Levels of Lanthanides and Natural Radionuclides in the Uncultivated Soils Near Industrial Area of Bangladesh

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LEVELS OF LANTHANIDES AND NATURAL RADIONUCLIDES IN THE UNCULTIVATED SOILS NEAR INDUSTRIAL AREA OF BANGLADESH

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Twenty-five uncultivated surface soil samples collected from the northern and southern regions of Dhaka Export Processing Zone (DEPZ), industrial area of Bangladesh, were analyzed for their contents of Y, lanthanides and natural radionuclides (Th and U) using an inductively coupled plasma mass spectrometer (ICP-MS). Analogous concentrations of the Y, lanthanides, Th and U were observed in the both regions of DEPZ around several kilometer distances. Further, the measured values showed no particular contamination. However, the concentrations of the light lanthanides (La, Ce and Nd) in the Bangladeshi soils were around twice the worldwide average value. But, the smooth curve of the chondrite normalized patterns of the lanthanides suggested that the lanthanide contents of the Bangladeshi soils in this area are the results of the natural dispersion process rather than anthropogenic activities. In addition, the relatively high Th and U concentrations and Th/U ratio were observed in Bangladeshi soils of this area, most likely due to the effect of their parent materials such as clay stones which have a high Th/U ratio. Since this is the first precise result for the Y, lanthanides, Th and U contents in Bangladeshi soils, it could be useful in understanding the background level and the characteristics of these elements in Bangladeshi soils.

Keywords: ICP-MS; Bangladeshi soil; Y; Lanthanides; Natural radionuclides; Th and U

INTRODUCTION

Environmental pollution for industrialization is now a serious problem throughout the world. With technological and industrial advances, wide varieties of elements are constantly being released into the living environment. Currently, the lanthanides are becoming more and more technologically significant elements. These elements comprise a total of 15 elements of which Pm does not occur naturally in the Earth's crust [1]. The lanthanides or rare earth elements (REE) possess nearly identical chemical and physical properties and form a geochemically coherent group [2]. Further, Y and lanthanides are associated in all natural matter, because the chemical behavior of Y is quite similar to that of the members of the group La–Lu. The Y and La–Lu elements

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are widely used in the frontier technologies such as, electronics, optoelectronics, super-conductors, super magnets, lasers, computers, rechargeable hydride batteries, artificial diamonds, glass and ceramics. Hence, REE technological materials are increasingly produced by industry and consequently also released into the environment where the trace levels of lanthanide elements are bio-accumulated by micro organisms [3]. Although, the bioavailability and the toxic properties of the REE are still not known well, it is reported that REE activate or inhabit metabolism or enzyme activity [4,5]. As a consequence, the basic information on the background level of lanthanide elements in the soil is essential to estimate the soil contamination due to anthropogenic activities. Further, analyses of lanthanide elements in soil samples are also geochemically important, because they can be used as an indicator for the identification of the origin of the soils. However, only a few reports are available for the distribution of lanthanide elements in soils [6–8].

In addition, natural radionuclides such as Th and U are used as a fuel in nuclear reactors. Further, a wide variety of industrial products contain radioactive nuclides (Th and U) that have been deliberately incorporated to satisfy a specific purpose. Uranium is used in inertial guiding devices, as shielding material, in photographic applications and in analytical chemistry. For example, porcelain used in dentistry. Optical lenses and alloys may contain significant amount of U. Compounds containing U are also used in the chemical industry as catalysts. Thorium also used in the preparation of incandescent mantles in electronic and electrical devices, such as gas-discharge lamps and vacuum tubes. Thorium is further used in ceramics and glassware. Thorium is an important alloying element in magnesium, and it is used to coat tungsten wire in electronic equipment. Glasses containing Th find application in lenses for cameras and scientific instruments. Thorium dioxide is a catalyst in several chemical processes. Therefore, the analysis of U and Th in the soil near industrial area is necessary for the control of natural radioactivity. Further, it is reported that the concentrations of U and Th in soil are closely related to the parent bedrock of the soil [6,9,10].

Dhaka Export Processing Zone (DEPZ), Savar is the largest industrial area in Bangladesh with 45 local and foreign industries including textile, dyeing, pharmaceuticals, leather, food processing, plastic and electrical product manufacturing factories etc. Outside this area, there are more 50 such factories. The industries of Savar generate a large amount of effluents everyday, which is directly discharged into the surrounding area, agricultural fields, irrigation channels, surface water and finally enter into the river. In the above mentioned contexts, a large number of villages around DEPZ area are now being threatened by the environmental degradation. Therefore, fish population and the crops, fruits and vegetables of this area might be affected by the industrial effluent. Further, the Atomic Energy Research Establishment (AERE) having a TRIGA Mark-II research reactor in operation is also located in this area. Generally, the possible release of hazardous contaminants from the industrial area are mostly dispersed into the environment through various media such as water, soil, mineral and vegetation and after passing through the food chain, these hazardous contaminants accumulate in the human body leading to various diseases. So, for the safety of the general people as well as to take remedial action of the contaminated area, it is necessary to establish the base line data for the radioactive and toxic elements in the environmental materials in the industrial area. However, no research work concerning the assessment of lanthanide elements and natural radionuclides in the environmental materials has been found yet due to the lack of proper facilities in Bangladesh.

Recently, inductively coupled plasma mass spectrometry has been used for accurate and precise determination of trace and ultra trace elements in variety of environmental samples. The main advantage of ICP-MS over other classical methods, such as Neutron Activation Analysis (NAA), Atomic Absorption Spectrometry (AAS), X-ray Florescence (XRF) and Atomic Emission Spectrometry (AES) are very low detection limit, high sensitivity for multielement detection, large dynamic range, limited interference effect and simplified sample preparation procedures [11–13]. In addition it possesses the capability of isotopic discrimination and measurement. So, in order to develop the base line data of the radioactive and hazardous contaminants, the background concentrations of Y, lanthanide and natural radioactive elements in the environmental samples around the industrial area of Bangladesh were estimated by the most advanced analytical techniques, ICP-MS and the study results were expected to be applicable as a reference in other sites of Bangladesh.

EXPERIMENTAL

Bangladesh, a country in South Asia, is located between latitude 20°34′ and 26°38′ N and longitude 88°3′ and 92°40′ E. It has a tropical climate characterized by three main seasons, (1) a dry season from November to March and a (2) rainy (monsoon) season from June to October. In addition to the summer monsoon, winter depressions originating from the Mediterranean and the so-called (3) "Nor Westers" in April and May contribute to annual precipitation. The climatic feature of Bangladesh varied from region to region and season to season.

Soils of Bangladesh have been formed from different kinds of parent materials occurring in various topographic and drainage conditions. They are spread over three major physiographic units: (i) Northern and eastern hills of tertiary formations, covering 12% of the total area; (ii) Pleistocene terraces of the Madhupur and Barind tracts, covering 8% of the total area; and (iii) Recent floodplains, covering 80% of the total area. Sandstone, siltstone, shale and clay stones are the main ocean sedimentary rock types existing all over the country of Bangladesh [14].

In this study, the sampling sites are located in the Madhupur and Barind tracts which contain Madhupur clay. Madhupur clay is considered to be a marine formation of Plio-Pleistocene age. It is remarkably homogeneous in appearance both vertically and laterally. Extensive areas of the Barind tract and parts of the Madhupur tract have almost level, terrace-like topography [15].

The soil samples were collected from 25 sites around 5 km distances and two directions (north and south) of the industrial area, DEPZ, Dhaka, Bangladesh (Fig. 1). The sampling sites selected for this study were uncultivated or forested areas assumed to receive pollution only from atmospheric deposition because of not using fertilizer or irrigation. In the northern and southern regions, around 11 and 14 surface soil samples (0–5 cm) were taken from the high lands mainly from the garden, forest and open areas from the boundary of the DEPZ to the rural villages respectively in June, 2001.

The soil samples were air dried, sieved (1 mm), and after oven dried at 80°C, ground to powder with an agate ball mill (FRITSCH, Planetary Ball Mill, Pulverisette 5). The finely ground soil samples (0.1 g) were digested in Teflon PFA pressure decomposition vessels with acids (HNO_3, HF, $HClO_4$). A microwave pressure digester (CEM, MARS-5) was used to decompose the soil samples. The decomposition and
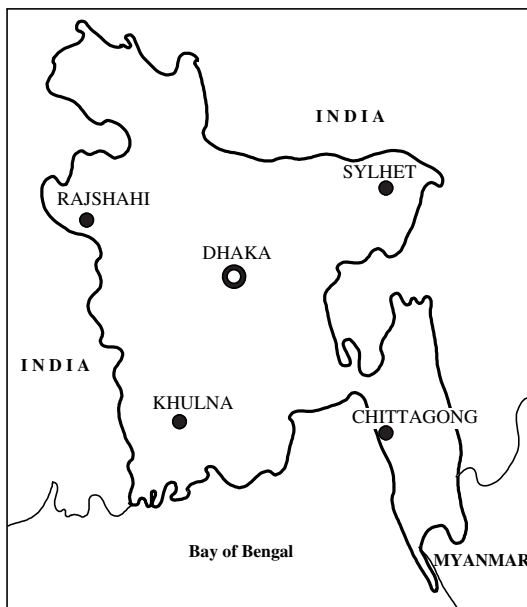
FIGURE 1   The map of Bangladesh.

analytical procedures are the same as in Yoshida *et al.* [6]. After digestion, the soil
sample solutions were evaporated to dryness. Then, the residues were dissolved in
2% HNO_3 to yield the final sample solutions of 50 mL. After 8-fold dilutions of the
final solution (dilution factor, 4000), the acid digests soil samples were analyzed by
ICP-MS (Agilent 7500 ICP-MS, Yokogawa Analytical Systems Inc. Japan) for 17
trace elements (Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th
and U) in the National Institute of Radiological Sciences, Chiba, Japan. The standard
solutions were prepared from SPEX Multi-Element Plasma Standards (XSTC-1 and
13), supplied by SPEX industries, Inc. (Metuchen, NJ, USA) and used to get calibration
curves. The elements In, Rh and Bi were chosen as the internal standards because of
their mass contents are nearly negligible in most of the soil samples [16]. The validity
of the analytical technique was examined by analyzing standard reference rock
sample, JB-1 (basalt) provided by the Geological Survey of Japan (GSJ).

RESULTS AND DISCUSSION

Accuracy of the Analytical Procedure

Standard Reference material JB-1 (basalt) which is one of the best certified reference
materials of the GSJ was used to check accuracy and precision in the analysis of
trace elements by the ICP-MS. Accuracies of the analytical results for the 17 trace ele-
ments were determined by comparing them with the certified values [17,18] of JB-1. The
average result of the nine individual determinations for JB-1 is shown in Table I. Good
agreements between the certified and measured values were observed in the reference
sample analyzed in this study.

TABLE I Analytical results of the certified reference material, JB-1, obtained by ICP-MS in comparison with certified values

m/z	Elements	Mean, n = 9 (mg/kg)	SD ±	RSD (%)	Certified value (mg/kg)	Meas./Cer.
89	Y	20.9	0.64	3.06	24.0	0.87
139	La	36.8	1.35	3.67	38.6	0.95
140	Ce	64.0	2.35	3.66	67.8	0.94
141	Pr	6.81	0.26	3.76	7.01	0.97
146	Nd	25.4	0.92	3.64	26.8	0.95
147	Sm	4.92	0.14	2.79	5.13	0.96
153	Eu	1.48	0.03	2.20	1.49	0.99
157	Gd	4.72	0.16	3.30	4.90	0.96
159	Tb	0.70	0.01	1.34	0.82	0.85
164	Dy	4.01	0.11	2.86	4.14	0.97
165	Ho	0.80	0.01	1.83	0.79	1.01
166	Er	2.23	0.06	2.64	2.27	0.98
169	Tm	0.32	0.00	0.91	0.35	0.92
174	Yb	2.04	0.06	2.76	2.10	0.97
175	Lu	0.30	0.01	2.32	0.31	0.97
232	Th	9.44	0.46	4.92	9.20	1.03
238	U	1.63	0.06	3.59	1.70	0.96

The errors of measured values were less than 10% of the certified values for 15 elements, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Th and U whereas the errors were less than 20% for 2 elements, Tb and Y. Precisions calculated using three independent runs of the samples were typically better than 3% RSD (relative standard deviation) for all the elements.

Concentrations of Y and Lanthanides in the Northern and Southern Regions of DEPZ

Total concentrations of Y and lanthanides found for the Bangladeshi soils in southern and northern regions of DEPZ are shown in Tables IIa and IIb, respectively.

Although the concentrations of the light lanthanides of the southern region (La: 39.9, Ce: 89.7, Pr: 33.6, Nd: 6.0) were slightly higher than the northern region (La: 34.1, Ce: 77.5, Pr: 28.7, Nd: 5.2), for most of the elements the differences between the two regions were very small. Further, no remarkable differences in lanthanide concentrations were observed with respect to the sample sites or soil utilizations such as garden, forest or open field soils. Therefore, it can be assumed that there is no apparent contamination in this area. The concentrations of Y and lanthanides in the present study area might be derived from the natural sources.

Comparison of the Present Data with the Data for Continental Crust and Worldwide Soils

The plot of the concentrations of La–Lu *versus* atomic number (Fig. 2) shows the striking differences in abundance between successive lanthanides with odd and even atomic numbers. These trends are consistent with the Odd-Harkins rule relating to the abundance of elements in the universe.

In this study, the lanthanide concentrations for the Bangladeshi soils are also compared with the recent data for Japanese soils [6], the average data for worldwide soils [1] and the data for continental crust [19] which are also shown in Fig. 2. The Japanese soils were selected, as they were analyzed with similar methods as our samples and the soils were mostly from forest or open field areas. On average, the

TABLE IIa   Concentrations of Y, lanthanides Th, and U (mg/kg) in Bangladeshi soils around southern region of DEPZ, Dhaka

Sample no	Soil Utal.	Location	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
S01	Garden	AERE	22.1	49.3	118	10.1	42.1	6.96	0.97	5.66	0.78	4.45	0.75	2.02	0.31	1.86	0.28	24.9	3.52
S02	Open area	EPZ	19.8	35.2	77.2	8.1	29.4	5.77	0.86	4.72	0.66	3.55	0.66	1.83	0.26	1.69	0.24	15.6	2.99
S03	Open area	EPZ	21.3	36.9	75.2	7.9	30.0	6.02	1.13	5.25	0.77	4.33	0.84	2.37	0.34	2.18	0.31	17.2	2.77
S04	Open area	AERE	21.7	35.1	71.8	8.1	30.3	6.01	1.13	5.14	0.73	4.05	0.77	2.17	0.30	1.91	0.27	15.0	2.40
S05	Garden	Ganak bari	24.2	45.9	89.5	8.3	38.0	5.94	1.03	5.08	0.72	4.80	0.72	1.95	0.28	1.70	0.25	20.0	2.50
S06	Forest	AERE	20.6	48.8	107	10.0	37.2	7.03	1.20	6.00	0.87	4.58	0.89	2.42	0.37	2.21	0.34	19.9	3.47
S07	Garden	Ganak bari	16.9	37.2	93.9	7.9	34.8	6.03	1.07	5.36	0.80	4.38	0.87	2.36	0.36	2.16	0.33	14.8	2.34
S08	Garden	Ganak bari	18.9	33.3	73.5	6.7	27.1	4.68	0.63	3.91	0.55	2.81	0.55	1.48	0.23	1.41	0.22	13.7	3.22
S09	Open area	AERE	19.7	39.0	81.4	9.0	32.1	5.92	0.88	4.70	0.65	3.42	0.64	1.73	0.24	1.54	0.22	20.4	2.56
S10	Forest	Ganak bari	19.5	39.7	93.4	9.0	32.7	6.17	0.88	5.05	0.71	3.65	0.68	1.87	0.26	1.72	0.24	18.0	3.11
S11	Garden	Ganak bari	18.6	33.3	96.5	7.7	33.1	5.44	0.84	4.62	0.69	3.64	0.71	1.92	0.30	1.78	0.28	16.0	3.38
S12	Forest	AERE	17.3	40.2	87.2	9.1	32.8	6.19	0.82	4.82	0.63	3.22	0.57	1.54	0.21	1.37	0.19	18.1	2.98
S13	Garden	AERE	10.6	42.8	107	9.7	35.4	6.67	1.07	5.57	0.80	4.32	0.83	2.29	0.35	2.12	0.32	19.5	3.22
S14	Garden	AERE	19.5	41.2	84.3	8.2	35.2	5.70	0.82	4.65	0.63	3.17	0.60	1.58	0.24	1.38	0.21	16.1	2.83
Min			10.6	33.3	71.8	6.7	27.1	4.68	0.63	3.91	0.55	2.81	0.55	1.48	0.21	1.37	0.19	13.7	2.34
Max			24.2	49.3	118	10.1	42.1	7.03	1.20	6.00	0.87	4.80	0.89	2.42	0.37	2.21	0.34	24.9	3.52
Median			19.6	39.4	88.4	8.3	33.0	6.02	0.93	5.07	0.72	3.85	0.72	1.94	0.29	1.75	0.26	17.6	2.99
Mean	All soils		19.3	39.9	89.7	8.5	33.6	6.04	0.95	5.04	0.71	3.88	0.72	1.97	0.29	1.79	0.26	17.8	2.95
Std(±)			3.2	5.3	14.0	1.0	3.9	0.60	0.16	0.53	0.09	0.61	0.11	0.32	0.05	0.30	0.05	3.0	0.40
Mean	Garden		18.7	40.4	94.7	8.4	35.1	5.92	0.92	4.98	0.71	3.94	0.72	1.94	0.30	1.77	0.27	17.9	3.00
Mean	Forest		19.1	42.9	95.9	9.4	34.2	6.46	0.97	5.29	0.74	3.82	0.71	1.94	0.28	1.77	0.26	18.7	3.19
Mean	Open area		20.3	35.9	75.8	7.9	29.8	5.68	0.93	4.74	0.67	3.63	0.69	1.92	0.27	1.75	0.25	16.4	2.79

TABLE IIb Concentrations of Y, lanthanides, Th, and U (mg/kg) in Bangladeshi soils around northern region of DEPZ, Dhaka

| Sample no	Soil Util.	Location	Y	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th	U
N01	Forest	Gajirchat-S	20.1	43.7	96.7	9.90	36.2	7.05	1.09	5.70	0.79	4.27	0.79	2.18	0.31	1.99	0.28	19.9	3.15
N02	Open area	Balivadra	16.9	35.2	77.2	8.08	29.4	5.77	0.86	4.72	0.66	3.55	0.66	1.83	0.26	1.69	0.24	15.6	2.99
N03	Open area	Bagabari	18.5	34.1	90.8	6.72	29.8	4.87	0.84	4.40	0.67	3.70	0.74	2.06	0.32	1.93	0.29	16.1	3.06
N04	Forest	Burirchar	17.4	24.3	64.0	5.34	19.2	3.52	0.46	2.91	0.42	2.17	0.42	1.18	0.19	1.17	0.18	11.1	2.90
N05	Open area	Ame. plaza	21.3	37.2	76.1	7.87	34.8	6.03	1.07	5.36	0.80	4.38	0.87	2.36	0.36	2.16	0.33	14.8	2.34
N06	Open area	Nayarhat	10.7	24.4	64.2	5.49	20.0	3.68	0.54	3.07	0.44	2.28	0.45	1.23	0.19	1.16	0.18	13.4	3.22
N07	Open area	Bagabari	13.6	33.3	73.5	6.68	27.1	4.68	0.63	3.91	0.55	2.81	0.55	1.48	0.23	1.41	0.22	13.7	3.22
N08	Open area	Gajirchat-N	14.8	41.2	84.3	8.20	35.2	5.70	0.82	4.65	0.63	3.17	0.60	1.58	0.24	1.38	0.21	16.1	2.83
N09	Forest	Balivadra	14.3	40.2	87.2	9.06	32.8	6.19	0.82	4.82	0.63	3.22	0.57	1.54	0.21	1.37	0.19	18.1	2.98
N10	Forest	Ashulia	13.4	35.3	83.3	8.06	29.6	5.75	0.88	4.77	0.68	3.58	0.68	1.84	0.27	1.68	0.24	16.8	2.90
N11	Open area	Burirchar	12.8	26.5	55.4	5.99	21.8	4.06	0.63	3.45	0.50	2.61	0.52	1.41	0.22	1.29	0.20	11.9	2.67
Min			10.7	24.3	55.4	5.34	19.2	3.52	0.46	2.91	0.42	2.17	0.42	1.18	0.19	1.16	0.18	11.1	2.34
Max			21.3	43.7	96.7	9.90	36.2	7.05	1.09	5.70	0.80	4.38	0.87	2.36	0.36	2.16	0.33	19.9	3.22
Median			14.8	35.2	77.2	7.87	29.6	5.70	0.82	4.65	0.63	3.22	0.60	1.58	0.24	1.41	0.22	15.6	2.98
Mean	All soils		15.8	34.1	77.5	7.40	28.7	5.21	0.78	4.34	0.62	3.25	0.62	1.70	0.25	1.57	0.23	15.2	2.93
Std(±)			3.3	6.6	12.6	1.47	6.1	1.13	0.20	0.91	0.13	0.74	0.14	0.39	0.06	0.35	0.05	2.6	0.26
Mean	Forest		16.3	35.9	82.8	8.09	29.4	5.63	0.81	4.55	0.63	3.31	0.62	1.69	0.25	1.55	0.22	16.5	2.98
Mean	Open area		15.5	33.1	74.5	7.00	28.3	4.97	0.77	4.22	0.61	3.21	0.63	1.71	0.26	1.57	0.24	14.5	2.90
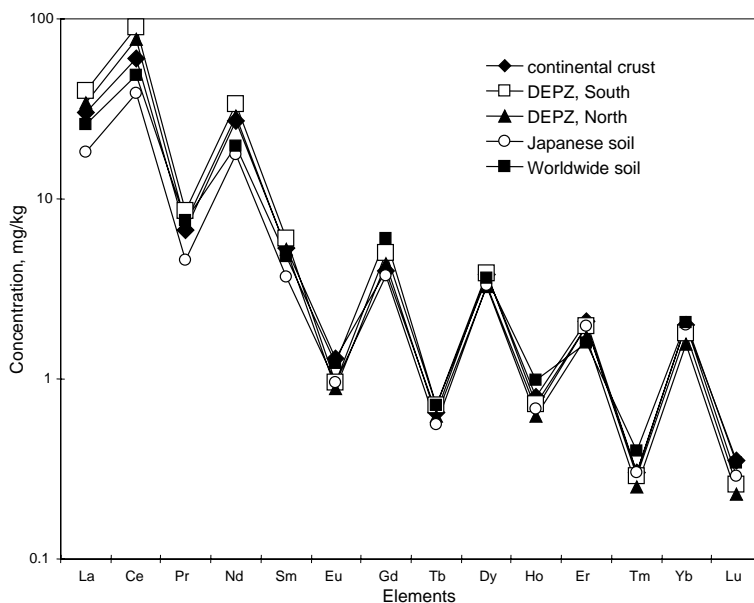
FIGURE 2   The plots of the concentrations of lanthanides *versus* elements.

concentrations of the light lanthanides La, Ce and Nd in Bangladeshi soils were about 2 times higher than the recent data for Japanese soils and the average data for worldwide soils whereas slightly higher than the data for continental crust. This is most likely due to the presence of naturally high level of light lanthanides in the parent materials (sedimentary rocks) of the soil in this region [20–22].

Chondrite Normalized Patterns of Lanthanides

A more precise method to compare the relative abundance of lanthanide elements in soils is the chondrite normalized patterns of lanthanides, where the abundance of each lanthanide elements in soil under investigation is divided by the abundance of the corresponding element in chondrites. In Fig. 3 chondrite normalized patterns of lanthanide elements in soils of the southern and northern regions of DEPZ are shown with the data for Japanese soils and also with the data for continental crust. Although Bangladeshi soils contain higher concentration of light lanthanides than the other soils, the chondrite normalize patterns of the Bangladeshi soils were very much similar to that of the Japanese soils and the average concentrations for continental crust. The smooth curve of the chondrite normalized patterns of the lanthanide contents observed in the Bangladeshi soils suggested that the lanthanide contents of the Bangladeshi soils in this area are the result of the natural dispersion process rather than anthropogenic activities. Further, the present experimental outcome pointed out that the lanthanide elements were quite resistant during the weathering and alteration process of parent rocks in the course of soil formation. This furthermore supports the previous hypothesis which was proposed by Yoshida *et al.* [6] for Japanese soils.
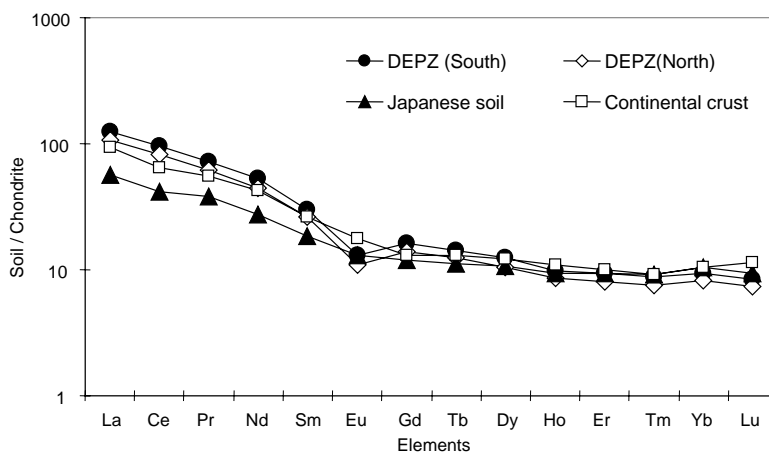
FIGURE 3   Chondrite normalized patterns of lanthanides in various soils.

TABLE III   Correlation coeficients (R^2) among Y, lanthanides, Th and U

Elements	Ce	Pr	Nd	Gd	Y	Tm	Yb	Lu	Th	U
La	0.73	0.88	0.91	0.79	0.35	0.23	0.21	0.18	0.82	0.03
Ce		0.69	0.72	0.54	0.2	0.19	0.15	0.16	0.73	0.25
Pr			0.78	0.82	0.33	0.21	0.21	0.16	0.81	0.04
Nd				0.79	0.39	0.3	0.26	0.24	0.74	0.02
Gd					0.72	0.57	0.02	0.5	0.64	0.004
Y						0.92	0.96	0.87	0.27	0.007
Tm							0.96	0.99	0.17	0.004
Yb								0.95	0.17	0.00
Lu									0.14	0.01
Th										0.07
U										

Correlation Among Y, Lanthanides, Th and U

Similarities among lanthanides, La to Lu are a consequence of the addition of electrons to the inner 4 f orbital rather than the outer shells. However, the lanthanide contraction which is the origin of gradual change in the crystal chemical behavior of the elements, forming at least two major groups which have long been distinguished as cerium dominant, light lanthanides which are more basic and yttrium-dominant, heavy lanthanides which are less basic [23–24]. A good correlation was observed among the lanthanide elements of the two group's cerium-dominant, light lanthanides and yttrium-dominant, heavy lanthanides in Bangladeshi soils (Table III and Fig. 4). The correlation coefficient (r^2) was 0.73, 0.69, 0.78 and 0.79 between La–Ce, Ce–Pr, Pr–Nd and Nd–Gd, respectively, for the light lanthanide elements whereas 0.95, 0.96, 0.92 and 0.72 between Lu–Yb, Yb–Tm, Tm–Y and Y–Gd for the heavy lanthanide elements respectively.

Thorium also showed a good correlation with cerium-dominant, light lanthanide elements, where correlation coefficient, r^2 was 0.82, 0.73, 0.81 and 0.74 between Th–La, Th–Ce, Th–Pr and Th–Nd respectively (Table III and Fig. 4). Thorium and U belong to the series of actinide elements which are characterized by an incomplete 5 f shell, analogous to the rare earth elements with incomplete 4 f shells. Thorium is
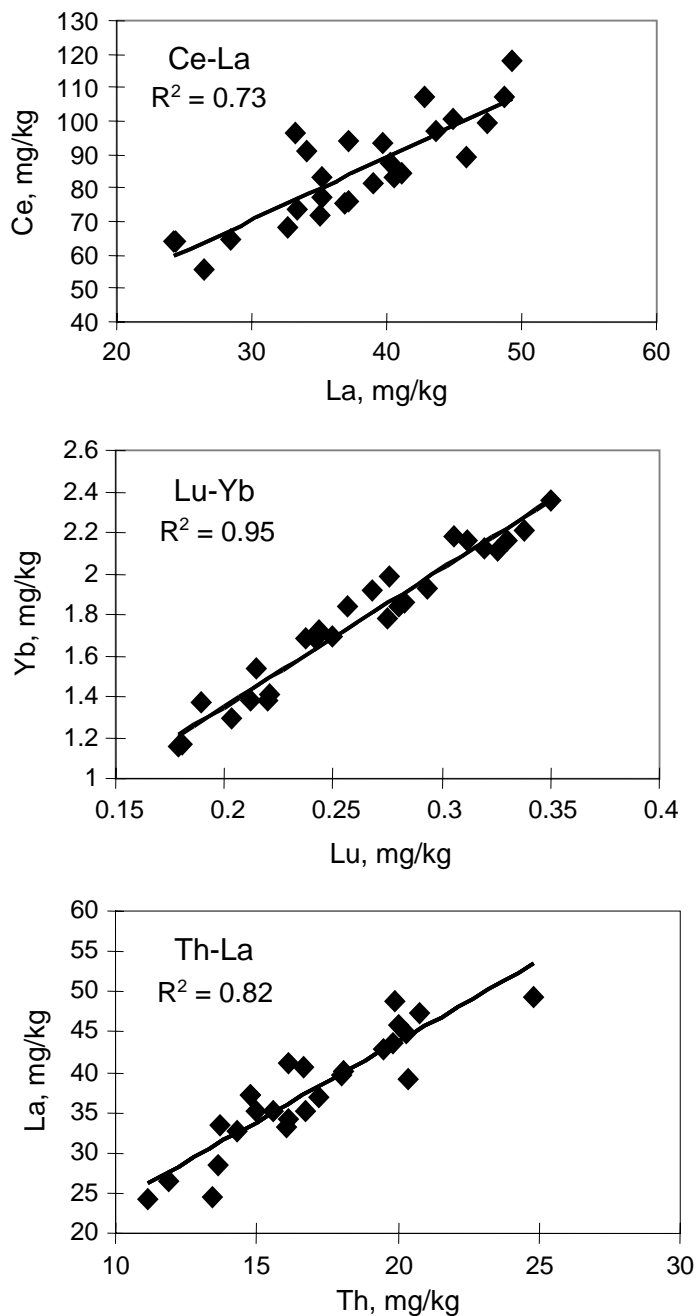
FIGURE 4 Correlations between La–Ce, Lu–Y and Th–La.

predominantly stable in the tetravalent state (Th^{4+}) which is the largest of the tetra-valent cations with an ionic radius comparable to that of U^{4+} and Ce^{4+}. Therefore, considering similarities in ionic size, outer electron configuration and bond character, the good correlation among the elements of Th, cerium-dominant, light lanthanides

and U can be expected. In contrast, however, in the present study, U showed a very poor correlation with lanthanides as well as Th (Table III). The poor correlation of U with Th and light lanthanides presumably due to the differences in resistivity to weathering of U, Th and light lanthanides in different stages of weathering and soil formation.

Th, U Contents and Th/U Ratio in the Bangladeshi Soils

The distribution patterns of Th and U in the northern and southern regions of DEPZ are shown in Fig. 5. Although the concentrations of Th in the southern region tended to be higher than the northern region, no significant difference was observed between the distribution patterns of Th and U in the both regions of DEPZ. The average concentrations were 17.8, 15.2 mg/kg for Th and 2.9, 3.0 mg/kg for U, respectively. The average Th and U content of the continental crust are 8.5 and 1.7 mg/kg [19] whereas the average value for worldwide soils are 9 and 2 mg/kg [25–29]. Therefore, the concentrations of Th and U in the soils of DEPZ area were about 2 times higher than the worldwide average value as well as the abundant in the continental crust.

Further, it is interesting to see that Bangladeshi soils have relatively higher average concentrations of Th (16.5 mg/kg) than U (2.9 mg/kg) where the ratio of Th/U is 5.6 (Fig. 5). It is reported that in the lithosphere the Th/U ratio is close to 3 [25], whereas in soils this ratio ranges from 2.5–5 [25,27,30,31]. It is known that the concentrations of Th and U in the soil are assumed to be influenced by the geological environment and the crystal structure of the minerals. It is found that the geochemical process of Th and U varied depending on their origin. A marked enrichment of Th (30 mg/kg) and U (4 mg/kg) relative to the abundance the continental crust with high Th/U ratio (7) was observed in clay stone [32,33] from which the soil in this area were originated. Hence, the high Th, U concentrations and Th/U ratio in Bangladeshi soils might be originated from the parent materials of the soil during the soil formation process.
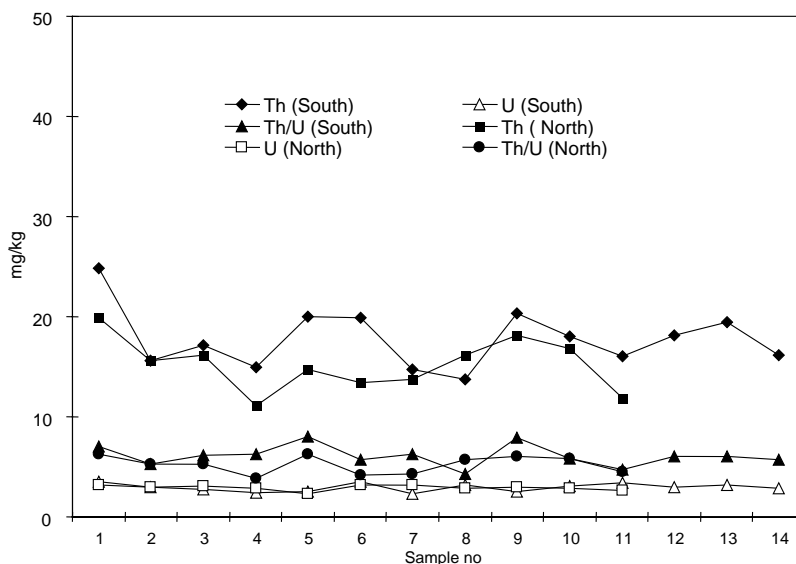

FIGURE 5 Distribution of Th, U and Th/U ratio in southern and northern regions of DEPZ, Bangladesh.

In addition, U is well leached during the weathering and alteration process. The tendency of U to be oxidized to the comparatively soluble uranyl ion permits U to be mobilized easily in surficial processes. The comparatively insoluble Th is concentrated in resistant minerals, whereas U is redistributed in surface and ground waters [34]. However, the observed high Th/U ratio in Bangladeshi soils of DEPZ area was correlated well with the higher content of Th in soil which originated from the parent materials rather than leaching of U content of the soil. Finally it can be assumed that the concentrations of Y, lanthanides, Th and U in the Bangladeshi soils are effected by the geological origin of the soil in the DEPZ area.

CONCLUSIONS

Twenty-five uncultivated surface soil samples collected from the northern and southern regions of Dhaka Export Processing Zone (DEPZ) area of Bangladesh were analyzed for their content of Y, lanthanides, Th and U using an inductively coupled plasma mass spectrophotometer, ICP-MS. Analytical results obtained are the first precise data for these elements in Bagladeshi soils which are useful in understanding the background level and characteristics of these elements in the Bangladeshi soils.

Although the concentrations of the light lanthanides (La, Ce, Pr and Nd) and Th in the southern region were slightly higher than the northern region, no remarkable difference was observed between the distribution patterns of the Y, Lanthanides, Th and U in the both regions of DEPZ around several kilometer distances. Further, the experimental results showed no particular contamination for these elements. It indicated that Y and lanthanide concentrations of the present study area were naturally derived.

The concentrations of the light lanthanides (La, Ce and Nd) in the Bangladeshi soils were around twice than the worldwide average value and slightly higher than the abundant of earth crusts. However, the smooth curve of the chondrite normalized patterns of lanthanides in the Bangladeshi soils also suggested that the lanthanides contents of the Bangladeshi soils in this area are the results of the natural dispersion process rather than anthropogenic activities. Further, a good correlation was observed among the members of the light and heavy lanthanides. The relatively high Th and U concentrations and Th/U ratio in the Bangladeshi soils of DEPZ area might be derived from the parent materials, such as clay stones during the soil formation process.

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