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Contamination Level of Different Chemical Elements in Top Soils of Barapukuria Coal Mine Area in Dinajpur, Bangladesh

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Abstract: The contents and contamination level of 17 different chemical elements (Rb, Cs, Sr, Ba, Y, Zr, Co, Ni, V, Nb, Sn, Nd, Ce, La, Pr, Sb and Th) along with major elemental composition in 19 top soils and three canal sediment samples of the Barapukuria coal mine area were studied by X-ray Fluorescence spectroscopy (XRF). The study results revealed that SiO_2, TiO_2, Fe_2O_3, MgO, CaO and P_2O_5 were within the limit of normal soil, while Al_2O_3, Na_2O and K_2O in soil, and MnO and Na_2O in sediment samples exceeded the maximum level of normal soil. Among the metals, the contents of Rb, Cs, Zr, Sn, Ce, La, Nd, Pr and Th in most of the top soils were higher compared to Earth's crust average, while Y and Sb contents were comparatively higher in sediment samples. Mine water discharge canal sediment samples had EFc values for Sb ranged from 24.72 to 57.09, indicating very severe to extremely severe contamination due to mining activities. Similarly, EFc values varied from 5 to <20 for Sb and Zr at 10 and 12 soil sampling locations, respectively indicating moderately severe to severe pollution load of the study area. EFc values for Sn, Th, La, Ce, Cs, Pr, Nd and Y were also >5 in several soil sampling locations indicating moderately severe contamination level in the study area. The study concluded that high EFc values indicate enrichment of metals, which might be originated from geogenic sources due to coal mining and coal based power generation related activities at the study area.

Key words: Contamination, major and trace elements, Barapukuria coal mine, Bangladesh.

Introduction

Barapukuria is one among the most important coal production base of Bangladesh, which is located at Phulbari Police Station of Dinajpur district. Coal extracted from Barapukuria has been used in a 250-megawatt coal-fired power plant, which is significantly contributing in socio economic benefits to the north western part of Bangladesh. The Barapukuria underground coal mine required continuous pumping and discharge of 1,500 m^3 of water per hour to keep the mine free from flooding. This waste water is disposed in the discharge canal, which is used directly for the irrigation of rice and vegetables by the local people of the area. Crops and vegetables grown on the mine waste can accumulate significant concentrations of metals with resulting adverse health effects (Sidenko et al., 2007). The suspended particles in mine water may carry a major fraction of metals, which may deposit to the downstream from their origin (Butler et al., 2008). As coal mine discharge is frequently acidic and contains high concentrations of metals and metalloids,

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it can create problems of groundwater, surface water and topsoil in the surrounding area of the mine (Akcil and Koldas, 2006). The release of mining waste to the environmental compartments can cause severe destruction of ecosystems, which in some cases may not be fully restored or rehabilitated (Bhuiyan et al., 2010).

The natural concentration of different chemical elements in soil is important for monitoring the impacts of human activity on the soil quality and for understanding the extent of anthropogenic influence on the environment. At present, many governments and environmental researchers are interested in establishing reliable soil quality criteria for different chemical elements that would enable the detection of polluted sites. Currently, contents and distribution patterns of different chemical elements participating in the soil forming processes and plant growth and development are fairly well established. At the same time, information about the elements exerting adverse impact on the environment is scarce, except for data on some toxic elements. Our previous study reports showed that the major contaminants in the surrounding soils of Barapukuria are Zn, Cu, Cd and Cr (Zakir et al., 2017a), and pollutants in surface water are Mn, Fe, Cu and K (Zakir et al., 2013).

However, data on the contents and distribution patterns of various transition, alkali, alkaline earth, and rare earth elements in soils and bedrocks of the study area are practically absent. According to Tyler (2004), determination of these chemical elements from soils is related to the difficulty with their identification by the application of expensive methods. But the environmental deterioration and contamination of the biosphere necessitate special studies on the measurement of the contents and distribution patterns of many chemical elements belonging to these groups (Asylbaev and Khabirov, 2016). Considering the fact stated above, present study was undertaken to assess major elemental composition and the contamination level of 17 different chemical elements in the surrounding top soils of Barapukiuria open coal mine area in Dinajpur, Bangladesh.

Materials and Methodology

Study Area

Barapukuria coal mine area is situated at the north western part of Bangladesh and the area lies between latitudes 25°31′N to 25°35′N and longitude 88°57′E to 88°59′E (Figure 1). The coal mine has a proved area of

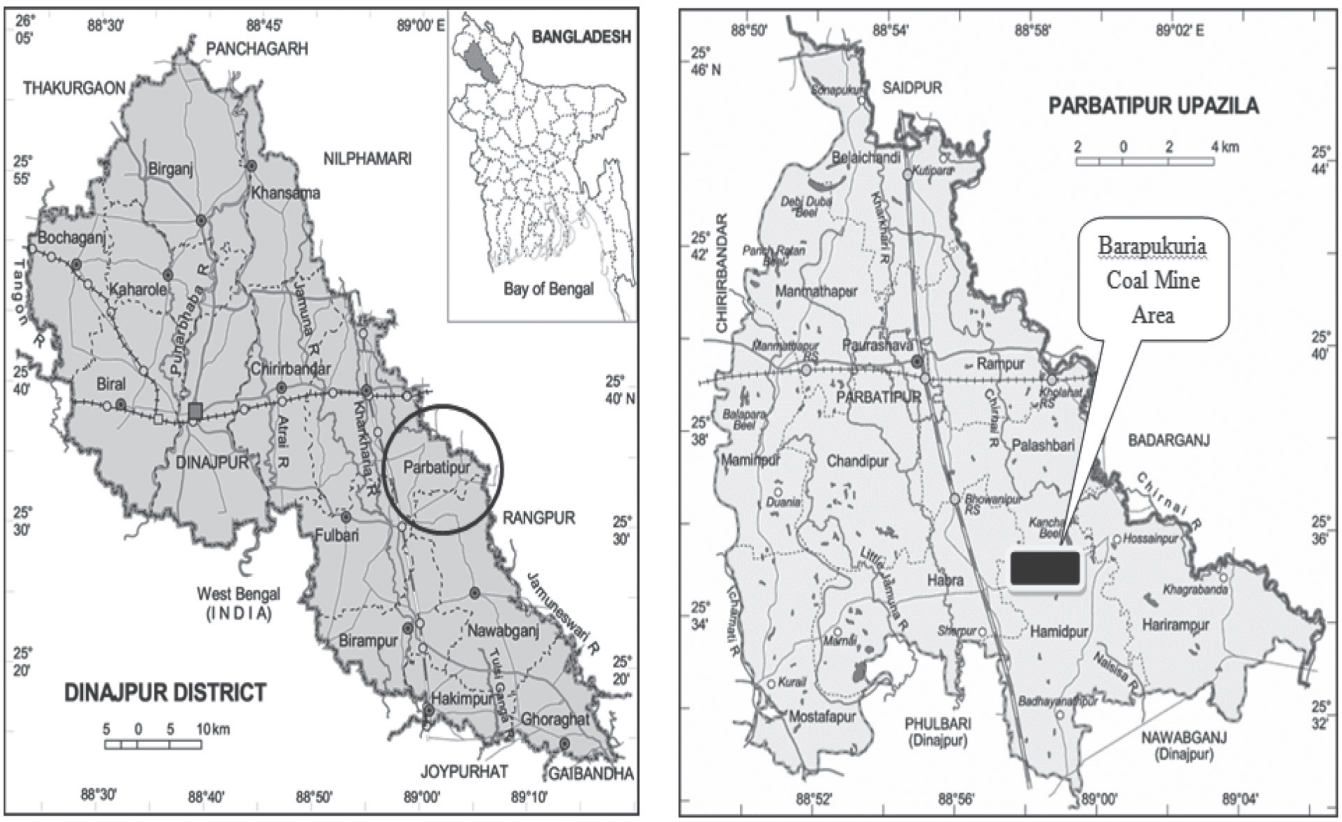

Figure 1: Map showing the location of Barapukuria open coal mine area in Dinajpur, Bangladesh.

6.68 square kilometre. The coalfield has a depth of coal deposit between 118 m and 509 m with an estimated reserve of coal 390 million metric ton (BCMCL, 2018). There are six coal containing seams (I to VI) in Barapukuria and among those seams II, IV and VI are more consistent and important. Furthermore, only seam VI contained about 90% of the total demonstrated reserve (Quamruzzaman et al., 2014). Presently coal is extracted from the mine by multi-slice longwall method and the thermal power plant, which is situated in the vicinity of the study area, is the main user of the produced coal.The coal-bearing sediments are comprised of Gondwana Permian-age sandstones, with subordinate siltstones and mudstones. The surface geology over the entire coal field area was covered by Barind Clay (Madhupur Clay). Ground water bearing strata (Dupi-Tila) uncomfortably overlays the Gondwana (Permian) coal bearing sediments(BCMCL, 2018).

Collection and Preparation of Soil Samples

Total 22 (19 top soil and 3 canal sediment) samples from 0-30 cm depth were collected from Barapukuria coal mine area of Dinajpur, Bangladesh (Table 1). Soil sampling was done maintaining a radius approximately 1 km from the origin of the mine and sampling distance from one site to another was at least about 100 m. From each location, about 500 g soil sample was collected and after collection quickly transferred the material into an airtight polythene bag. Then the materials were brought to the laboratory of the Department of Agricultural Chemistry, Bangladesh Agricultural University, Mymensingh. Sub-samples of the material were air dried first and then oven dried at 50°C for 24 hrs. After drying, soil samples were ground and sieved (aperture 125 μm) to remove stones and plant fragments. In order to normalize the variations in grain size, the lower particle size fraction was homogenized by grinding in an agate mortar and stored in glass bottles for chemical analyses. Analytical reagent grade quality chemicals and reagents were used during analysis. Before use, all glass and plastic ware were soaked in 14% HNO_3 for 24 hrs and the washing was completed with Millipore water rinse.

Determination of Available Concentration of Major Nutrients

The content of available phosphorus in soil samples was determined by Olsen method using 0.5 M sodium bicarbonate ($NaHCO_3$) solution adjusted to pH at 8.5 as outlined by Ghosh et al. (1983).Then the phosphate extracted in solution was determined colorimetrically using a spectrophotometer at 660 nm wavelength. Available fraction of sulphur in soil was measured turbidimetrically using calcium chloride dihydrate ($CaCl_2.2H_2O$) 0.15% solution as an extractant (Ghosh et al., 1983). The extracted sulphur was measured colorimetrically using a spectrophotometer at 425 nm wavelength. Exchangeable cations (Na, K, Ca and Mg) in soil samples were extracted by neutral ammonium acetate (CH_3COONH_4) solution. Then the contents of calcium and magnesium in aqueous extract were determined titrimetrically using standard Na_2-EDTA. On the other hand, the amounts of sodium and potassium in extract were measured by using a flame photometer(Ghosh et al., 1983).

Determination of Major Elemental Constituents

Quantitative determination of major elements as oxide of the collected top soil samples was carried out by X-ray Fluorescence spectroscopy (XRF) (Rigaku RIX 1000, Tokyo, Japan) at the Laboratory of Geochemistry, Keio University, Yokohama, Japan. For the preparation of beads, exactly 0.4 g dry oxidized (at 900°C for 14 hrs) soil samples, 4.0 g lithium tetraborate and 50 mg lithium iodide were mixed together and then a Bead Sampler NT-2100 (Tokyo, Japan) was used. Plate calibration was performed using standards of Geological Survey of Japan (JB-3, JF-1, JG-2, JGb-2, JH-1 and JSy-1) following the manufacturer's recommendations. The results are calculated considering the loss on ignition and expressed in mass percent. Analytical recoveries for the major elements from JSd-2 ranged 94-108%.

Determination of Minor Chemical Elements

The collected soil samples were ground for 30 minutes using a ball mill to prepare powder. The powder samples were then pulverized in a pulverizer machine. The finely ground powder (<75 μm) was then put in a porcelain crucible and dried at 100°C in an oven overnight to remove moisture. Then the dried powder samples were mixed with binder (at a ratio of stearic acid:sample = 1:10) and pulverized again for two minutes. The resulting mixture was spooned into an aluminum cap (30 mm). The cap was sandwiched between two tungsten carbide pellets using a manual hydraulic press with 10 tons in^{-2} for 2 minutes and finally pressure was released slowly. The pellet was then ready for X-Ray analysis. The minor chemical elements were determined by X-ray Fluoresecence spectroscopy (XRF) (Rigaku RIX 1000, Tokyo, Japan) following the standard procedures as recommended by the manufacturer.

Table 1: Description of locations and available concentration of major nutrients in soil samples collected from Barapukuria open coal mine area, Dinajpur, Bangladesh

Sample ID	*Location from the mine*	*Land type*	*Available concentration of major nutrients (μgg^{-1})*					
			P	*Na*	*K*	*S*	*Ca*	*Mg*
1	North	Medium high land	0.93	99.12	35.49	0.06	1241.98	2.40
2	North	Fallow land	1.06	107.53	92.60	0.30	801.28	4.80
3	North	Medium high land	0.94	58.80	60.19	0.04	761.21	2.40
4	East	Medium high land	0.92	42.00	75.63	0.08	1522.43	2.40
5	East	Medium high land	0.93	58.80	32.41	0.21	600.96	2.40
6	South	Medium high land	1.30	168.01	69.45	6.56	801.28	4.80
7	South	Medium high land	0.61	126.01	84.89	6.09	1201.92	2.40
8	South	High land	1.21	67.20	27.78	0.62	681.08	2.40
9	North	Fallow land	0.97	92.40	67.91	0.06	801.28	2.40
10	West	Medium high land	1.49	164.65	106.49	0.06	1362.17	7.20
11	West	Medium high land	1.51	104.16	32.41	1.23	841.34	2.40
12	West	Medium high land	1.22	102.48	60.19	1.21	881.40	2.40
13	South	Sediment from canal	1.07	60.48	33.95	8.26	841.34	2.40
14	South	Sediment from canal	1.20	75.60	35.49	12.53	1001.60	4.80
15	East	Low land	1.00	144.49	134.28	7.26	1241.98	2.40
16	East	Medium high land	0.61	55.44	24.69	0.71	520.83	2.40
17	South	Medium high land	0.92	87.36	33.95	7.00	1001.60	16.80
18	South	High land	0.65	50.40	24.69	0.78	440.70	2.40
19	South	High land	0.49	57.12	23.15	0.04	600.96	4.80
20	West	Medium high land	1.45	85.68	50.93	1.17	560.89	4.80
21	West	Medium high land	1.67	87.36	23.15	0.84	721.15	2.40
22	East	Sediment from canal	1.31	78.01	50.93	7.69	1806.08	7.20
Mean	-	-	1.07	89.69	53.67	2.85	919.79	4.04
Range	-	-	0.61-1.67	42.00-168.01	23.15-134.28	0.04-12.53	600.96-1806.08	2.40-16.80

Determination of Enrichment Factor (EFc)

Crustal enrichment factors (EFc) of elements are frequently used to determine the degree of modification in soil composition (Atgin et al., 2000), which is usually computed relative to the abundance of species in source material to that found in the Earth's crust. The following equation was used to calculate the EFc:

$$EFc = (C_M/C_{Fe})\ \text{sample}/(C_M/C_{Fe})\ \text{Earth's crust}$$

where (C_M/C_{Fe}) sample is the ratio of concentration of metal (C_M) to that of Fe (C_{Fe}) in the soil sample and (C_M/C_{Fe}) Earth's crust is the same reference ratio in the Earth's crust. The average abundance of metal in the reference Earth's crust was taken from Taylor (1964) and Fe was selected as the reference element, due to its crustal dominance and its high immobility. EFc values were interpreted as outlined by Acevedo-Figueroa et al. (2006) where EFc<1 indicates no enrichment; 1-3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe and >50 is extremely severe.

Assessment of Pollution Load Index (PLI)

The pollution load index (PLI) was measured in this study for the surface soils of Barapukuria open coal mine area in Dinajpur, Bangladesh. According to Tomlinson et al. (1980), the PLI for a single site is the *n*th root of *n* number of multiplied together contamination factor (CF) values. The content of Earth's crust average as described by Taylor (1964) was used in this study as baseline concentration of different chemical elements. The CF and PLI are the quotient obtained as follows:

$CF = C_{\text{Metal concentration}}/C_{\text{Baseline concentration of the same metal}}$ and

$$\text{PLI for a site} = n\text{th} \sqrt{CF1 \times CF2 \ldots \times CFn},$$

where n equals the number of contamination factors and sites, respectively. A number of contamination factors were calculated for different chemical elements at each site. To calculate a site pollution index, the five highest contamination factors were selected and then deriving the fifth root of the five factors multiplied together (Tomlinson et al., 1980).

Results and Discussions

Available Concentration of Major Nutrients

The available concentration of major nutrient elements in top soils of Barapukuria open coal mine area has been presented in Table 1. The available P content in top soils of the study area varied from 0.61 to 1.67 μgg^{-1} with the mean value of 1.07 μgg^{-1}. Available P status of Bangladesh soils is in general poor. Portch and Islam (1984) reported that 41% of the soils of Bangladesh contained P below the critical level and 35% of the soils contained P above the critical level but below the optimum level. Sodium is not an essential plant nutrient but can replace part of the K requirement of some plant species. Saline soils are problem for plants because the high osmotic potential of the soil solution makes it unavailable for plants. The content of exchangeable Na in top soils of the study area ranged from 42.00-168.01 μgg^{-1} with an average value of 89.69 μgg^{-1}. Potassium is the third major nutrient deficient in most of Bangladesh soils. The maximum and minimum concentrations of exchangeable K in top soils of Barapukuria coal mine area were 134.28 and 23.15 μgg^{-1}, respectively (Table 1).

The average concentration of exchangeable K in soil was 53.67 μgg^{-1}. According to Portch and Islam (1984), the optimum level of K in agricultural soils of Bangladesh is 0.4 mmol per 100 mL. Among the secondary macro nutrients, deficiency of S is the most common in soils of Bangladesh. Portch and Islam (1984) reported that 68% of the soils of Bangladesh contained S below the critical level (26.0 μgg^{-1}). The available S content in top soils of the study area varied from 0.04 to 12.53 μgg^{-1} with the mean value of 2.85 μgg^{-1}. It is apparent from this study that available S contents in most of the soils are far below than the critical limit (Table 1).

Calcium and Mg are not at all a problem for crop production in Bangladesh except some hill and terrace soils. Calcareous soils occurring in Ganges floodplain of Bangladesh have a moderate to high exchangeable Ca reserve. But, decalcification and acidification processes have been going on even in young floodplain soils due to ferrolysis (Ahsan and Karim, 1988). Portch and Islam (1984) found that 14 and 21% of the soils were below the critical level for Ca and Mg, respectively. The maximum and minimum concentrations of exchangeable Ca in top soils of Barapukuria coal mine area were 1806.08 and 600.96 μgg^{-1}, respectively (Table 1). The average concentration of exchangeable Ca in soil was 919.79 μgg^{-1}. The optimum level of Ca for agricultural soils is 4.0 mmol per 100 mL (Portch and Islam, 1984). The exchangeable Mg content in top soils of the study area varied from 2.40 to 16.80 μgg^{-1} with the mean value of 4.04 μgg^{-1}. Magnesium was found to be deficient in the coarse-textured soils of Old Himalayan Piedmont plain, Brown hill soils, and Grey floodplain soils of the northern part of the country.

According to Portch and Islam (1984), the optimum level of Mg in agricultural soils of Bangladesh is 2.0 mmol per 100 mL. Present study results inferred that although the sediment samples (ID # 13, 14 and 22) contained comparatively higher amount of available major nutrient elements but use of mine water for irrigating top soils of the study area has no positive contribution in available major nutrient elements. However, the variations in available nutrient contents in top soils of Barapukuria mine area might be due to physicochemical properties of soil, organic matter content, nature of parent materials, temperature, rainfall and topography of the area.

Major Elemental Composition of the Top Soils

There are certain major element oxides (i.e., SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5) in soils which are mainly released from parent material mostly overlain by igneous or sedimentary rocks (Ramussen, 2007; Nael et al., 2009). Other than the geological components, these elements may also release from anthropogenic sources like fertilizers, sewage sludge, chemical industries, irrigation water, pesticides and coal combustion residues (Senesi et al., 1999). The geochemical pattern of soil pollution in the environment is a matter of great concern over the last few decades (Soylak et al., 2000). Major element oxides such SiO_2, Al_2O_3, Fe_2O_3 and TiO_2 are the major components of soil showing resistance to weathering, while CaO is less resistant to weathering and can be easily eroded (Orescanin et al., 2009). However, major element oxide components of top soils of Barapukuria coal mine area are listed in Table 2.

Table 2: Major elemental composition of soil samples collected from Barapukuria open coal mine area, Dinajpur, Bangladesh

Sample ID	*Oxides of major elements (wt.%)*										*Ignition loss (%)*
	SiO_2	*TiO_2*	*Al_2O_3*	*$T\text{-}Fe_2O_3$*	*MnO*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*P_2O_5*	
1	66.49	0.87	17.00	2.89	0.03	0.39	0.26	1.34	1.88	0.05	4.71
2	66.47	0.76	19.38	4.54	0.06	0.47	0.25	0.87	2.19	0.04	4.46
3	65.02	0.86	18.43	3.74	0.04	0.44	0.18	0.76	1.98	0.04	3.76
4	69.29	0.75	12.77	1.87	0.01	0.20	1.58	1.12	1.61	0.06	3.61
5	66.50	0.83	14.01	1.81	0.01	0.27	0.22	1.15	1.73	0.03	4.59
6	64.36	0.91	21.35	3.68	0.04	0.40	0.30	1.31	1.92	0.04	4.96
7	68.36	0.91	17.33	2.40	0.02	0.24	0.96	1.07	1.70	0.05	6.93
8	71.18	0.82	14.45	1.73	0.01	0.17	0.18	0.38	1.49	0.04	3.84
9	58.38	0.78	22.78	3.90	0.08	0.30	0.23	1.17	1.75	0.04	4.50
10	58.56	0.70	23.07	3.78	0.06	1.01	0.88	0.04	2.25	0.08	4.35
11	67.14	0.80	17.30	2.07	0.03	0.17	0.23	1.07	1.61	0.06	4.38
12	56.38	0.95	25.72	2.62	0.01	0.28	0.20	1.16	1.80	0.05	5.51
13	28.87	0.94	22.39	4.94	0.16	0.02	0.31	1.52	0.84	0.40	67.89
14	16.77	0.81	18.24	6.64	0.18	0.06	0.81	1.51	0.47	0.49	78.40
15	51.72	0.97	29.23	4.25	0.08	0.35	1.79	1.06	1.78	0.07	9.56
16	56.56	1.00	27.41	4.27	0.09	0.33	0.12	0.73	1.78	0.05	5.36
17	61.14	0.93	26.34	3.08	0.03	1.65	0.18	1.47	1.53	0.05	4.49
18	46.42	1.08	36.84	5.04	0.11	0.61	0.36	1.17	1.28	0.06	5.71
19	48.94	0.57	27.75	3.84	0.06	0.38	0.26	1.27	2.14	0.11	3.12
20	49.35	0.72	28.93	4.84	0.07	0.22	0.29	1.32	2.26	0.10	2.38
21	51.55	0.95	29.14	3.32	0.06	0.24	0.21	1.05	1.55	0.05	4.80
22	31.32	1.10	32.01	5.83	0.15	1.05	1.05	1.33	1.39	0.12	26.00
Mean	55.49	0.86	22.81	3.69	0.06	0.42	0.49	1.09	1.68	0.09	11.97
Range	16.77-71.18	0.57-1.10	12.77-36.84	1.73-6.64	0.01-0.18	0.02-1.65	0.12-1.79	0.04-1.52	0.47-2.26	0.03-0.49	2.38-78.40
Crustal average*	60.18	1.06	15.61	3.14	-	3.56	5.17	3.91	3.19	-	-
Normal soil**	70.29	0.88	13.22	0.5-5.0	< 0.1	0.99	< 1.44	0.99	1.20	0.18	-

* Taylor (1964); ** Bohn et al. (2001)

Silica (SiO_2) is essential element for soil, rock and mineral structures, and has great effect on physical and chemical properties of soil (Kebede, 2009). Silicon is also essential for plants and animals in trace amounts. Silica content in top soils of the study area varied from 16.77 to 71.18 wt.% with the mean value of 55.49 wt.% (Table 2). It is evident from Table 2 that mine canal sediments contained lesser amount of SiO_2 and the range was 16.77-31.32 wt.% (Sample # 13, 14 and 22). The SiO_2 concentration in the normal soil is 70.29 wt.% (Bohn et al., 2001), but crustal average of silica is 60.18 wt.% (Taylor, 1964). The obtained data suggest that SiO_2 concentration of the soils of Barapukuria mine area were within the range of normal soil and are, therefore, considered safe for agricultural use. TiO_2 in soils is normally contributed from the minerals like rutile, sphenes, titanomagnetite etc. of all the major rock types. TiO_2 content in top soils of the study area varied from 0.57 to 1.10 wt.% with the mean value of 0.86 wt.% (Table 2). The normal soil has up to 0.88 wt.% TiO_2 (Bohn et al., 2001) while the crustal average is 1.06 wt.% (Taylor, 1964) and therefore, no need to take precautionary measure for the soil of the study area.

The content of Al_2O_3in soil is essential for understanding about the soil forming process, soil chemistry and physicochemical properties of soils (Bera et al., 2005). The maximum and minimum concentrations of Al_2O_3 in top soils of Barapukuria coal mine area were 36.84 and 12.77 wt.%, respectively with an average content of 22.81 wt.% (Table 2). The normal soil usually has 13.22 wt.% of Al_2O_3 (Bohn et al., 2001) while the crustal average is 15.61 wt.% (Taylor, 1964). All top soil samples of the Barapukuria coal mine area had Al_2O_3 contents higher than the normal soil. Furthermore, 86% soil samples contained Al_2O_3 higher than the crustal average (Table 2). All of these are indications of contamination of Al_2O_3 and, therefore, need precautionary measure for agricultural use. Iron (Fe_2O_3)is common constituent in many primary and secondary minerals and is usually not deficient in soils. It is one among the major constituent of soils with iron content between 0.5 and 5 wt.% depending on the type of parent material (Bohn et al., 2001). Iron content in top soils of the study area varied from 1.73 to 6.64 wt.% with the mean value of 3.69 wt.% (Table 2). It is apparent from Table 2 that mine canal sediments contained comparatively higher amount of Fe_2O_3 and the range was 4.94-6.64 wt.% (Sample # 13, 14 and 22). However, Fe_2O_3 contents obtained by the study suggest that there is no iron deficiency or toxicity in the top soils of Barapukuria coal mine area, as because Fe_2O_3 contents were within the normal range.

In nature Mn chemically behaves similar to that of Fe. In the reducing condition Mn (II) species are most stable, while in oxidizing environments the most stable form is MnO_2. According to Bohn et al. (2001), the MnO contents in the normal soil are generally below 0.1 wt.%, and all top soil samples of the study area contained MnO within this limit (range is 0.01-0.11 wt.%) except three canal sediment samples (range is 0.15-0.18 wt.%) (Table 2), which indicates mine discharge water contained significant amount of Mn. This finding is at par with our previous report (Zakir et al., 2013).The MgO concentration in top soils of the study area varied from 0.02 to 1.65 wt.% with the mean value of 0.42 wt.% (Table 2). The MgO in the normal agricultural soil is 0.99 wt.% (Bohn et al., 2001), while the crustal average is 3.56 wt.% (Taylor, 1964). However, the MgO contents in most of the soil samples of the study area were lower than that of the normal agricultural soil. Calcium is an essential element for plants and animals and the amounts are rarely deficient in soils. According to Bohn et al. (2001), the CaO concentration in the normal agricultural soil is upto 1.44 wt.%, while the crustal average is 5.17 wt.% (Taylor, 1964). Similar to MgO, CaO contents in most top soils of Barapukuria coal mine were lower than the normal agricultural soil and, therefore, considered safe for agricultural use (Table 2).

The maximum and minimum concentrations of Na_2O in top soils of Barapukuria coal mine area were 1.52 and 0.04 wt.%, respectively with an average content of 1.09 wt.% (Table 2). The concentration of Na in the normal agricultural soil is 0.99 wt.% as reported by Bohn et al. (2001). 74% top soil samples and all canal sediment samples of the study area contained higher amount of Na_2O than that of normal agricultural soil. This increasing content of Na in the top soils of the study area can pose threat to the ecosystem of the region. Many soils of humid regions are unable to supply sufficient K for agronomic crop. The concentration of K_2O in normal agricultural soil is 1.2 wt.% (Bohn et al., 2001). The K_2O concentration in top soils of the study area varied from 0.47 to 2.26 wt.% with the mean value of 1.68 wt.% (Table 2). So, it can be inferred that 100% top soils samples of the study area contained higher amount of K_2O than that of normal agricultural soil. P_2O_5 content in top soils of the study area varied from 0.03 to 0.49 wt.% with the mean value of 0.09 wt.% (Table 2). It is apparent from Table 2 that mine canal sediments contained comparatively higher amount of P_2O_5 and the range was 0.12-0.49 wt.% (Sample # 13, 14 and 22). The normal agricultural soil contained about 0.18 wt.% of P_2O_5 (Bohn et al., 2001). However, P_2O_5 contents obtained by the study suggest that there is no problem in the top soils of Barapukuria coal mine area, as because P_2O_5 contents were within the normal range.

Concentration of Different Types of Metals in the Top Soils

Coal fly ash, which when not utilised is considered waste, has been regarded as the possible source of many elements, including rare earth elements (REE) (Franus et al., 2015). XRF result presented in Table 3 gives the total metal concentration for individual element, which is useful for determining the vertical and horizontal extent of contamination and for measuring any net change (leaching to ground water, surface runoff, erosion) in soil metal concentration over time (Humsa and Srivastava, 2015). But, this does not give an indication of chemical form of the metals in the soil. Some of these metals may exist in soil in more than one oxidation state. The oxidation state, chemical complexation with inorganic and organic ligands and redox reactions of these metals determine their relative mobility, bioavailability and toxicity (Violante et al., 2010). However, concentration of 17 different metals in top soils of Barapukuria coal mine area are discussed under the following headings:

Alkali Metals (Rb and Cs)

Rubidium (Rb) occurs in the main types of mountain soils, its geochemical features are similar to lithium, and its content is higher in felsic igneous rocks and sedimentary alumino silicates (Asylbaev and Khabirov, 2016). The maximum and minimum concentrations of Rb in top soils of Barapukuria coal mine area were 139.26 and 10.93 μgg^{-1}, respectively with an average content of 101.74 μgg^{-1}, while the crustal average of Rb is 90.0 μgg^{-1} (Table 3). The overall mean total content of Rb in tropical Asian paddy soils is 75 μgg^{-1}, while the mean content of Rb in 53 samples of Bangladesh soil is 22 μgg^{-1} with a range of 0-63 μgg^{-1} (Domingo and Kyuma, 1983). On the other hand, according to Shacklette and Boerngen (1984), the surficial soils in the USA have a geometric mean of Rb 67.0 μgg^{-1} and a range of <20-210 μgg^{-1}. Cesium (Cs) is mainly accumulated in felsic igneous rocks and clay sediments. The Cs content is 1.5-5.93 μgg^{-1} in soils and 1.8-12 μgg^{-1} in parent materials (Asylbaev and Khabirov, 2016). The Cs content in the top soils of Barapukuria varied from 1.23 to 7.46 μgg^{-1} with the mean value of 5.51 μgg^{-1} (Table 3). The concentration of Cs in an uncultivated Cambisol in central Scania of South Sweden is 7.90±0.20 μgg^{-1} (Tyler and Olsson, 2001). So, it can be inferred from the study results that the distribution of both Rb and Cs in the studied soil profiles attests to their major supply from the parent materials and underlying bedrocks.

Alkaline Earth Metals (Ba and Sr)

Barium (Ba) mainly occurs in nature as barite ($BaSO_4$) and witherite ($BaCO_3$) and its content in soil is highly variable (Asylbaev and Khabirov, 2016). The Ba content in the top soils of Barapukuria varied from 152.22 to 428.90 μgg^{-1} with the mean value of 353.61 μgg^{-1} (Table 3). The earth crust average of Ba is 425 μgg^{-1} (Taylor, 1964). Bowen (1979) reported that Ba concentrations in soils ranged from 100-3000 μgg^{-1}, and the median being about 500 μgg^{-1}. Surficial soils in the USA have a geometric mean of 580 μgg^{-1} and a range of 10-5000 μgg^{-1} (Shacklette and Boerngen, 1984). The concentration of Ba in an uncultivated Cambisol in central Scania of South Sweden is 646±13.60 μgg^{-1} (Tyler and Olsson, 2001). According to our data, Ba content was also highly variable in top soils of the study area.

Strontium (Sr) mainly occurs in nature assulfate and carbonate compounds like $SrSO_4$ (celestine) and $SrCO_3$ (strontianite). This element is assigned to the third hazard category according to the current State Standard of Russia. In the arable soils, the accumulation of Sr may be related to the application of the high rates of phosphorus fertilizers and lime (Asylbaev and Khabirov, 2016). The Sr content in the Earth's crust is 375 μgg^{-1} (Taylor, 1964). The maximum and minimum concentrations of Srin top soils of Barapukuria coal mine area were 157.70 and 40.04 μgg^{-1}, respectively with an average content of 62.94 μgg^{-1} (Table 3). The concentration of Sr in an uncultivated Cambisol of South Sweden is reported 74±0.9 μgg^{-1} (Tyler and Olsson, 2001), while in soils and other surficial materials have a geometric mean of 240 μgg^{-1} and a range of <5-3000 μgg^{-1} (Shacklette and Boerngen, 1984). According to Domingo and Kyuma (1983), the median total content of Sr for Asian paddy soils is 108 μgg^{-1}, and the content of Sr for Bangladesh soils varied from 0 to 147 μgg^{-1} with a mean value of 66 μgg^{-1}. Thus, it can be assumed that both Ba and Sr contents in the study area are mainly determined by their contents in the parent material and bedrocks.

Lanthanoids and Actinoids (Ce, La, Nd, Pr and Th)

The cerium (Ce) content in the top soils of Barapukuria coal mine area ranged from 49.22 to 139.33 μgg^{-1} with the mean value of 105.93 μgg^{-1} (Table 3). The earth crust average of Ce is 60 μgg^{-1} (Taylor, 1964). The abundance of Cein soil is almost the same as environmentally much more studied elements, such as Cu and Zn (Tyler, 2004). The concentration of Ce in an uncultivated Cambisol developed from a mixed shale-gneiss moraine in central Scania, South Sweden is 76±1.6 μgg^{-1} (Tyler and Olsson, 2001). Soils and other surficial materials in the United States have a geometric mean of Ce 75 μgg^{-1} and a range of <150-300 μgg^{-1} (Shacklette and Boerngen, 1984). Lanthanum (La) is the third-most abundant of all the lanthanides, it is the most reactive among them, tarnishing slowly in air and burning readily to form lanthanum (III) oxide (La_2O_3), which is almost as basic as CaO. The content of La in the top soils of the study area varied from 25.81 to 72.67 $\mu gg^{-1}$with an average value of 56.29 μgg^{-1}, which is almost twice than the earth crust average value (30 μgg^{-1}) (Table 3). According to Shacklette and Boerngen (1984), the surficial soils have a geometric mean of La 37 μgg^{-1} and a range of <30-200 μgg^{-1}. Similarly, Tyler and Olsson (2001) reported that the concentration of La in an uncultivated soil of South Sweden is

Table 3: Concentrations (μgg^{-1}) of different types of metals (transition, alkali, alkaline earth and rare earth) in collected soil samples of Barapukria open coal mining area, Dinajpur, Bangladesh

Sample ID	*V*	*Co*	*Ni*	*Rb*	*Sr*	*Y*	*Zr*	*Nb*	*Sn*	*Sb*	*Cs*	*Ba*	*La*	*Ce*	*Pr*	*Nd*	*Th*
1	62.50	5.59	31.09	119.66	43.34	40.02	414.82	15.47	4.91	0.30	6.53	374.18	60.42	110.03	13.51	45.55	24.65
2	70.28	10.15	32.54	130.70	48.55	40.53	431.46	13.37	4.95	0.32	6.33	406.50	72.67	139.33	16.38	55.68	24.35
3	62.80	7.28	30.42	133.42	42.06	37.55	376.81	14.74	4.52	0.16	7.17	386.72	57.16	103.03	12.54	44.13	22.71
4	41.08	3.46	20.61	88.70	42.33	39.34	551.65	14.10	3.96	0.86	4.23	326.09	61.09	113.39	12.42	45.69	23.24
5	54.13	3.02	21.50	97.90	44.95	42.16	579.88	17.71	5.30	0.66	5.67	358.76	67.55	125.29	13.87	52.16	23.97
6	66.14	7.57	30.89	128.13	46.65	42.46	529.23	20.46	6.20	0.58	7.39	428.90	66.17	122.91	12.63	48.31	25.94
7	51.21	4.25	28.78	94.52	52.45	41.58	605.21	18.29	5.24	1.06	5.91	367.18	69.39	128.81	13.85	51.82	24.15
8	44.75	5.59	17.98	83.64	41.74	42.38	698.80	16.66	4.61	0.63	4.35	324.42	72.06	134.81	14.26	53.16	25.93
9	59.02	7.76	32.59	115.71	42.54	36.53	438.25	14.68	5.08	0.46	6.60	381.10	59.33	112.40	10.83	45.11	22.73
10	54.43	7.90	24.97	139.26	72.82	38.36	372.14	12.08	5.21	0.29	6.17	402.93	64.74	119.86	13.70	50.16	22.46
11	43.40	3.68	18.58	88.41	45.23	42.27	624.16	16.54	4.82	0.57	4.40	351.31	68.53	125.21	14.66	49.99	24.69
12	60.32	4.78	29.67	122.33	44.36	35.88	487.79	18.52	5.89	1.09	7.46	408.44	65.58	119.94	14.19	49.35	25.31
13	32.45	2.00	39.65	24.60	97.42	44.66	343.88	29.29	4.56	7.01	1.35	207.27	34.38	59.85	6.46	21.44	10.57
14	20.26	2.06	29.88	10.93	99.34	42.38	269.83	25.98	2.94	5.30	1.23	152.22	25.81	49.22	3.96	17.56	7.93
15	70.09	8.35	45.88	117.20	55.41	22.46	477.77	18.63	5.77	0.89	6.95	396.91	63.83	119.00	13.25	49.46	23.07
16	70.37	8.73	36.63	122.44	40.04	40.01	492.43	17.89	5.53	1.21	6.38	364.53	54.89	110.27	10.32	39.52	21.43
17	56.97	6.62	35.99	115.26	42.37	29.05	406.77	14.60	3.96	0.31	5.08	304.38	42.82	84.46	9.54	31.02	20.95
18	88.34	11.98	43.44	105.96	44.30	35.33	419.51	16.84	4.42	0.35	6.37	323.41	59.58	116.07	15.37	47.44	22.29
19	67.86	8.98	32.72	108.33	139.36	20.01	171.37	8.47	3.11	0.75	5.36	393.06	51.99	65.75	6.85	37.99	16.60
20	73.48	11.97	38.37	119.72	157.70	23.65	202.62	9.75	3.09	0.32	6.79	410.46	36.49	71.58	10.52	27.93	12.30
21	83.85	11.49	34.11	109.29	45.75	35.06	401.49	15.10	4.70	0.52	5.40	341.86	49.52	101.69	10.15	38.93	20.52
22	46.82	3.12	44.58	62.25	96.00	42.18	529.79	21.52	4.50	2.04	4.10	368.74	34.37	97.49	6.11	25.57	10.82
Mean	58.21	6.65	31.86	101.74	62.94	36.99	446.62	16.85	4.69	1.17	5.51	353.61	56.29	105.93	11.61	42.18	20.76
Range	20.26-88.34	2.00-11.98	17.98-45.88	10.93-139.26	40.04-157.70	20.01-44.66	171.37-698.80	8.47-29.29	2.94-6.20	0.16-7.01	1.23-7.46	152.22-428.90	25.81-72.67	49.22-139.33	3.96-16.38	17.56-55.68	7.93-25.94
ECA*	135.0	25.00	75.00	90.00	375.0	33.00	165.0	20.00	2.00	0.20	3.00	425.0	30.00	60.00	8.20	28.00	9.60

* Earth Crust Average (Taylor, 1964)

40.6±0.8 μgg^{-1}. It is apparent from Table 3 that mine canal sediments contained comparatively lower amount of La and the range was 25.81-34.37 μgg^{-1} (Sample # 13, 14 and 22), which means La contents in top soils of the study area are mainly derived from the parent material and bedrocks.

Neodymium (Nd) is one of the rare earth metals that have a bright silvery metallic lustre. It is one of the more reactive rare-earth metals, which is quickly oxidized in air. It is rarely found in nature as a free element, but rather it occurs in ores. Its abundance in the Earth's crust is 28 μgg^{-1} (Taylor, 1964). The maximum and minimum concentrations of Nd in top soils of Barapukuria coal mine area were 55.68 and 17.56 μgg^{-1}, respectively with the mean value of 42.18 μgg^{-1} (Table 3). Extensive analyses of soil and other surficial materials in United States by Shacklette and Boerngen (1984) reported a mean concentration of Nd 46 μgg^{-1} with a range of <70 to 300 μgg^{-1}. On the other hand, according to Tyler and Olsson (2001), the content of Nd in an uncultivated Cambisol in central Scania, South Sweden is 17.80±0.14 μgg^{-1}. Praseodymium (Pr) content in the top soils of Barapukuria coal mine area ranged from 3.96 to 16.38 μgg^{-1} with the mean value of 11.61 μgg^{-1}, while the Earth's crust average value is 8.20 μgg^{-1} (Table 3). Thorium (Th) is a naturally occurring radioactive metal found at low levels in soils, rocks and water. The Th content in the top soils of Barapukuria ranged from 7.93 to 25.94 μgg^{-1} with the mean value of 20.76 μgg^{-1} (Table 3). Soils and other surficial materials in the USA have a geometric mean of Th 9.4 μgg^{-1} and a range of 2.2-31.0 μgg^{-1} (Shacklette and Boerngen, 1984). The concentration of Th in an uncultivated Cambisol in central Scania of South Sweden is 12.6±0.2 μgg^{-1} (Tyler and Olsson, 2001). Similar to La, it can be inferred from this study that Nd, Pr and Th contents in top soils of Barapukuria coal mine area originated from the parent material and bedrocks, and mine waste did not contribute to the higher amount of these metals to the study area.

Transition Metals (Co, Ni, Nb, Sn, V, Y and Zr)

Cobalt is not an essential element to plants but its level in plant tissue is of general concern because of its essentiality in animal nutrition. Usually it occurs in high amounts in ultrabasic rocks where it is associated with olivine minerals (Adriano, 2001). The Co content in the top soils of Barapukuria mine area ranged from 2.00 to 11.98 μgg^{-1} with the mean value of 6.65 μgg^{-1} (Table 3). In the conterminous US, the mean Co content of soils and other surficial materials is 9.1 μgg^{-1}, with a range of <3-70 μgg^{-1} (Shacklette and Boerngen, 1984). According to Domingo and Kyuma (1983), the median total content of Co for Asian paddy soils is 56 μgg^{-1}, while an average content of Co in 53 soil samples of Bangladesh is 58 μgg^{-1} with a range of 24-96 μgg^{-1}. Li et al. (2009) indicated that plants can accumulate small amounts of Co, and there are few toxicity data for higher plants. Nickel (Ni) is potentially toxic elements and the content in the soils are quite variable, which are caused by several factors, including soil parent material. For world soils, an average concentration of Ni is likely around 20 μgg^{-1} (Adriano, 2001). The maximum and minimum concentrations of Niin top soils of Barapukuria coal mine area were 45.88 and 17.98 μgg^{-1}, respectively with the mean value of 31.86 μgg^{-1} (Table 3). The earth crust average of Ni is 75 μgg^{-1} (Taylor, 1964). The mean total content of Ni in Bangladesh soils as well as the median total content for Asian paddy soils is 22 μgg^{-1} (Domingo and Kyuma, 1983). The concentration of Ni in an uncultivated Cambisol in central Scania of South Sweden is 11.40±1.38 μgg^{-1} (Tyler and Olsson, 2001).

Niobium (Nb) is a soft, grey, crystalline metal often found in the minerals pyrochlore and columbite. The content of Nb in the top soils of the study area varied between 8.47 and 29.29 μgg^{-1} with an average value of 16.85 μgg^{-1} (Table 3). Extensive analyses of soil and other surficial materials in USA by Shacklette and Boerngen (1984) reported a mean concentration of Nb 11 μgg^{-1} with a range of <10 to 100 μgg^{-1}. On the one hand, according to Tyler and Olsson (2001), the content of Nb in an uncultivated Cambisol in central Scania, South Sweden is 0.17±0.01 μgg^{-1}. On the other hand, according to Peterson and Girling (1981), trace amounts of Sn is present in soils and plants, and a common range in soil is 1.0-10.0 μgg^{-1}. The Sn content in the top soils of Barapukuria mine area ranged from 2.94 to 6.20 μg g^{-1} with the mean value of 4.69 μgg^{-1}, while the Earth's crust average value is 2.0 μgg^{-1} (Table 3). Shacklette and Boerngen (1984) reported a mean concentration of Sn 1.3 μgg^{-1} with a range of <0.10 to 10.0 μgg^{-1} for soils and other surficial materials in United States. Thus, the data obtained by the present study indicates Sn contamination in the top soils of the area.

Vanadium (V) is an essential trace element for living organisms, but excessive amount of V is harmful to human beings, animals and plants (Crans et al., 2004). The mean concentration of V for Asian paddy soils is 166 μgg^{-1} (Domingo and Kyuma, 1983), while Bowen (1979) reported that V concentrations in soils ranged from 3-500 μgg^{-1}, and the mean being about

90 µg g^{-1}. However, this study obtained V contents for the top soils of Barapukuria coal mine area within a range of 20.26-88.34 µgg^{-1} with an average value of 58.21 µgg^{-1} (Table 3). According to Domingo and Kyuma (1983), average V content in Bangladesh soils is 109 µgg^{-1} with a range of 50-209 µgg^{-1}. Vanadium in soil is derived from parental rocks and deposits, and soil properties clearly affect the fate of vanadium in soil. It is mainly iron and aluminum oxides and hydroxides that determine vanadium mobility in soils and waters (Wallstedt et al., 2010; Naeem et al., 2007).

Yttrium (Y) contents in the top soils of Barapukuria coal mine area varied from 20.01 to 44.66 µgg^{-1} with the mean value of 36.99 µgg^{-1} (Table 3). Present study revealed that mine canal sediments contained comparatively higher amount of Y and the range was 42.18-44.66 µgg^{-1} (Sample # 13, 14 and 22). Similar results was also reported by Luo et al. (2018), who stated that exogenous Y has no significant effect on soil physical properties but a significantly negative impact on soil chemical properties. They also stated that among the critical elements yttrium (Y) contents was the highest in fly ash and a clear correlation between them was observed. Zirconium (Zr) is mined from the mineral zircon which is highly resistant to weathering. The maximum and minimum concentrations of Zrin top soils of Barapukuria coal mine area were 171.37 and 698.80 µgg^{-1}, respectively with the mean value of 446.62 µgg^{-1} (Table 3). Shacklette and Boerngen (1984) reported a mean concentration of Zr 230 µgg^{-1} with a range of <20 to 2000 µgg^{-1}. According to Domingo and Kyuma (1983), the median total content of Zr for Asian paddy soils is 209 µgg^{-1}, while an average content of Zr in 53 soil samples of Bangladesh is 175 µgg^{-1} with a range of 26-521 µgg^{-1}. They also stated that Zr is one of the least mobile elements in the process of weathering; it therefore tends to accumulate in well-weathered soils.

Metalloids (Sb)

Antimony (Sb) is the bluish white, lustrous, very brittle metal, which is found in nature in more than 100 minerals. The major commercial sources of Sb are stibnite and antimonial Pb ores with minor contribution from antimonoxides (Adriano, 2001). The maximum and minimum concentrations of Sbin top soils of Barapukuria coal mine area were 7.01 and 0.16 µgg^{-1}, respectively with an average content of 1.17 µgg^{-1}, while the crustal average is only 0.20 µgg^{-1} (Table 3). It is apparent from Table 3 that mine canal sediments contained comparatively higher amount of Sb and the range was 2.04-7.01 µgg^{-1} (Sample # 13, 14 and 22). Surficial soils of the USA have a geometric mean of Sb 0.66 µgg^{-1} with a range of <1.0-8.8 µgg^{-1} (Shacklette and Boerngen, 1984). The concentration of Sb in an uncultivated Cambisol in central Scania of South Sweden is 0.40±0.03 µgg^{-1} (Tyler and Olsson, 2001). According to Adriano (2001), the geochemical behaviour of Sb is similar to that of As, but plants are more tolerant to Sb than As, and in soils, a median value of Sb is 1.0 µgg^{-1} (range of 0.20 to 10 µgg^{-1}). Biogeochemical redox processes strongly influence mobility of Sb in soil and it may locally represent an important contaminant, for example in the vicinity of copper and lead ore smelters (Violante et al., 2010).

Assessment of Soil Pollution Level

Enrichment Factor (EFc)

To evaluate the level of contaminants in the soil and sediments, the enrichment factors were computed relative to the abundance of metal species in source material to that found in the Earth's crust (Atgin et al., 2000; Zakir et al., 2017b; Zakir et al., 2018). If the EFc value of a metal is greater than unity, this indicates that the metal is more abundant in the sample relative to that found in the Earth's crust. According to Atgin et al. (2000), EFc value <5 may not be considered significant, they are indicative of metal accumulation, because such small enrichments may arise from differences in the composition of local sample material with respect to the reference Earth's crust ratio values used in the EFc calculations. If the EFc values are >5, samples are considered contaminated. However, Acevedo-Figueroa et al. (2006) classify contamination level using EFc values, where EFc<1 indicates no enrichment; 1-3 is minor; 3-5 is moderate; 5-10 is moderately severe; 10-25 is severe; 25-50 is very severe and >50 is extremely severe. Figure 2 represents the EFc values of 17 metals measured in the top soil samples of Barapukuria coal mine area. It is evident from Figure 2 that canal sediment samples (ID # 13, 14 and 22) had EFc values for Sb ranged from 24.72 to 57.09, indicating very severe to extremely severe sediment quality. On the other hand, EFc values varied from 5 to <20 for Sb and Zr at 10 and 12 sites, respectively indicating moderately severe to severe pollution load to the top soils of the study area.

It is also apparent from Figure 2 that EFc values for Sn, Th, La and Ce were within the range of 5 to <15 at 13, 10, 7 and 7 locations, respectively. Similarly, EFc values were within the range of 5 to <10 for Cs, Pr, Nd and Y at 9, 6, 6 and 3 sites, respectively indicating moderately severe contamination level to the top soils

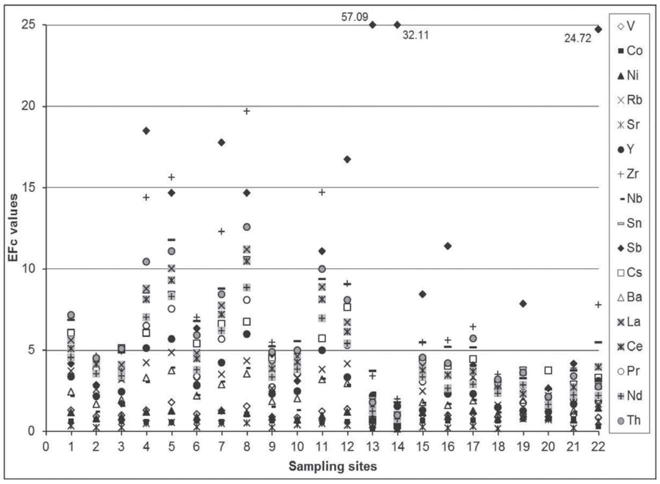

Figure 2: Enrichment factors (EFc) of different chemical elements in top soil samples collected from surrounding areas of Barapukuria open coal mine, Dinajpur, Bangladesh.

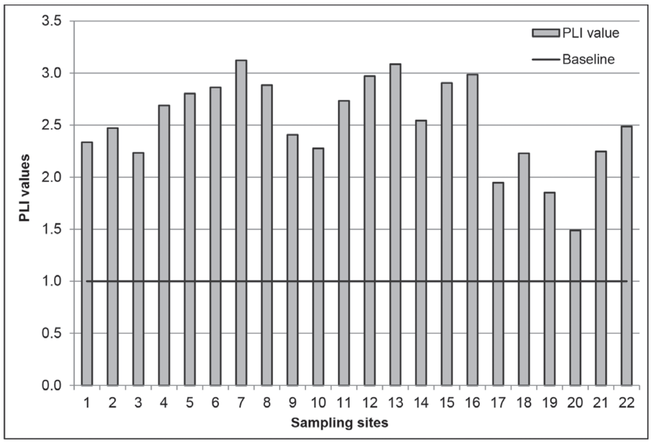

Figure 3: Pollution load index (PLI) at different soil sampling sites of Barapukuria open coal mine, Dinajpur, Bangladesh.

of Barapukuria coal mine area. It is presumed that high EFc values indicate an anthropogenic source of metals, and for this case mainly from coal mining and coal based power generation related activities. Since, the bioavailability and toxicity of any metal in soil and sediments depend upon the chemical form and concentration of the metals (Kwon et al., 2001), it can be inferred that metals in soil and sediment samples with the highest EFc values have a potential for mobility and bioavailability on the surrounding ecosystems.

Pollution Load Index (PLI)

While computing the contamination factor (CF) as mentioned in methodology for pollution load index (PLI) of top soils of Barapukuria coal mine area, earth crust average value for each metal described by Taylor (1964) was considered as background concentration. Computed contamination factors and PLI values for 17 metals are presented in Table 4 and Figure 3, respectively. According to Tomlinson et al. (1980), the concept of a baseline is a fundamental issue to the formation of a PLI. The PLI values ranged from 1.49 to 3.12 for soil and sediment samples collected from 22 locations of Barapukuria open coal mine area. According to Tomlinson et al. (1980), the PLI provides a simple and comparative means for assessing a site quality. If a PLI value is zero that indicates perfection, a value of one (1.0) represents only baseline levels of pollutants, and values >1.0 would indicate progressive deterioration of the site. So, it can be inferred from Figure 3 that the PLI for all sampling sites had value higher than 1.0, which indicates progressing worsening of top soil quality by several metals at Barapukuria open coal mine area.

Conclusion

The present study determined the concentration of 17 different chemical elements along with major elemental composition in soils and sediments of the Barapukuria coal mine area. The study results revealed that SiO_2, TiO_2, Fe_2O_3, MgO, CaO and P_2O_5 were within the limit of normal soil, while Al_2O_3, Na_2O and K_2O in soil, and MnO and Na_2O in sediment samples exceeded the permissible level of normal soil. Among the metals, the contents of Rb, Cs, Zr, Sn, Ce, La, Nd, Pr and Th in most of the top soils were higher compared to Earth's crust average, while Y and Sb contents were comparatively higher in sediment samples. The study assessed the contamination level in soils and sediments by computing EFc and PLI. Mine water discharge canal sediment samples had EFc values for Sb ranged from 24.72 to 57.09, indicating very severe to extremely severe contamination due to mining activities. On the other hand, EFc values varied from 5 to <20 for Sb and Zr at 10 and 12 soil sampling locations, respectively indicating moderately severe to severe pollution load of the study area.

The computed EFc values for Sn, Th, La, Ce, Cs, Pr, Nd and Y were also >5 in several soil sampling locations indicating moderately severe contamination level in the study area. Similarly, the calculated PLI for all sampling sites had value higher than 1.0, which also indicates progressing deterioration of top soils by several metals at Barapukuria open coal mine area.The study results inferred that top soils of the coal mining area has been

Table 4: Contamination factors (CF) of different minor elements in top soil samples collected from surrounding areas of Barapukuria open coal mine, Dinajpur, Bangladesh

Sample ID	*V*	*Co*	*Ni*	*Rb*	*Sr*	*Y*	*Zr*	*Nb*	*Sn*	*Sb*	*Cs*	*Ba*	*La*	*Ce*	*Pr*	*Nd*	*Th*
1	0.463	0.224	0.415	1.330	0.116	1.213	2.514	0.774	2.455	1.500	2.177	0.880	2.014	1.834	1.648	1.627	2.568
2	0.521	0.406	0.434	1.452	0.129	1.228	2.615	0.669	2.475	1.600	2.110	0.956	2.422	2.322	1.998	1.989	2.536
3	0.465	0.291	0.406	1.482	0.112	1.138	2.284	0.737	2.260	0.800	2.390	0.910	1.905	1.717	1.529	1.576	2.366
4	0.304	0.138	0.275	0.986	0.113	1.192	3.343	0.705	1.980	4.300	1.410	0.767	2.036	1.890	1.515	1.632	2.421
5	0.401	0.121	0.287	1.088	0.120	1.278	3.514	0.886	2.650	3.300	1.890	0.844	2.252	2.088	1.691	1.863	2.497
6	0.490	0.303	0.412	1.424	0.124	1.287	3.207	1.023	3.100	2.900	2.463	1.009	2.206	2.049	1.540	1.725	2.702
7	0.379	0.170	0.384	1.050	0.140	1.260	3.668	0.915	2.620	5.300	1.970	0.864	2.313	2.147	1.689	1.851	2.516
8	0.331	0.224	0.240	0.929	0.111	1.284	4.235	0.833	2.305	3.150	1.450	0.763	2.402	2.247	1.739	1.899	2.701
9	0.437	0.310	0.435	1.286	0.113	1.107	2.656	0.734	2.540	2.300	2.200	0.897	1.978	1.873	1.321	1.611	2.368
10	0.403	0.316	0.333	1.547	0.194	1.162	2.255	0.604	2.605	1.450	2.057	0.948	2.158	1.998	1.671	1.791	2.340
11	0.321	0.147	0.248	0.982	0.121	1.281	3.783	0.827	2.410	2.850	1.467	0.827	2.284	2.087	1.788	1.785	2.572
12	0.447	0.191	0.396	1.359	0.118	1.087	2.956	0.926	2.945	5.450	2.487	0.961	2.186	1.999	1.730	1.763	2.636
13	0.240	0.080	0.529	0.273	0.260	1.353	2.084	1.465	2.280	35.050	0.450	0.488	1.146	0.998	0.788	0.766	1.101
14	0.150	0.082	0.398	0.121	0.265	1.284	1.635	1.299	1.470	26.500	0.410	0.358	0.860	0.820	0.483	0.627	0.826
15	0.519	0.334	0.612	1.302	0.148	0.681	2.896	0.932	2.885	4.450	2.317	0.934	2.128	1.983	1.616	1.766	2.403
16	0.521	0.349	0.488	1.360	0.107	1.212	2.984	0.895	2.765	6.050	2.127	0.858	1.830	1.838	1.259	1.411	2.232
17	0.422	0.265	0.480	1.281	0.113	0.880	2.465	0.730	1.980	1.550	1.693	0.716	1.427	1.408	1.163	1.108	2.182
18	0.654	0.479	0.579	1.177	0.118	1.071	2.542	0.842	2.210	1.750	2.123	0.761	1.986	1.935	1.874	1.694	2.322
19	0.503	0.359	0.436	1.204	0.372	0.606	1.039	0.424	1.555	3.750	1.787	0.925	1.733	1.096	0.835	1.357	1.729
20	0.544	0.479	0.512	1.330	0.421	0.717	1.228	0.488	1.545	1.600	2.263	0.966	1.216	1.193	1.283	0.998	1.281
21	0.621	0.460	0.455	1.214	0.122	1.062	2.433	0.755	2.350	2.600	1.800	0.804	1.651	1.695	1.238	1.390	2.138
22	0.347	0.125	0.594	0.692	0.256	1.278	3.211	1.076	2.250	10.200	1.367	0.868	1.146	1.625	0.745	0.913	1.127
Range	0.150-0.654	0.080-0.479	0.240-0.612	0.121-1.547	0.107-0.421	0.606-1.353	1.039-4.235	8.47-29.29	1.470-3.100	0.800-35.05	0.410-2.487	0.358-1.009	0.860-2.422	0.820-2.322	0.483-1.998	0.627-1.989	0.826-2.702

severely contaminated due to Sb and Zr, and moderately polluted by several chemical elements, which might be originated from geogenic sources due to coal mining and coal based power generation related activities at the study area. Thus, if such activities are continued by ignoring protective measures, the concentration of different chemical elements will increase to intolerable limits, which may create severe impacts on the soil environment and finally to the food chain.

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