF < 1 – refers to low contamination
2. 1 < CF < 3 indicates moderate contamination
3. 3 < CF < 6 implies considerable contamination
4. CF > 6 denotes high contamination

The region's average CF values for Cu, Ni, and Mn exceed 1, indicating low levels of contamination (Table 5). Though the whole area is slightly contaminated with these elements, for Cu 18 offshore samples and for Ni 21 offshore samples have

Table 4 — Enrichment Factor (EF) of heavy metals

Sample No.	Enrichment Factor					Sample No.	Enrichment Factor				
	Cu	Zn	Ni	Cr	Mn		Cu	Zn	Ni	Cr	Mn
1/G/1	1.087	1.223	0.719	2.309	0.820	2/G/1	0.376	0.356	0.622	2.349	0.866
1/G/2	0.578	1.049	0.764	1.781	0.489	2/G/2	0.664	0.853	0.816	1.848	0.401
1/G/3	0.562	1.286	0.743	1.732	0.461	2/G/3	0.500	0.789	0.882	2.416	0.679
1/G/4	0.703	0.965	0.837	1.827	0.260	2/G/4	0.518	0.327	0.915	2.419	0.558
1/G/5	0.529	1.453	0.630	2.009	0.896	2/G/5	0.755	0.715	1.071	2.266	0.388
1/G/6	0.685	1.330	0.816	1.815	0.221	2/G/6	0.473	0.522	0.730	1.969	0.784
1/G/7	0.419	1.192	0.625	1.940	0.799	2/G/7	0.550	0.456	0.728	2.064	0.772
1/G/8	0.839	1.622	1.017	2.621	0.255	2/G/8	0.694	0.576	0.804	2.083	0.671
1/G/9	0.389	2.576	0.771	2.331	0.596	2/G/9	0.457	0.432	0.680	1.940	0.798
1/G/10	0.661	1.292	0.875	1.860	0.341	2/G/10	0.680	0.609	0.900	1.852	0.216
1/G/11	0.407	1.541	0.808	2.373	0.711	2/G/11	0.834	0.503	0.803	2.350	0.289
1/G/12	0.698	1.587	0.924	1.885	0.266	2/G/12	0.753	0.678	0.897	1.882	0.251
1/G/13	0.394	1.990	0.695	2.298	0.709	2/G/13	0.713	0.826	0.892	1.863	0.285
1/G/14	0.746	1.378	0.839	1.753	0.292	2/G/14	0.714	0.634	1.004	1.741	0.354
1/G/15	0.659	1.795	0.872	2.884	0.654	2/G/15	0.710	0.523	0.835	1.774	0.246
1/G/16	0.818	1.227	0.902	1.840	0.267	2/G/16	0.819	1.129	0.936	2.048	0.233
1/G/17	0.661	3.129	0.874	2.395	0.568	2/G/17	0.754	0.794	0.887	1.885	0.288
1/G/18	0.819	1.100	0.904	1.229	0.217	2/G/18	0.734	0.974	0.875	1.909	0.191
1/G/19	0.782	0.976	0.894	1.883	0.237	2/G/19	0.731	0.900	0.919	1.754	0.201
1/G/20	0.651	1.849	0.861	2.521	0.646	2/G/20	0.822	0.814	0.940	1.869	0.202
Average	*0.658*	*1.099*	*0.838*	*2.039*	0.460						

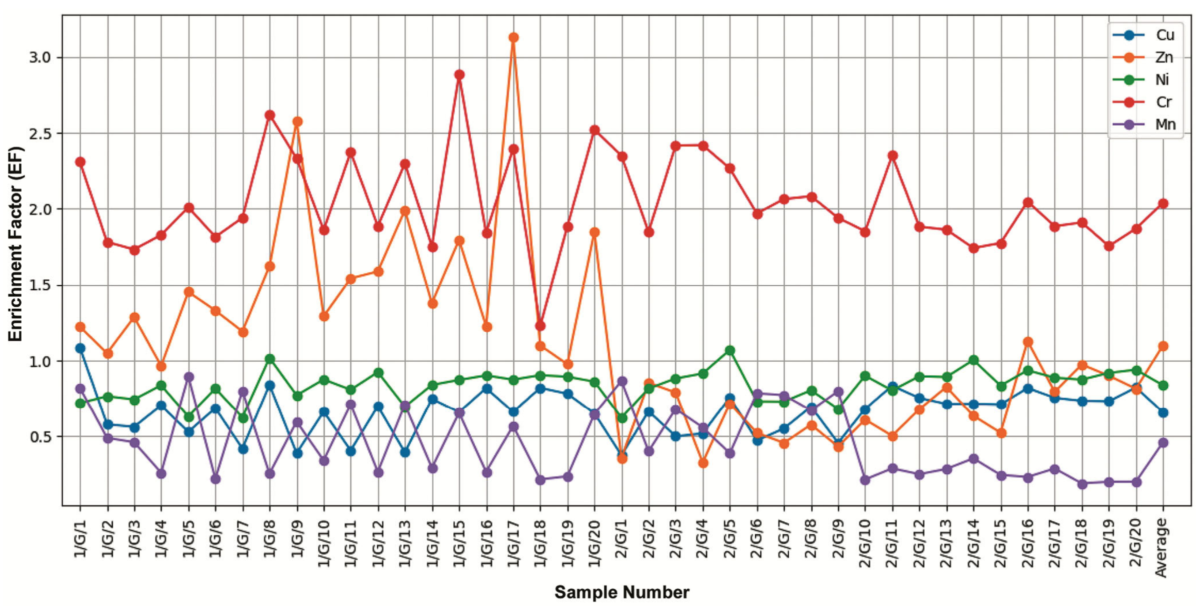

Fig. 4 — Variation in the EF values of heavy metals in the area

contamination factor 1 < CF < 3, which indicates moderate contamination in this area. Moderate pollution is indicated by the average CF of Zn and Cr in the area, which is 1 < CF < 3. The following is the order of the average CFs of heavy metals: Cr > Zn > Ni > Cu > Mn.

Pollution Load Index (PLI)

Heavy metals in sediments typically occur as complex mixtures and exhibit considerable variability, hence the PLI, which is an indication of integrated pollution status of the area, was calculated using equation (4) by calculating

Table 5 — Contamination Factor (CF) and Pollution Load Index (PLI) of heavy metals

Sample No.	Contamination Factor (CF)					PLI	Sample No.	Contamination Factor (CF)					PLI
	Cu	Zn	Ni	Cr	Mn			Cu	Zn	Ni	Cr	Mn	
1/G/1	0.89	1	0.59	1.89	0.67	0.921	2/G/1	0.22	0.21	0.37	1.39	0.51	0.414
1/G/2	0.67	1.21	0.88	2.06	0.56	0.963	2/G/2	0.78	1	0.96	2.17	0.47	0.946
1/G/3	0.67	1.53	0.88	2.06	0.55	1.002	2/G/3	0.33	0.53	0.59	1.61	0.45	0.596
1/G/4	1.11	1.53	1.32	2.89	0.41	1.217	2/G/4	0.33	0.21	0.59	1.56	0.36	0.470
1/G/5	0.56	1.53	0.66	2.11	0.94	1.022	2/G/5	0.78	0.74	1.1	2.33	0.4	0.900
1/G/6	1.11	2.16	1.32	2.94	0.36	1.274	2/G/6	0.33	0.37	0.51	1.39	0.55	0.546
1/G/7	0.44	1.26	0.66	2.06	0.85	0.917	2/G/7	0.44	0.37	0.59	1.67	0.62	0.631
1/G/8	1.33	2.58	1.62	4.17	0.41	1.566	2/G/8	0.44	0.37	0.51	1.33	0.43	0.545
1/G/9	0.11	0.74	0.22	0.67	0.17	0.290	2/G/9	0.44	0.42	0.66	1.89	0.78	0.711
1/G/10	0.89	1.74	1.18	2.5	0.46	1.158	2/G/10	1	0.89	1.32	2.72	0.32	1.005
1/G/11	0.33	1.26	0.66	1.94	0.58	0.794	2/G/11	1.22	0.74	1.18	3.44	0.42	1.091
1/G/12	1.11	2.53	1.47	3	0.42	1.393	2/G/12	1.11	1	1.32	2.78	0.37	1.086
1/G/13	0.33	1.68	0.59	1.94	0.6	0.826	2/G/13	1	1.16	1.25	2.61	0.4	1.086
1/G/14	1.11	2.05	1.25	2.61	0.44	1.265	2/G/14	0.89	0.79	1.25	2.17	0.44	0.965
1/G/15	0.44	1.21	0.59	1.94	0.44	0.770	2/G/15	1	0.74	1.18	2.5	0.35	0.945
1/G/16	1.33	2	1.47	3	0.44	1.386	2/G/16	1.22	1.68	1.4	3.06	0.35	1.250
1/G/17	0.44	2.11	0.59	1.61	0.38	0.805	2/G/17	1	1.05	1.18	2.5	0.38	1.034
1/G/18	1.33	1.79	1.47	2	0.35	1.199	2/G/18	1.11	1.47	1.32	2.89	0.29	1.125
1/G/19	1.22	1.53	1.4	2.94	0.37	1.232	2/G/19	1.11	1.37	1.4	2.67	0.31	1.116
1/G/20	0.44	1.26	0.59	1.72	0.44	0.758	2/G/20	1.22	1.21	1.4	2.78	0.3	1.115
Average	*0.8*	*1.23*	*1*	*2.3*	*0.5*	*0.958*							

the n^{th} root of the product of n CFs for the tested metals:

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \cdots \times CF_n)^{1/n} \quad \ldots (4)$$

Where, CF_n is the CF of n^{th} metal.

Tomlinson *et al.*[17] classified PLI into two as:

1. Polluted – PLI > 1
2. Unpolluted – PLI < 1

The average PLI of all the samples in the area is 0.96, indicating no heavy metal pollution throughout the area. Nevertheless, 20 samples have PLI >1, suggesting that heavy metal contamination exists in this clayey-covered area. A two-dimensional surface depiction of the area's PLI is displayed in Figure 5. The region away from the coast and the Netravati River mouth has a PLI > 1 and is heavily metal-polluted (Fig. 5).

Source of heavy metals

The sources of these heavy metals are analysed using Pearson's correlation coefficient in XLSTAT version 20.1.49878.0 (Table 5). Al shows a significant positive correlation with Cu, Zn, Ni, Cr, Mg, and Fe, indicating that these metals are originated from a common source. It shows a negative correlation with Mn, Sr, Ca, and Ti. Ti shows a strong positive correlation with Mn, indicating a common source and a relatively weak correlation with Sr. Moreover, it shows a negative correlation with all other metals. The distribution of these heavy metals is directly related to sediment distribution in the area. Positive correlations of Cr, Cu, Ni, and Zn with Al, Mg, and Fe indicate that these are adsorbed in the clay, and a smaller amount of clay may be the reason for the low concentration of these heavy metals near the coast covered by sand. Cu and Zn may substitute Fe^{2+} and Mg^{2+} in ferromagnesian minerals. The correlation of these metals with Mn is negligible, indicating that Mn occurs in the crystal structure of other minerals rather than as hydroxides, as evidenced by its negative correlation with Fe (Table 6).

Principal component analysis (PCA) was performed to identify the potential sources of heavy metals. The first three components were employed to identify the factors influencing sediment contamination in the study area. The cumulative variance explained by the first three components, along with the rotated loadings of the first two principal components (PCs) representing maximum variance, are presented in Table 7. The total variance accounted for by the first three PCs is 81.6 %. Component 1 was heavily loaded with high

Table 6 — Pearson correlation coefficient among heavy metals (N = 40 and the result is significant at $p < 0.05$)

Variables	**Cu**	**Zn**	**Ni**	**Cr**	**Mn**	**Sr**	**Al**	**Mg**	**Ca**	**Fe**	**Ti**
Cu	1										
Zn	0.540	1									
Ni	0.956	0.562	1								
Cr	0.871	0.585	0.884	1							
Mn	-0.397	-0.108	-0.432	-0.231	1						
Sr	-0.720	-0.465	-0.732	-0.702	0.188	1					
Al	0.955	0.498	0.979	0.849	-0.465	-0.715	1				
Mg	0.905	0.426	0.946	0.820	-0.480	-0.650	0.958	1			
Ca	-0.213	-0.295	-0.211	-0.275	-0.259	0.746	-0.192	-0.079	1		
Fe	0.943	0.571	0.964	0.883	-0.266	-0.728	0.965	0.937	-0.236	1	
Ti	-0.217	-0.009	-0.243	-0.072	0.942	0.057	-0.288	-0.274	-0.239	-0.062	1

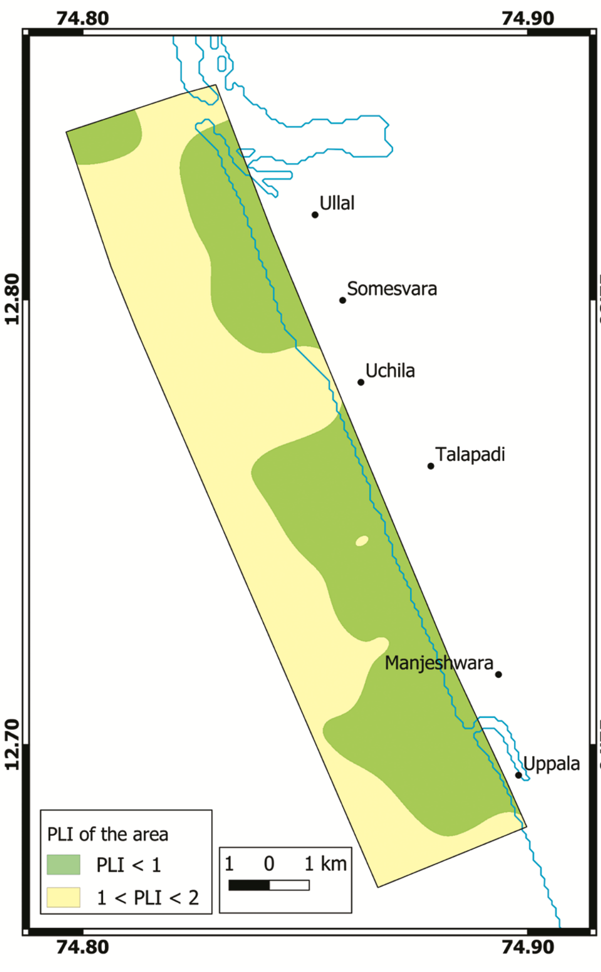

Fig. 5 — Representation of PLI

concentrations of Cu, Zn, Ni, Cr, Al, Mg and Fe with a variance of 62.087 %. This indicates that more of these metals may have originated from common sources (parent rock materials) and accumulated in the sediments[18,19]. Component 1 shows negative loadings for Mn, Sr, Ca, and Ti, indicating different

Table 7 — Principal components of heavy metals in the area

Variables	**F1**	**F2**
Cu	0.963	-0.015
Zn	0.609	0.240
Ni	0.983	-0.038
Cr	0.905	0.147
Mn	-0.439	0.840
Sr	-0.800	-0.345
Al	0.976	-0.089
Mg	0.937	-0.146
Ca	-0.300	-0.678
Fe	0.962	0.111
Ti	-0.258	0.862
Variability (%)	*62.087*	*19.554*

sources for these metals. Similarly Component 2 is heavily loaded with Mn and Ti with a variability of 19.554 %. Further, it is negatively loaded for Cu, Ni, Sr, Al, Mg, and Ca. As indicated in the varimax rotated components of the metals in Figure 6, Mn and Ti (heavy minerals present in the area); Sr and Ca (may be the biogenous material); and Zn, Cr, Fe, Cu, Al and Mg (clay minerals) have a common sources of origin.

Cr values in the area are higher than the average shale value, and according to the EF and I_{geo} the area is moderately contaminated with Cr. Cr has widespread use in industries for the manufacturing of steel and other alloys, preservation of wood, tanning of leather, used in high-temperature furnaces as refractory materials, as well as in pigments, dyes, drilling muds, rust and corrosion inhibitors, textiles, and photocopier toners. Because of these, Cr may be added to air, water, or sediments, and in sediments it will be adsorbed onto clay particles. To correctly identify the hazard posed by metals like Cr in

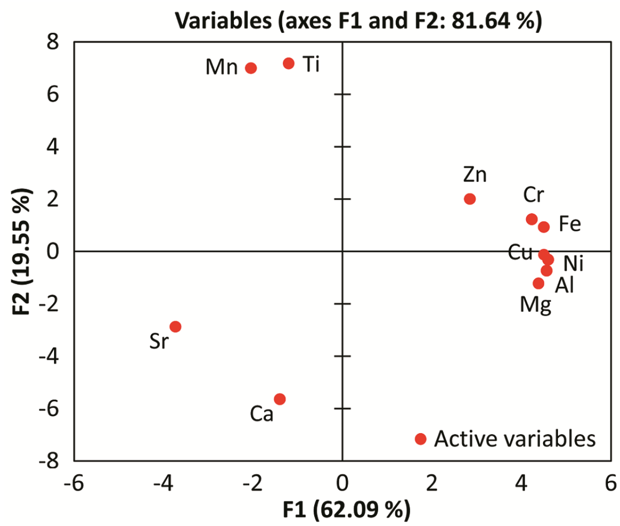

Fig. 6 — Varimax rotated components of the heavy metals of the area

sediments, it is necessary to evaluate their exposure potential, including bioavailability[20]. Even relatively high contamination levels may have limited or no biological impact if the metals are not readily bioavailable.. Cr exists in marine sediments in two oxidation states, trivalent [Cr(III)] and hexavalent [Cr(VI)] with distinct characters. It is established that exposure to Cr(VI) at certain levels can cause significant health hazards; in contrast, Cr(III) is not toxic. So before establishing the Cr toxicity of sediments, a study on Cr chemistry has to be conducted, as the threshold of Cr toxicity is correlated with the valence state of Cr[(ref. 21)]. However, the bioavailability of Cr in the area north of Netravati River mouth is reported as 50 %[(ref. 2)], signifying its association with organic matter.

Conclusion

Mg, Fe, Cu, Zn, Cr, and Ni show the same pattern of spatial distribution, while the distribution pattern of Ti and Mn is opposite. Concentration of all heavy metals, along with Al and Fe, is high near the mouth of the Netravati River and in the area away from the coast. This suggests that a significant quantity of the heavy metals may be carried by the Netravati and Gurupura Rivers and debouched into the sea. These might be partitioned and adsorbed onto clay particles in the offshore environment soon after their discharge into the sea. Average Cr values in the area are above the average shale value. The pollution indices indicate that the area is not contaminated with Cu, Ni, and/or Mn. CF of Zn and Cr show moderate contamination. Based on these pollution indices, it can be said that the area is contaminated with Cr. According to the calculated PLI, though the area as a whole is not polluted, areas away from the coast and near the mouth of the Netravati River show PLI > 1, *i.e.*, they are polluted. This area matches the zone of high concentration of heavy metals. Al, Mg, and Fe show a strong positive correlation with Cu, Zn, Ni, and Cr, indicating that these heavy metals are adsorbed onto the clay particles. Further Ti and Mn show a positive correlation, indicating their source as heavy minerals. Similar is the case with Ca and Sr, which indicates a biogenous source. Many of the industries in the Mangalore region are located near the Gurupura and Netravati Rivers. Cr may be a byproduct of these industries and may be added to river water, and which may ultimately reach the sea. In addition, Mangalore port is handling all types of cargo, including sulphur, crude oil, fertilizer, etc. These may also contaminate the coastal and nearshore sediments off Mangalore. But since Cr can exist in two chemical states and Cr toxicity depends on its oxidation states, it is essential to conduct a study on Cr chemistry in the area to establish the extent of pollution.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contributions

The first (SRBK) and third (BG) authors were responsible for data processing, data analysis, and drafting of the manuscript. The second (LGS) author carried out the fieldwork.

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