Distribution and Contamination of Trace Elements in Core Sediments of the Karnaphuli River using Neutron Activation Analysis

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Abstract

The present study investigates the distribution and contamination of trace elements in core sediments collected from 3 locations of the Karnaphuli river. Total concentrations of 15 major and trace elements (Na, Al, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Rb, Th and U) were determined in sediments of the Karnaphuli river by neutron activation analysis (NAA) method. When compared with upper continental crustal (UCC) values, it is observed that mean concentrations of Al, Ti, V, Zn, Rb and that most of the cores show elevated values. In this study, pollution level of pollutants in core sediments evaluated by different pollution indices suggests that recent pollution level of the sediments is higher than the previous levels. This study will be helpful to quantify levels of trace elements pollution, to identify their tentative sources as well as to mitigate future pollution risks of the river.

***Keywords*:** Trace element, core sediments, neutron activation analysis, Karnaphuli river

1. Introduction

Sediments are important carriers of trace elements in the hydrological cycle. Since trace elements are partitioned with the surrounding waters, they reflect the quality of an aquatic system. Moreover, sediments play a major role in determining pollution pattern of aquatic systems [1, 2], reflecting the history of pollutants deposition and providing a record of catchment inputs into aquatic ecosystems [3, 4]. Therefore, by analyzing sediments, it is possible to determine the provenance, distribution and possible hazards of element contaminations in the river system [5-7]. The concentration of trace elements in sediments are varied according to the rate of particle sedimentation, the rate of heavy metals deposition, the particle size and the presence or absence of organic matter in the sediments.

Environmental research using nuclear techniques for the determination of trace and ultra-trace element pollutions has a great potential in relation to human health. Generally, different analytical techniques have been extensively employed for elemental pollution monitoring of sediments like atomic absorption spectrometry, inductively coupled plasma optical emission spectrometry, and inductively coupled plasma mass spectrometry. These chemical methods involve digestion of the samples. There are also some other methods that use only finely grinded homogenized powder samples without further chemical treatments [8]. Neutron activation analysis (NAA) is one of them. NAA is a specific and accurate analytical technique due to its high sensitivity and multi-element determination nature [9, 10], recently classified as a primary ratio method by metrology [11].

The increasing urbanization and industrialization of Bangladesh have negative implications in river sediment and water quality. The Karnaphuli is the principal river of the Chattogram region. A water treatment plant has been set up by Chattogram Port Authority to source water from the Karnaphuli river for its uses. The plant will make the port self-reliant in its water needs. Like many rivers in Bangladesh, Karnaphuli is heavily polluted by agricultural runoff and industrial effluents. Although some studies on spatial metal distributions of the Karnaphuli river have been carried out [12, 13], but core sediment analysis of this river is rare. Therefore, in this study an attempt has been taken to investigate the concentration and distribution of major and trace elements in core sediments of the Karnaphuli river using NAA technique. This study also assesses the depth-wise elemental pollution status of the river by calculating different environmental pollution indices.

2. Experimental Details

2.1 Study area and sample collection

The Karnaphuli river is located (22 ° 12 ′33 ′′ N to 91 °48 ′54 ′′E) in the southeastern region of Bangladesh. Karnaphuli river is the major watercourse of the Chattogram region of Bangladesh. Rising in the Mizo Hills of Mizoram state, northeastern India, flows about 270 km south and southwest through the southeastern arm of Bangladesh to empty into the Bay of Bengal, 19 km below the city of Chittagong. Three core sediment samples were collected from 3 locations of the Karnaphuli river (Core-1: 22 °37 ′1 ′′N and 91 °88 ′6 ′′E, Core-2: 22 °35 ′3 ′′N and 91 °87 ′8 ′′E, Core-3:22 °35 ′2"N and 91 °86'9 ′′E). The sediment samples were collected using an acrylic pipe sampler during ebbs. Each core sample was sliced into 5 cm interval (for example, K-1.1=surface (0-5cm), K-1.2= 5-10 cm, K-1.3=10-15 cm etc.) to study depth-wise distribution of trace elements in the cores and each sediment slice was stored in cleaned polyethylene bag. The length of core-1 was 60 cm whereas core-2 and core-3 were 70 cm.

2.2 Sample preparation

The aggregates and organic species from the sediment samples were removed and dried at about 50 °C in an

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electric oven in the laboratory to obtain constant weight. The dried samples were then ground into small grain size and homogeneously mixed using anagate mortar and pestle. The homogenous powdered samples were sieved and stored in labeled glass bottles as stock samples for elemental analyses.

2.3 Sample irradiation and analysis

Approximately 50 mg of each dried powder sample was weighed in polyethylene bag and heat sealed. For relative standardization approach of instrumental neutron activation analysis (INAA), two certified reference materials (CRMs) from International Atomic Energy Agency (IAEA): IAEA-Soil-7 and IAEA-SL-1 (Lake Sediment) and one standard reference material NIST-1633b along with the sediment samples were analyzed in this study. IAEA-Soil-7 was used as the standard, while IAEA-SL-1 and NIST-1633b were used as the control samples. Two types of neutron irradiation (short and long) were performed at 3 MW TRIGA MARK II research reactor of Bangladesh Atomic Energy commission. Short irradiation was perform to investigate the short-lived radionuclidesof the elements Na, K, Al, Mn,Ti, V which was performed separately for each sample with the thermal neutrons (flux:~5.28×10^{12} cm^{-2} s^{-1}) for 1min. at 250 kW reactor power. The dead time of the counting system was kept within 10%.

Long irradiation was perform to investigate medium and long lived radionuclidesof the elements which was performed simultaneously with all the samples and standards with the thermal neutrons (flux: ~2.11×10^{13} cm^{-2} s^{-1}) for 7 minutes at 2.4 MW power of the reactor. In that irradiation tube, three Al-0.1% Au (0.1 mm foil) were also stacked at the top, middle and bottom of the samples and standards for monitoring neutron flux variation in the tube. After long irradiation, two timesgamma ray countingswith different decay intervals were performed for medium and long-lived radionuclides with a high purity germanium (HPGe) detector (40% relative efficiency, 1.8 keV resolution at 1332.5 keV of ^{60}Co source) coupled with a gamma spectrometer (ORTEC, DSPEC JrTM). Peak counts were calculated using Hypermet PC software. For the calculation of trace element concentrations, the considered product radionuclides with their half-lives and gamma-ray energies are given in Table 1.

Table 1. Radionuclides with their half-lives and gamma ray energies for NAA determination of the elements [22]

Elements	Product nuclide	Half-life	Gamma-ray energy (keV)
Na[a]	^{24}Na	14.7 h	1369
Al[a]	^{28}Al	2.24 min	1779
K[a]	^{42}K	12.4 h	1525
Sc	^{46}Sc	83.8 d	889 , 1121
Ti[a]	^{51}Ti	5.76 min	320
V[a]	^{52}V	3.75 min.	1434
Cr	^{51}Cr	27.7 d	320
Mn[a]	^{56}Mn	2.58 h	847, 1811
Fe	^{59}Fe	44.5 d	1099,1292
Co	^{60}Co	5.27 y	1173, 1332
Zn	^{66}Zn	244 d	116
As	^{76}As	26.3 h	559
Rb	^{86}Rb	18.7 d	1077
Th	^{233}Pa	27 d	312
U	^{239}Np	2.36 d	106 , 278

[a]Elements are determined by short irradiation

2.4 Quantification of sediment pollution

2.4.1 Enrichment factor (*EF*)

Metal contamination in the studied sediments can be evaluated in more comprehensive way by using enrichment factor (EF), which can be calculated by using the following equation [14].

$$EF = \frac{\left(\frac{Metal}{Al}\right)sample}{\left(\frac{Metal}{Al}\right)Background}$$

In this study, Al was used as reference element for geochemical normalization and upper continental crustal (UCC) average values from literature [15] were used as the geochemical background concentration. EF values 1.5-3.0, 3.0-5.0, 5.0-10 and >10 are the evidence of minor, moderate, severe and very severe enrichment of the elements in sediments, respectively.

2.4.2 Geo-accumulation index (I_{geo})

Geo-accumulation index (I_{geo}) can be defined by the following equation [14]:

$$I_{geo} = Log_2\left(\frac{C_x}{1.5\ XB_x}\right)$$

Where, C_x is the measured concentration of the metal x, B_x is the geochemical background concentration of metal x.

Factor 1.5 is the background matrix correction factor due to lithospheric effects. The I_{geo} consists of seven classes. Class 0 (practically uncontaminated): $I_{geo}<0$; Class 1 (uncontaminated to moderately contaminated): $0 < I_{geo}<1$; Class 2 (moderately contaminated): $1 < I_{geo}< 2$; Class 3 (moderately to heavily contaminated): $2 < I_{geo}< 3$; Class 4 (heavily contaminated): $3 < I_{geo}< 4$; Class 5 (heavily to extremely contaminated): $4 < I_{geo}< 5$; Class 6 (extremely contaminated): $5 <I_{geo}$.

2.4.3 Pollution load index **(***PLI***)** *and modified degree of contamination* **(***mC_d***)**

Pollution load index (PLI) is calculated from the contamination factors (CF) of the studied elements for a specific sampling site, which can be defined as follows [16]:

$$CF = \frac{(Metal\ concentration)_{Sample}}{(Metal\ concentration)_{Background}}$$

Then, PLI is represented by the following equation [16]

$$PLI = (CF_1 X\ CF_2 X\ CF_3\ X \dots\dots\dots\ CF_n)^{1/n}$$

Where, CF_1 to CF_n represents the contamination factors for the studied elements and n is the total number of contamination factors considered.

The modified degree of contamination (mC_d) index can be calculated as follows [14]:

$$mC_d = \frac{1}{n}\sum_{i=1}^{n} CF_i$$

Where, n is the total number of contaminants; CF is the contamination factor of each element at a point. The mC_dconsists of following gradation: $mC_d<1.5$ is nil to a very low degree of contamination; $1.5\leq mC_d< 2$ is a low degree of contamination; $2\leq mC_d<4$ is a moderate degree of contamination; $4\leq mC_d<8$ is a high degree of contamination; $8\leq mC_d<16$ is a very high degree of contamination; $16\leq mC_d<32$ is an extremely high degree of contamination; $mC_d\leq 32$ is an ultra-high degree of contamination.

3. Results and Discussion

3.1 Elemental concentration in sediments

In this study, total concentrations of 15 major and trace elements (Na, Al, K, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, As, Rb, Th and U**)** in core sediments of the Karnaphuli river are determined by NAA. To ensure quality of the analytical data, comparisons of trace element analyses results for single measurement in this study to the certified/ information values of the reference materials are given in Table 2. It is observed that concentrations for most of the studied elements obtained in this study are within 10% deviation from their certified/information values which assures accuracy of the analysis. The elemental concentrations, their descriptive statistics, PLI values as well as the literature data of UCC [15] for the respective elements in core sediments of the Karnaphuli river are given in Table 3-5. If we observe the concentration variations of the elements in different cores, it is observed that for core-1, most of the element contents do not vary over a long range (RSD: 6.8–46.7%), whereas Al and Rb contents vary widely(RSD: 61.4% and 69.4% respectively,Table 3); for core-2 all element contents varywith RSD: 4.3-39.4% except Al and Rb contents (RSD: 42.4% and 45.1%, respectively, Table 4) whereas for core-3 element contents vary with RSD: 10-36.8% except Al contents (RSD: 46.9%, Table 5) varies over a relatively long range.

Table 2. Comparison of results (mg kg^{-1}) of the element analyses in this study to the certified values of those elements in the reference materials

Element	IAEA-CRM-SL-1			NIST-SRM-1633b		
	Study value	certified value	ratio	study value	certified value	ratio
Na	1707 ± 60.1	1700 (1600-1800)	1.00	2159 ± 25.3	2010	1.07
Al	96625 ± 3091	89000	1.09	151478 ± 4821	150500	1.01
K	12623 ± 675	14500 (12400-16600)	0.87	20861 ± 1065	19500	1.07
Sc	14.9 ± 0.48	17.3 (16.2-18.4)	0.86	39.0 ± 1.26	41.0	0.95
Ti	5937 ± 413	5170 (4740-5600)	1.15	7799 ± 459	7910	0.99
V	186 ± 8.78	170	1.09	237 ± 10.7	296	0.80
Cr	92.6 ± 4.24	104 (95-113)	0.89	183 ± 7.82	198	0.92
Mn	3529 ± 121	3460	1.02	145 ± 6.26	132	1.09
Fe	58649 ± 2119	67400	0.87	74252 ± 2649	77800	0.95
Co	19.5 ± 1.03	19.8 (18.3-21.3)	0.99	49.8 ± 2.6	50	1.00
Zn	207.9 ± 14.88	223	0.93	200.2 ± 15.1	210	0.95
As	29.2 ± 1.20	27.6 (24.7-30.5)	1.06	9 ± 0.3	136	0.07
Rb	96 ± 8.50	113 (102-124)	0.85	145 ± 11	140	1.04
Th	12.4 ± 0.5	14 (13-15)	0.89	26.1 ± 1.0	25.7	1.02
U	4.13 ± 0.3	4.02 (3.69-4.35)	1.03	9.01 ± 0.41	8.79	1.03

ratio = **s**tudy value/certified value

Table 3. Concentrations of the elements (mg kg^{-1}) in sediments of core-1 of the Karnaphuli river

Sample	Na	Al	K	Sc	Ti	V	Cr	Mn	Fe	Co	Zn	As	Rb	Th	U	PLI
K-1.1	7933	166622	25615	18.2	7257	168	165	749	61307	19.1	116	10.9	393	31.9	4.25	1.52
K-1.2	8581	192687	21742	15.5	7379	190	161	877	53723	16.2	96.6	7.17	318	30.6	2.65	1.46
K-1.3	6915	223716	24719	15.7	7844	208	102	883	46034	19.9	102	9.05	153	20.4	3.95	1.32
K-1.4	7935	215763	25267	16.7	7409	198	101	816	48235	21.6	113	8.25	155	19.1	3.53	1.34
K-1.5	8580	177954	22578	12.9	6064	156	82.4	647	37018	17.0	110	5.35	119	15.7	4.05	1.12
K-1.6	8597	217343	23400	12.4	9051	181	78.2	663	34923	15.6	97.6	4.36	111	14.9	3.33	1.15
K-1.7	8608	281713	22975	12.0	7230	189	77.5	635	33808	15.8	80.8	4.81	111	15.7	2.97	1.13
K-1.8	7714	157548	22210	11.9	6317	140	62.5	665	31247	17.0	82.9	5.94	82.7	11.6	2.52	1.00
K-1.9	7558	156169	22395	13.4	6345	147	68.8	699	35034	18.8	101	5.46	96.6	12.8	2.48	1.05
K-1.10	7647	257490	22954	13.1	9300	216	68.8	720	34972	18.6	110	4.11	73.1	12.5	1.96	1.14
K-1.11	7525	268285	24383	13.5	7205	207	66.2	796	34828	18.3	89.7	4.62	77.7	11.5	2.62	1.11
K-1.12	8151	238502	24384	11.7	7928	177	60.7	718	30862	17.6	87.3	3.64	64.6	10.7	3.03	1.04
Min	6915	156169	21742	11.7	6064	140	60.7	635	30862	15.6	80.8	3.6	64.6	10.7	1.96	1.00
Max	8607	281713	25615	18.2	9300	216	165	883	61307	21.6	116	10.9	393	31.9	4.25	1.52
UCC	24300	81500	23200	14	3800	97	92	775	39200	17.3	67	4.8	84	10.5	2.7	
Mean	7979	125617	22664	12	4896	116	74	722	32159	17	88	4	98	14	3	1.20
SD	542	43322	1280	2	997	25	36	86	9798	2	12	2	103	7	1	
RSD,%	6.8	61.4	11.1	20.9	43.7	44.8	37.3	12.7	27.4	11.7	18.3	46.7	69.4	38.3	28.5	

UCC= Upper continental crustal average; SD= Standard deviation; RSD= Relative standard deviation; PLI = Pollution load index

Uncertainties associated with elemental concentrations due to estimated uncertainty budget of NAA are**:** Na, Al, K, Sc, Mn, Fe, As, Th and U = 3-4%; V, Cr and Co = 4-5%; Ti, Zn and Rb = 6-7%

Table 4. Concentrations of the elements (mg kg^{-1}) in sediments of core-2 of the Karnaphuli river

Sample	Na	Al	K	Sc	Ti	V	Cr	Mn	Fe	Co	Zn	As	Rb	Th	U	PLI
K-2.1	6744	155864	18596	7.87	5361	114	53.9	631	21746	13.8	73.2	2.05	47.5	8.28	1.86	0.78
K-2.2	6993	197654	21454	8.90	6720	151	45.8	653	23266	15.5	80.9	3.20	49.4	7.33	1.60	0.85
K-2.3	7339	178303	19178	7.47	6727	143	39.4	616	19459	13.1	72.9	2.06	33.2	7.47	1.53	0.76
K-2.4	896	216092	19837	7.18	6616	146	35.0	553	18881	12.9	72.4	2.17	34.6	7.46	1.99	0.65
K-2.5	7123	178695	19922	9.40	7251	143	34.9	697	23871	15.7	80.4	2.30	49.5	8.05	1.97	0.84
K-2.6	7561	84990	20417	8.27	4657	93.5	40.7	650	20644	14.1	73.3	2.22	33.1	6.88	1.92	0.70
K-2.7	6588	99547	19651	10.9	3703	84.4	87.4	654	33694	16.7	62.6	6.32	122	16.8	3.04	0.90
K-2.8	7167	121251	21598	12.5	3933	102	105	777	36435	17.6	91.2	6.00	136	17.1	3.03	1.03
K-2.9	7458	85828	20645	10.8	3464	76.9	88.0	635	30932	15.1	60.8	4.91	100	14.9	2.49	0.86
K-2.10	7105	92211	20708	11.3	3237	85.6	78.3	729	31206	16.6	84.3	3.89	96.6	12.9	2.65	0.88
K-2.11	5919	112242	20997	11.8	3676	94.0	86.6	739	33511	17.6	89.6	3.88	95.3	15.0	2.75	0.93
K-2.12	7782	57853	20970	11.2	2549	59.2	86.3	657	30413	16.4	84.4	4.70	90.1	13.5	2.49	0.81
K-2.13	6730	44317	20754	11.6	2322	50.1	78.8	655	31994	18.0	80.6	3.79	99.0	13.7	2.59	0.78
K-2.14	7355	120437	21318	11.1	3768	94.2	76.3	793	30878	17.3	73.2	3.57	92.1	13.0	2.79	0.91
Min	896	44317	18596	7.18	2322	50.1	34.9	553	18881	12.9	60.8	2.05	33.1	6.88	1.53	0.65
Max	7782	216092	21597	12.5	7251	151	105	793	36435	18.0	91.2	6.32	136	17.1	3.04	1.03
UCC	24300	81500	23200	14	3800	97	92	775	39200	17.3	67	4.8	84	10.5	2.7	
Mean	6626	124663	20432	10	4570	103	67	674	27638	16	77	4	77	12	2	0.84
SD	1714	52861	885	2	1664	33	24	66	6012	2	9	1	35	4	1	
RSD,%	25.9	42.4	4.3	17.8	36.4	31.8	36.0	9.7	21.8	10.9	11.7	39.4	45.1	33.0	21.9	

Table 5. Concentrations of the elements (mg kg^{-1}) in sediments of core-3 of the Karnaphuli river

Sample	Na	Al	K	Sc	Ti	V	Cr	Mn	Fe	Co	Zn	As	Rb	Th	U	PLI
K-3.1	8049	39087	25858	13.8	4039	105	84.1	1015	37558	19.3	104	4.30	101	15.0	3.63	0.97
K-3.2	8071	40148	22829	13.0	3086	76.3	77.8	745	35785	18.7	112	4.22	102	14.8	2.80	0.89
K-3.3	8260	48162	22977	12.7	2764	62.5	78.8	651	33983	16.6	97.9	4.87	96.9	15.2	2.95	0.85
K-3.4	7995	38935	22267	12.7	3775	91.6	76.6	725	33988	18.7	83.4	4.98	88.1	14.2	3.05	0.87
K-3.5	8393	4153	23139	12.0	3420	65.6	67.8	801	31356	17.7	99.0	<0.82	87.4	12.7	<1.5	0.84
K-3.6	8390	40331	25434	12.7	3133	80.4	69.5	793	33525	19.3	104	3.88	96.9	13.1	2.62	0.88
K-3.7	8768	39894	2658	11.9	2783	69.4	72.9	764	31510	17.8	98.8	3.83	88.6	12.7	2.65	0.84
K-3.8	9523	43410	24289	10.5	2407	56.8	59.3	718	26095	16.4	85.4	3.45	59.1	11.1	2.69	0.74
K-3.9	8636	40087	27099	12.7	2390	59.4	63.3	860	31292	19.9	91.1	3.71	73.8	12.1	2.93	0.81
K-3.10	9803	31662	26623	11.5	2618	46.6	63.4	750	28478	17.7	103	4.03	66.9	10.6	2.72	0.76
K-3.11	8899	51095	25371	10.4	2412	60.8	58.3	796	27123	17.3	96.2	3.34	58.0	14.4	3.81	0.79
K-3.12	9282	116318	26313	11.0	3766	104	54.1	724	26808	17.6	72.2	3.52	57.9	10.5	3.06	0.86
K-3.13	647	96584	15934	7.70	3173	79.8	43.4	662	20386	14.0	46.9	2.60	44.8	8.57	2.23	0.66
K-3.14	7525	58343	23184	7.99	2758	58.6	42.5	569	19537	13.4	60.0	1.96	46.4	9.01	2.55	0.64
Min	6477.3	31662	15934	7.70	2390	46.6	42.5	569	19537	13.4	46.9	<0.82	44.8	8.57	<1.5	0.64
Max	9803.1	116318	27099	13.8	4039	105	84.1	1015	37558	19.9	112.2	5.0	102.4	15.2	3.8	0.97
UCC	24300	81500	23200	14	3800	97	92	775	39200	17.3	67	4.8	84	10.5	2.7	
Mean	8434	51828	24136	11	3037	73	65	755	29816	17	89	3	76	12	3	0.82
SD	846	24305	2877	2	545	18	13	104	5392	2	18	1	21	2	1	
RSD,%	10.0	46.9	11.9	15.8	17.9	24.6	19.6	13.8	18.1	10.7	20.6	36.8	26.9	17.7	32.6	

When compared with UCC values, it is observed that mean concentrations of Al, Ti, V, Zn, Rb and Th (core-1), mean concentration of Al, Ti, V, Zn and Th (core-2) and mean concentration of K, Co, Zn and Th (core-3) show elevated values. Recently, distributions of trace elements in surface sediments of the Buriganga and Poshur rivers have been reported [5, 9]. The elevated concentration levels of Ti, V, Th and U are also reported in those studies. The overall mean elemental concentrations for rest of the studied elements in this study are comparable to that of their concentrations in surface sediments of the Bangladeshi rivers [17, 18].

For core-1, the concentration of Al varied from 156169 (K-1.9) to 281713mg kg^{-1} (K-1.7), with a mean concentration of 125617 mg kg^{-1}. The concentration of Ti varied from 6064(K-1.5) to 9300mg kg^{-1} (K-1.10), with a mean concentration of 4896mg kg^{-1}. The concentration of V varied from 140 (K-1.8) to 216mg kg^{-1} (K-1.10), with a mean concentration of 116mg kg^{-1}. The concentration of Zn varied from 80.8 (K-1.7) to 116mg kg^{-1} (K-1.1), with a mean concentration of 88mg kg^{-1}. The concentration of Rb varied from 64.6 (K-1.12) to 393mgkg^{-1}(K-1.1), with a mean concentration of 98 mg kg^{-1}. The concentration of Th varied from 10.7 (K-1.12) to 31.9 (K-1.1) mg kg^{-}1, with a mean concentration of 14mg kg^{-1}. For core-1, relatively higher concentrations of trace elements were found in K-1.1 (surface, 0-5 cm), whereas K-1.12 (55-60 cm depth) shows the overall lowest concentrations of the studied trace elements. The higher concentrations of the trace elements in surface sediments of core-1 indicate more contamination in the present time than previous periods in the Karnaphuli river. In core-2, the concentration of Al varied from 44317(K-2.13) to 216092 mg kg^{-1} (K-2.4), with a mean concentration of 124663 mg kg^{-1}. The concentration of Ti varied from 2322 (K-2.13) to 7251 mg kg^{-1} (K-2.5), with a mean concentration of 4570 mg kg^{-1}. The concentration of V varied from 50.1 (K-2.13) to 151 mg kg^{-1} (K-2.2), with a mean concentration of 103 mg kg^{-1}. The concentration of Zn varied from 60.8 (K-2.9) to 91.2mg kg^{-1} (K-2.8), with a mean concentration of 77 mg kg^{-1}. The concentration of Th varied from 6.88 (K-2.6) to 17.1mg kg^{-1} (K-2.8), with a mean concentration of 12mg kg^{-1}. For core-2, relatively higher concentrations of the studied elements were found in K-2.8 (35-40 cm), whereas lowest concentrations were found in K-13 (60-65 cm). In the case of core-3, the concentration of K varied from 15934 (K-3.13) to 27099mg kg^{-1} (K-3.9), with a mean concentration of 24136 mg kg^{-1}. The concentration of Co varied from 13.4 (K-3.14) to 19.9 mg kg^{-1} (K-3.9), with a mean concentration of 17 mg kg^{-1}. The concentration of Zn varied from 46.9 (K-3.13) to 112 mg kg^{-1} (K-3.2), with a mean concentration of 89 mg kg^{-1}. The concentration of Th varied from 8.57 (K-3.13) to 15.2 mg kg^{-1} (K-3.3), with a mean concentration of 12 mg kg^{-1}. For core-3, the relatively higher concentrations of the studied trace elements were found in K-3.9 (40-45 cm) and lower concentrations were found in K-3.13 (60-65 cm).

3.2 Assessment of elemental contamination

Various pollution indices have been developed to assess the environmental contamination and risk of trace elements in sediments based on their total contents. Among the contamination indices, the enrichment factors (EFs) of trace elements have been commonly used to assess human-made contamination. In general, EF values of 0.5–1.5 reflect regional rock compositions, whereas EF>1.5 indicates non-crustal contributions and/or anthropogenic influences.

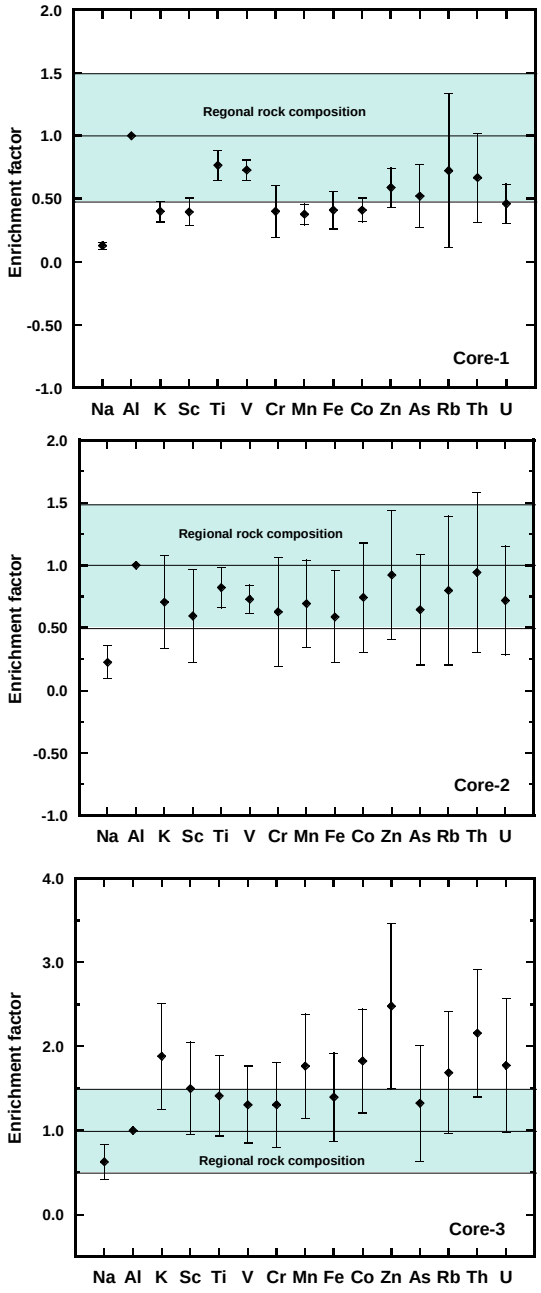

Fig. 1 The average enrichment factor values of the studied elements for sediments core-1, core-2 and core-3 of the Karnaphuli river

In this study, for core-1, the range of EF value for the studied elements are as follows: Na, 0.09–0.16; K, 0.29-0.54; Sc, 0.25-0.64; Ti, 0.55-0.93; V, 0.56-0.85; Cr, 0.22-0.88; Mn, 0.24-0.48; Fe, 0.25-0.76; Co, 0.26-0.57; Zn, 0.35-0.85; As, 0.26-1.12; Rb, 0.26-2.29; Th, 0.33-1.49 and U, 0.23-0.77. The average EF values along with standard deviations of the studied elements for core-1, core-2 and core-3 of the Karnaphuli river are shown in Fig. 1. The average and standard deviation values were calculated for core-1, n=12 and for core-2 and core-3, n=14. For core-1, the average EF values of all elements are below 1.5 indicates no pollution by these elements.

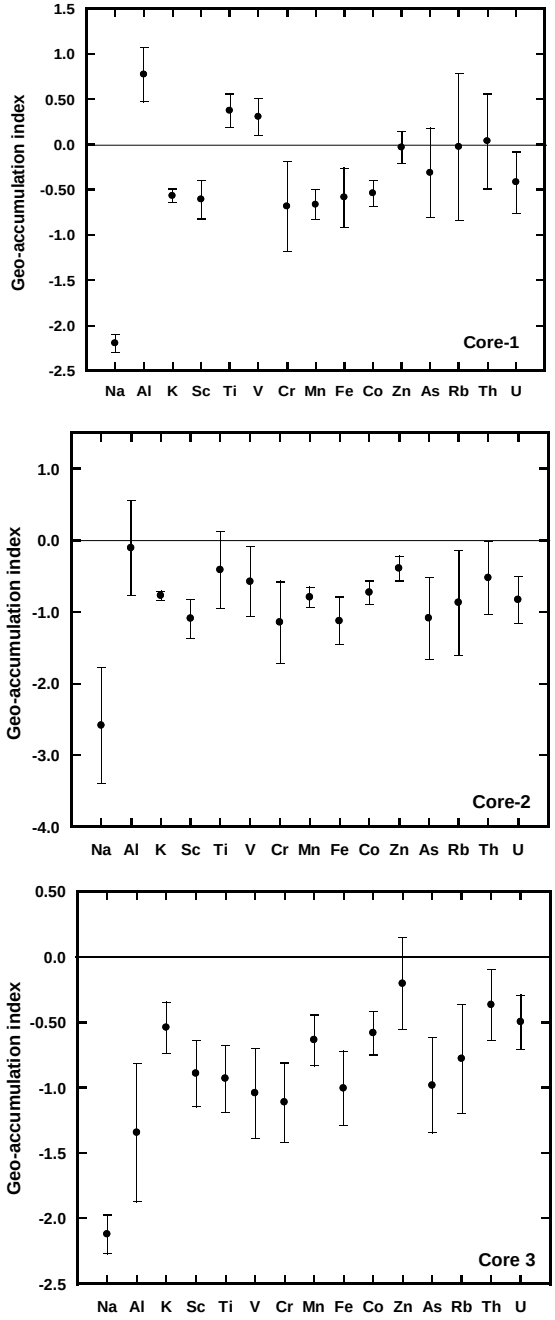

Fig. 2 Theaverage geo-accumulation index values of the studied elements forsediments core-1, core-2 and core-3 of the Karnaphuli river

For core-2, the range of EF value for the studied elements are as follows: Na, 0.01–0.51; K, 0.32-1.65; Sc, 0.19-1.53;

Ti, 0.66-1.18; V, 0.57-0.95; Cr, 0.14-1.58; Mn, 0.27-1.55; Fe, 0.18-1.50; Co, 0.28-1.91; Zn, 0.41-2.21; As, 0.17-1.45; Rb, 0.16-2.17; Th, 0.27-2.41 and U, 0.24-1.77. From EF values, it is observed that Co, Zn, Rb, Th and U at some layers, especially at K-2.13 layer, are minorly enriched.

For core-3, the range of EF value for the studied elements are as follows: Na, 0.22–1.04; K, 0.58-2.95; Sc, 0.46-2.12; Ti, 0.69-2.22; V, 0.69-2.27; Cr, 0.4-1.91; Mn, 0.65-2.73; Fe, 0.44-2.00; Co, 0.68-2.63; Zn, 0.59-3.95; As, 0.0-2.17; Rb, 0.45-2.50; Th, 0.69-2.98 and U, 0.0-2.80. For core-3, at most of the layers K, Sc, Mn, Co, Zn, Rb, Th and U are above 1.5 which indicates contamination of the sediments at this area of the Karnaphuli river by these elements. The depth-wise trace elemental distribution at core-3 indicates that this area is contaminated by these elements from previous time to still now. This study also indicates that rest of the elements Na, Ti, V, Cr, Fe, As are not a major concern for the contamination of the sediments of the river at this area. From Fig.1, it is also observed that the EF values of Na is significantly lower than unity, which indicate elemental mobilization of this element in sediments of this river. The highest EF value is observed for Zn (EF = 3.95) and ranges from 0.59 to 3.95. The high contents of Zn in the sediments of the Karnaphuli river may be due to the precipitation of Zn in the river system from effluents of battery, paints and different chemical industries like fertilizer and tannery [19]. The higher level of Th and U in the sediments may be due to the contamination of these elements from chemical fertilizer used in the agricultural fields of that area [20]. The degree of contamination with studied elements as indicated by EF was: Zn>Th> K>Co> U>Mn>Rb>Sc>Ti>Fe>As>V>Cr>Al>Na (high to low).

The calculated average geo-accumulation index (I_{geo}) values along with standard deviation of each core for the studied elements are shown in Fig. 2. According to I_{geo} classification, the average I_{geo}values ($0<I_{geo}<1.0$)of core-1 indicate that sediments of the core-1 are uncontaminated to moderately contaminated by Al, Ti, V and Th. For core-2 and core-3 sediments are practically uncontaminated.

PLI values at all layers of core-1 are ≥1.0, ranging from 1.00 to 1.52 withaverage PLI = 1.20. The highest PLI value is observed in the sampling point K-1.1 (PLI = 1.5). PLI values in all layers of core-2 are<1.0, except at K-2.8 (PLI = 1.03), ranging from 0.65 to 1.03 with average PLI = 0.84. PLI values at all layers for core-3 are <1.0. According to the classification adopted by Tomlinson et al. (1980) [21], PLI> 1.0 indicates deterioration of the sediment quality. From this study, estimated PLI values indicate the deterioration of the sediment quality at all layers of the core-1 (Table 3). For core-2 and core-3, there is no pollution in the sediment layers (except at K-2.8). The range of calculated modified degree of contamination (mC_d) for core-1, 1.1 to 1.8 with mean 1.3; for core-2, 0.73 to 1.12 with mean 0.91 and for core-3, 0.67 to 1.05 with mean 0.87. According to the gradation of mC_d, sediments at top three layers (K-1.1=1.81, K-1.2=1.63 and K-1.3=1.51) of core-1 represent low degree of contamination, whereas other deeper layers of this core represent nil to very low degree of contamination. For core-2 and core-3, all layers of sediments represent nil to very low degree of contamination. In this study, the PLI and mC_d values indicate that contamination of surface sediments at core-1 and core-3 is relatively higher than the deeper layers indicating that recent pollution level of the sediments is higher than the past in the Karnaphuli river.

4. Conclusion

In this study, 15 major and trace elements are determined in core sediments of the Karnaphuli river by NAA. It is observed that mean concentrations of Al, Ti, V, Zn, Rb and Th (core-1), mean concentration of Al, Ti, V, Zn and Th (core-2), mean concentration of K, Co, Zn and Th (core-3) show elevated values with respect to UCC. Among the studied 15 elements, the highest EF value is observed for the Zn (EF = 3.95) and ranges from 0.59 to 3.95 (core-3). The degree of contamination with studiedtrace elements as indicated by EF was: Zn>Th> K>Co > U>Mn>Rb>Sc> Ti>Fe>As>V>Cr>Al>Na (high to low). The calculated PLI and mC_d values indicate that sediments at core-1 are deteriorated. This study recommends that continuous monitoring of trace elements in sediment and other aquatic biota of Karnaphuli river should be directed to assess the risk of these elements to safe ecology of this river.

Acknowledgement

The authors thank personnel of the Center for Research Reactor (CRR) of Bangladesh Atomic Energy Commission for sample irradiation to perform NAA. The technical personnel of NAA, RNPD are gratefully acknowledged for their kind help during sample preparation and analysis for this study.

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