Assessment of Trace Contaminants in Sediments of the Poshur River Nearby Mongla Port of Bangladesh

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Abstract

The present study investigates the distribution and contamination of trace elements in the sediments of the Poshur river nearby Mongla port of Bangladesh. Total 24 major, minor and trace elements were determined in sediments of the Poshur river by instrumental neutron activation analysis (INAA) method. Quality control of the analysis was performed by analyzing certified reference materials IAEA-Soil-7 and IAEA-SL-1 (Lake Sediment). The irradiation of the samples and standards were performed using 3 MW TRIGA Mark-II Research Reactor and the gamma-ray spectrometry was performed by high resolution HPGe detector system. In this study, pollution level of pollutants evaluated by different pollution indices suggests that Poshur river sediments are minorly contaminated with Ga, As, Sb, Cs, Th and U. The calculated pollution load index values also suggest the deterioration of the sediment quality. This study will be helpful to set a picture of metal contamination of the river and the nearby Sundarban mangrove forest area.

Keywords: INAA, trace element, sediment contamination, Poshur river

1. Introduction

Pollution of the natural environment by toxic elements is a universal problem because these elements are nondestructible and most of them have toxic effects on living organisms, when permissible levels are exceeded [1]. Trace elements are either naturally or through anthropogenic sources introduced into rivers. Elements that are naturally introduced, come primarily from sources such as rock weathering, soil erosion and the dissolution of water-soluble salts. Naturally occurring metals (especially the trace metals) move through aquatic environments independent of human activities and usually without any detrimental effects [2]. Anthropogenic pollutants are discharged from industrial, domestic and agricultural wastewater into river water system [3, 4]. Sediment served as sinks for most of the metals in aqueous phase [5-6]. The concentrations 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 soils. Several analytical techniques have been extensively employed for sediment metal pollution monitoring. Instrumental neutron activation analysis (INAA) is one of the most extensively used methods for environmental and geochemical studies due to its high sensitivity, precision, versatility and multi-elemental character [4].

The increasing urbanization and industrialization of Bangladesh have negative implications for river sediment and water quality. The pollution from industrial, urban waste effluents, port activities and agrochemicals in some water bodies and rivers has reached at an alarming level. Since our country is networked with small and big rivers, the pollution load from different sites has been added up and finally destroyed the fresh water aquatic ecosystem of the country. In river system, water and sediment are the most vital compartments and are crucial for the survival of all living organisms. In order to follow the extent of pollution, a baseline data should be established which will be helpful in future for assessment of the influence of the toxic metals on the river environment. In the last few years, port activities, industrial effluents discharge and several cargo accidents occurred at the Poshur river caused metal contamination of the river. In view of this consideration, in this study an attempt has been taken to investigate the concentration level of the trace elements in the sediments of the Poshur river nearby Mongla port.

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2. Materials and Methods

2.1 Study Area and Sample Collection

Mongla is an Upazila of Bagerhat District in the Division of Khulna, Bangladesh. Mongla is located at 22.4833°N 89.6083°E. There is a sea port at Mongla which is the second largest sea port in Bangladesh. Basically it derives with Poshur channel and is situated beside the Sundarban mangrove forest. The name Mongla originated from Mongla river presently known as Mongla Nulla. Mongla river originated from the Poshur river. The surface sediment samples (0-5 cm) were collected from 7 different locations in the Poshur river near the Mongla sea port, Khulna (longitude: 89°35′29″, latitude: 22°29′23″). Three replicate samples were taken at each point and mixed into a composite sample. The sediment samples were collected using an acrylic pipe sampler during ebbs and stored in cleaned polyethylene bag.

2.2 Sample Preparation

The collected samples were air dried under laboratory temperature. Each soil sample was sieved to remove the aggregates and organic species and dried at about 50°C in an electric oven for 2 days in the laboratory to obtain

constant weight. For making small grain size and homogeneous mixture, each of the samples was ground with an agate mortar and pestle.

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 INAA, two certified reference materials (CRMs): IAEA-Soil-7 and IAEA-SL-1 (Lake Sediment) along with the sediment samples were analyzed in this study. Two irradiation schemes were performed using pneumatic transfer (rabbit) system at the 3 MW TRIGA Mark -II research reactor of Bangladesh Atomic Energy Commission, Savar, Dhaka: (i) Long irradiation was performed simultaneously with all the samples and standards with the thermal neutron flux of 2.11×10^{13} $cm^{-2}s^{-1}$ for 7 minutes at 2.4 MW and (ii) Short irradiation was performed separately for each sample and standard with the thermal neutron flux of 5.28×10^{12} $cm^{-2}.s^{-1}$ for 1 min at 250 kW. To determine the neutron flux gradient within the sample stack, three IRMM-530RA Al – 0.1% Au (0.1 mm foil) monitor foils were also irradiated by placing them at the bottom, middle and top of the sample stack for the long irradiation scheme. After irradiation, gamma-ray counting was performed with a high purity germanium (HPGe) detector (CANBERRA, 25% relative efficiency, 1.8 keV resolution at 1332.5 keV of ^{60}Co source) coupled with a digital gamma spectrometer (ORTEC, DSPEC JrTM). For long irradiated samples, first counting was performed for 1 hour after a decay time of 2 days while the second counting was performed for 1.5 hours after a decay time of 7-10 days followed by third counting for 2 hours after 4 weeks decay. For short irradiation, first counting was performed for 300 s after a decay time of about 10 minutes and second counting for 600 seconds after a decay time of 2 to 3 hours. Peak counts were calculated using Hypermet PC software.

2.4 Quantification of Sediment Pollution

2.4.1 Enrichment Factor (EF)

Enrichment factor can be used to evaluate the metal contamination in the studied sediment in more comprehensive way. This method generally normalizes the measured elemental concentration with respect to a reference metal such as Fe or Al [7].Fe and Al usually have relatively high natural concentrations, and are therefore not expected to be substantially enriched from anthropogenic sources inestuarine sediments [8]. Currently, Al is the most frequently used geochemical normalizer in estuarine and coastal sediments [9]. This factor estimates the anthropogenic impact on sediments by calculating metal concentrations above uncontaminated background levels. Thus EF can be calculated by using the following equation [10]:

$$EF = \frac{(Metal/Al)_{Sample}}{(Metal/Al)_{Background}} \quad (1)$$

In this study, Aluminium (Al) was used as the reference element for geochemical normalization. For this study, Upper Continental Crustal (UCC) average values from literature [11] are used as the geochemical background concentration. The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals, whereas EF>1.0 indicates that the element is of anthropogenic origin. 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 sediment, respectively.

2.4.2 Geo-accumulation Index (I_{geo})

The geo-accumulation index (Igeo), originally defined by Muller [12] is a quantitative measure of the metal pollution in aquatic sediments. To characterize the pollution levels of sediments, Igeo is an effective tool which can be defined by the following equation [13]

$$I_{geo} = \mathrm{Log}_2\left(\frac{C_n}{1.5\times B_n}\right) \quad (2)$$

Where, C_n is the measured concentration of the metal n, B_n is the geochemical background concentration of metal n. Factor 1.5 is the background matrix correction factor due to lithospheric effects. The geo-accumulation index consists of seven grades or classes. Class 0 (practically uncontaminated): Igeo≤0; Class 1 (uncontaminated to moderately Contaminated): 0<Igeo<1; Class 2 (moderately contaminated): 1<Igeo<2; Class 3 (moderately to heavily contaminated): 2<Igeo<3; Class 4 (heavily contaminated): 3<Igeo<4; Class 5 (heavily to extremely contaminated): 4<Igeo<5; Class 6 (extremely contaminated): 5<Igeo. Class 6 is an open class and comprises all values of the index higher than Class 5. The elemental concentrations in Class 6 may be hundred fold greater than the geochemical background value.

2.4.3 Pollution Load Index (PLI)

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 [14]:

$$CF = \frac{(Metal\ concentration)_{Sample}}{(Metal\ concentration)_{Background}} \quad (3)$$

Then, PLI is represented by the following equation [14]:

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

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

3. Results and Discussion

3.1 Elemental Concentrations in Sediments

Total 24 major and trace elements were determined in the sediments of the Poshur river by INAA. A typical gamma-ray spectrum of an irradiated sediment sample is shown in Fig. 1. The gamma-ray peaks from the radioisotopes of Eu, Ce, Th, Cr, Hf, Cs, Sc, Fe and Co are observed in the spectrum. Quality control of the analyses is always performed by analyzing reference standard materials. The determined concentration of the studied elements in IAEA-SL-1(lake sediment) relative to IAEA-Soil-7 indicates that for most of the studied element concentrations are within

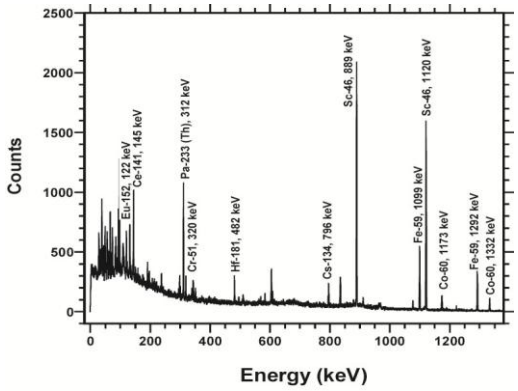

Fig. 1: A typical gamma-ray spectrum of an irradiated sediment sample (sample mass 62.2mg, irradiation time 7 min, decay time 1 month, counting time 9000 s)

10% deviation from their certified values which assures accuracy of the analysis [15].

The total concentrations of the studied elements in surface sediments in all sampling points of the Poshur river are tabulated in Table 1. Average concentrations, standard deviations as well as the literature data of the UCC for the respective elements are also given in Table 1. The range of concentration of the studied elements are Na(0.866-1.23%), Al(7.05-8.50%), K(2.35-2.82%), Ca(0.718-2.66%), Sc(12.3-17.8µg/g), Ti(0.442-0.524%), V (84.1-120µg/g), Cr(64.03-82.35 µg/g), Mn(505-737µg/g), Fe(3.59-4.90%), Co(14.6-15.2 µg/g), Zn(46.8-88.8µg/g), Ga(15.3-29.9 µg/g), As(3.40-9.04 µg/g), Sb(0.576-1.24 µg/g), Cs(8.59-13.5µg/g), La(45.0-55.3 µg/g), Ce(109-137 µg/g), Eu(1.17-1.47 µg/g), Dy(6.01-7.56 µg/g), Yb(3.09-3.81 µg/g), Hf(5.50-10.1µg/g), Th(20.8-26.7µg/g), U(4.08-7.88 µg/g). It is observed that distributions of the elemental concentrations vary from one sampling point to another. When compared with UCC values, it is observed that mean concentrations of Ga, As, Sb, Cs, REEs, Th and U show elevated values with respect to UCC. A previous study on metal assessment of sediments of the Poshur river reported that concentration of Fe, Cr and Zn varied from 1.65-3.19%, 2.8-31.9 µg/g and 26.3-71.9 µg/g, respectively [16]. Present study indicates that concentration levels of these elements in the Poshur river increased accordingly. When concentrations of the studied elements are compared with UCC values, it is observed that mean concentrations of K, Ti, Ga, As, Sb, Cs, REE, Hf, Th and U show elevated values with respect to UCC value.

Table 1: Elemental abundances (in µg/g, otherwise specified) in Poshur river sediments

Element	P-1	P-2	P-3	P-4	P-5	P-6	P-7	Mean	SD	UCC[a]
Na (%)	1.23	0.866	1.22	1.13	1.19	1.15	0.960	1.11	0.14	2.43
Al (%)	7.46	8.50	7.05	8.28	8.02	7.05	8.05	7.77	0.59	8.15
K (%)	2.35	2.82	2.45	2.54	2.44	2.46	2.60	2.52	0.15	2.32
Ca (%)	2.66	0.718	2.23	2.46	2.36	2.04	1.15	1.95	0.73	2.57
Sc	13.5	17.8	14.1	12.9	12.3	13.5	16.0	14.4	1.9	14.0
Ti (%)	0.464	0.442	0.486	0.492	0.524	0.456	0.470	0.476	0.027	0.38
V	84.1	119	87.1	96.4	89.4	84.8	103	95.1	13.0	97.0
Cr	68.0	82.1	78.0	64.0	68.1	64.9	82.4	72.5	8.1	92.0
Mn	723	510	707	737	667	688	504	649	99	775
Fe (%)	4.11	4.90	4.00	3.97	3.59	3.91	4.62	4.16	0.45	3.92
Co	15.2	15.0	15.2	14.7	14.7	14.8	14.6	14.9	0.2	17.3
Zn	58.1	88.8	68.7	46.8	64.8	83.6	77.8	69.8	14.8	67.0
Ga	24.9	29.9	23.5	22.7	15.4	19.9	26.0	23.2	4.6	17.5
As	6.80	9.04	7.15	7.42	5.80	3.40	7.48	6.73	1.76	4.80
Sb	0.620	1.24	0.718	0.702	0.576	0.624	0.952	0.776	0.239	0.40
Cs	10.4	13.6	10.5	10.3	8.59	9.35	11.9	10.7	1.6	4.90
La	45.6	48.6	55.3	44.9	48.7	47.8	47.4	48.3	3.4	31.0
Ce	113	112	137	112	112	109	111	115	10	63.0
Eu	1.31	1.25	1.47	1.34	1.17	1.21	1.28	1.29	0.10	1.00
Dy	6.82	6.60	7.56	6.56	6.82	6.90	6.01	6.75	0.47	3.90
Yb	3.30	3.09	3.81	3.35	3.13	3.59	3.74	3.43	0.29	2.00
Hf	7.22	5.50	10.1	7.54	8.00	7.90	6.58	7.54	1.41	5.30
Th	21.7	22.2	26.7	20.8	21.6	23.3	21.9	22.6	1.97	10.5
U	4.22	7.88	5.21	4.28	4.17	4.08	6.02	5.12	1.41	2.70

P = sampling point, SD = standard deviation (n = 7)and [a]UCC = Upper continental crust [11]

3.2 Assessment of Elemental Contamination

To quantify the sediment pollution of the Poshur river, the EF values are calculated and given in Table 2.The highest EF value is observed for the Sb (EF = 2.97) and ranges from 1.46 to 2.97 which indicates the anthropogenic origin of this element [17]. The EF values for Ga, As, Sb, Cs, REE, Th and U are significantly higher than 1. The EF values of the environmentally toxic elements As, Sb, Th and U are between 1.5-3.0 which implies that Poshur river sediments are minorly enriched with these elements. These elements are more likely to have the anthropogenic origin rather than a simple crustal origin. The port activities, chemical fertilizer used in agricultural field and fish

Table 2: Enrichment factor (EF) of the elements in sediments of the Poshur river

Element	P-1	P-2	P-3	P-4	P-5	P-6	P-7
Na	0.55	0.34	0.58	0.46	0.50	0.55	0.40
K	1.11	1.17	1.22	1.08	1.07	1.22	1.14
Ca	1.13	0.27	1.00	0.94	0.93	0.92	0.45
Sc	1.09	1.22	1.17	0.91	0.9	1.11	1.16
Ti	1.33	1.11	1.48	1.27	1.4	1.39	1.25
V	0.95	1.18	1.04	0.98	0.94	1.01	1.09
Cr	0.81	0.86	0.98	0.68	0.75	0.82	0.91
Mn	1.02	0.63	1.06	0.94	0.88	1.03	0.66
Fe	1.14	1.2	1.18	1.00	0.93	1.15	1.19
Co	0.96	0.83	1.01	0.84	0.86	0.99	0.85
Zn	0.95	1.27	1.19	0.69	0.98	1.44	1.17
Ga	1.56	1.64	1.55	1.28	0.89	1.32	1.51
As	1.55	1.8	1.72	1.52	1.23	0.82	1.58
Sb	1.69	2.97	2.08	1.73	1.46	1.8	2.41
Cs	2.32	2.65	2.48	2.07	1.78	2.21	2.46
La	1.61	1.5	2.06	1.43	1.6	1.78	1.55
Ce	1.96	1.71	2.52	1.75	1.81	2.01	1.8

Element	P-1	P-2	P-3	P-4	P-5	P-6	P-7
Eu	1.43	1.2	1.69	1.32	1.19	1.4	1.29
Dy	1.91	1.62	2.24	1.65	1.78	2.05	1.56
Yb	1.8	1.48	2.20	1.65	1.59	2.08	1.89
Hf	1.49	0.99	2.19	1.4	1.54	1.72	1.26
Th	2.26	2.03	2.94	1.95	2.09	2.57	2.11
U	1.71	2.8	2.23	1.56	1.57	1.75	2.26

aquaculture run off discharges to the Poshur river may be the sources of these elements. Moreover, hydrodynamic conditions and landform can affect the physical properties of sediments in the Poshur river, further affecting heavy metal concentrations and spatial distribution [18]. Except for these elements, other elements like Na, Ca, Cr, Mn and Co seem to have crustal origin.

Table 3: Geo-accumulation Indices (I_{geo}) and PLI values in sediments of the Poshur river

Index	Element	P-1	P-2	P-3	P-4	P-5	P-6	P-7
I_{geo}	Na	-0.432	-0.642	-0.411	-0.517	-0.477	-0.438	-0.574
	Al	-0.176	-0.176	-0.176	-0.176	-0.176	-0.176	-0.176
	K	-0.131	-0.109	-0.089	-0.143	-0.148	-0.088	-0.121
	Ca	-0.122	-0.748	-0.176	-0.201	-0.206	-0.213	-0.519
	Sc	-0.139	-0.089	-0.109	-0.216	-0.224	-0.129	-0.112
	Ti	-0.051	-0.129	-0.007	-0.071	-0.029	-0.034	-0.078
	V	-0.199	-0.103	-0.16	-0.186	-0.205	-0.172	-0.141
	Cr	-0.269	-0.244	-0.185	-0.34	-0.3	-0.265	-0.219
	Mn	-0.168	-0.376	-0.153	-0.205	-0.233	-0.164	-0.357
	Fe	-0.117	-0.098	-0.104	-0.177	-0.207	-0.114	-0.099
	Co	-0.194	-0.256	-0.171	-0.253	-0.241	-0.182	-0.245
	Zn	-0.199	-0.072	-0.102	-0.339	-0.183	-0.017	-0.106
	Ga	0.016	0.039	0.015	-0.07	-0.225	-0.057	0.002
	As	0.014	0.08	0.06	0.006	-0.087	-0.263	0.022
	Sb	0.053	0.297	0.141	0.061	-0.011	0.08	0.206
	Cs	0.189	0.247	0.219	0.139	0.075	0.167	0.215
	La	0.03	0.00	0.138	-0.022	0.027	0.075	0.013
	Ce	0.116	0.056	0.225	0.067	0.082	0.127	0.079
	Eu	-0.02	-0.096	0.053	-0.056	-0.10	-0.029	-0.065
	Dy	0.105	0.034	0.174	0.043	0.074	0.135	0.017
	Yb	0.08	-0.005	0.167	0.041	0.026	0.141	0.101
	Hf	-0.003	-0.179	0.165	-0.03	0.01	0.061	-0.076
	Th	0.178	0.131	0.293	0.114	0.144	0.233	0.148
	U	0.056	0.271	0.172	0.017	0.020	0.067	0.178
PLI		1.203	1.274	1.298	1.199	1.152	1.152	1.236

To quantify the sediment pollution of the Poshur river, the values of the Geo-accumulation Indices, I_{geo} are also calculated and given in Table 3. According to I_{geo} value, the sediments are uncontaminated to moderately contaminated ($0<I_{geo}<1$) byGa, As, Sb, Cs, REE, Hf, Th and U whereas the Poshur river sediments are practically uncontaminated by rest of the elements. The PLI is used to determine the comprehensive pollution effect at different stations by the metals. The calculated PLI values at different sampling stations are shown in Fig. 2. The range of literature data [19] for PLI values (PLI = 0.90-1.16) of the Poshur river (shaded area) are also shown in Fig. 2. Values of PLI = 1 indicate metal loads close to background, and values above 1 indicate progressive pollution of the sediments [20]. In this study, the calculated PLI values among the sampling points varied from 1.20-1.30 indicating the progressive deterioration of the sediment quality of the river. A recent study has shown that PLI values for the Korotoa river varied from 1.6-7.2 [21] which is significantly higher than the PLI values of this study.

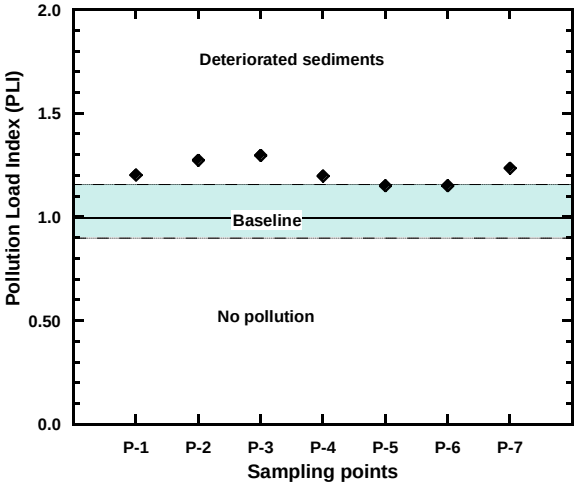

Fig. 2: Pollution load index values for surface sediments of the Poshur river

4. Conclusion

In this study, 24 major, minor and trace elements are determined in the sediments of the Poshur river by INAA. Mean concentrations of Ga, As, Sb, Cs, REEs, Th and U are higher than those of UCC values. Different sediment contamination indices-enrichment factor and geo-accumulation index suggest that Poshur river sediments are poorly contaminated with Ga, As, Sb, Cs, Th and U.

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