

Assessment of Metallic Pollution along with Geochemical Baseline of Soils at Barapukuria Open Coal Mine Area in Dinajpur, Bangladesh

H.M. Zakir*, M.Y. Arafat and M.M. Islam

Department of Agricultural Chemistry, Faculty of Agriculture, Bangladesh Agricultural University
Mymensingh – 2202, Bangladesh
✉ zakirhm.ac.bau@gmail.com

Received April 26, 2017; revised and accepted September 6, 2017

Abstract: A total 42 (5 + 37) soil samples surrounding 4 km² of Barapukuria open coal mine area were collected to determine the geochemical baseline and concentrations of different metals after digestion with aqua regia. The mean total concentration and geochemical baseline values of Cu, Zn, Pb, Cd and Cr in soil samples were 28.43, 44.83, 20.94, 0.19 and 55.79 $\mu\text{g g}^{-1}$, and 20.40, 32.80, 20.47, 0.12 and 42.69 $\mu\text{g g}^{-1}$, respectively. Out of 37 sampling stations, 92-100% locations had the values higher for Cu, Zn, Cd and Cr, while it was 65% for Pb, than that of the geochemical baseline value. The deposition of outlet fly ash and waste water may be responsible to increase metal concentrations in surface soils around the coal mining area. Copper, Zn, Cd, Cr and Pb concentrations upto carbonate bound fraction were 2.52-17.12, 2.62-40.67, 0, 1.47-17.62 and 4.53-16.10 $\mu\text{g g}^{-1}$, respectively. Zinc, Cu, Cd and Cr were the major pollutants in the surrounding soils of Barapukuria because these metals have contamination factor >1.0 for most sampling stations. Study also revealed moderate pollution level by these metals after calculated I_{geo} values. According to risk assessment code, although adjacent soils of Barapukuria are contaminated with Cu, Zn, Cd, Cr and Pb but these metals are relatively strongly bound to the soils and are of *low risk* (<10% for these metals) as regards to mobilization. The study results inferred that if proper attention is ignored, the concentration of metals will increase to intolerable limits that may have severe impacts on the soil environment.

Key words: Geochemical baseline, metallic pollution, Barapukuria coal mine, Bangladesh.

Introduction

Mining activities are responsible for different types of serious problem to the environment in all over the world. Open pit type coal mining activities in Barapukuria produce huge quantities of solid and liquid wastes that may be contaminated with different metals. Furthermore, open pit mine system requires dewatering and depressurization of the aquifers through continuous pumping out of water to keep the mine pit dry and keep secure working conditions (Zaman, 2009). Discharge of

contaminated water from such activities mix with both surface and ground water, and deteriorate their quality (Khan et al., 2005; Singh et al., 2008; Singh et al., 2010; Zakir et al., 2013). This contaminated water is also responsible for the degradation of soil and aquatic environment by allowing heavy metals to seep into the sites (Fang et al., 2003; Coulthard and Macklin, 2003; Xi-Jun et al., 2008). Discharge of untreated mine water, fly ash, waste water and effluents from different industries are responsible for toxic metallic contamination in water and agricultural soils. Higher

*Corresponding Author

concentration of toxic metals in soils can harmfully affect crop growth by interfering with metabolic functions in plants (Monni et al., 2000; Pietraszewska, 2001) and cause changes in the composition of soil microbial community (Giller et al., 1998; Kurek and Bollag, 2004), adversely affecting soil characteristics. Considerable amounts of potentially toxic metals get into the food chain if crops are grown in such metal contaminated soils (Agoramoorthy et al., 2009; Naaz and Pandey, 2010).

Natural variations in concentration for an element in the surficial environment may refer as its geochemical baseline (Salminen and Tarvainen, 1997). But the natural element concentration of a substance is known as the geochemical background. The baseline represents the on-the-spot measured concentration of an element in some sites under anthropogenic activities. Natural spatial variations in the Earth's surface materials can define using baseline value which is very much useful for policy makers and others interested in different environmental issues (Darnley, 1997). The geochemical baseline may be used as a reference standard to monitor environmental changes in spite of either natural or anthropogenic comparative standards or scales (Yanguo et al., 2001). Hence, the purpose of baseline study is to take the geochemical picture of an area. Environmental changes in geochemical landscape can be monitored using this in future (Eppinger et al., 2001). Usually, in geochemical environment natural and human made anomalies coexist. Hence, in environmental impact appraisal it is important to differentiate anthropogenic anomaly from natural variation (Chaffee et al., 1997; Chaffee and Carlson, 1998). Geochemical baselines and related indices can be used to distinguish anthropogenic influence from natural one. Therefore, in the present study, soil samples collected from surrounding areas

of Barapukuria open coal mine area were analysed to determine concentrations of different metals and assess pollution level along with geochemical baseline of metals.

Study Area

Barapukuria is one among the most important coal production base of Bangladesh, which is located at Phulbari Police Station in Dinajpur district. Geological Survey of Bangladesh (GSB) first discovered the mine in 1985 and a treaty was signed between Petrobangla and a Chinese consortium (M/S China National Machinery Import and Export Corporation) in 1994, and accordingly the physical works for implementation of the project was commenced in June 1996. According to Barapukuria Coal Mining Company Limited (BCMCL), it has a proved area of 6.68 square kilometre. The coalfield has a depth of coal deposit between 118 m and 509 m with an estimated reserve of coal as 390 million metric ton. 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, situated in the vicinity of the study area, is the main user of the produced coal. The main components of the geology of Barapukuria coal mine basin are shown in Table 1 and Figure 1.

Materials and Methodology

Collection and Preparation of Soil Samples

Total 37 soil samples were collected from the surrounding area within a radius of 1 km from the origin

Table 1: Stratigraphic succession of the Barapukuria coal basin (after Quamruzzaman et al., 2014)

<i>Age</i>	<i>Group</i>	<i>Formation</i>	<i>Member</i>	<i>Lithology</i>	<i>Thickness (m)</i>
Holocene		Alluvium		Silty clay	1.83
Pleistocene		Barind clay residuum		Clay and sandy clay	10.36
Pliocene		Dupi tila	Upper	Sandstone, pebbly sandstone and clay/mudstone	126.82
			Lower	Sandstone, claystone and mudstone with silica and white clay	
Permian	Gondwana			Feldspathic sandstone, carbonaceous sandstone and shale, ferruginous sandstone, conglomerates and coal beds	457.32
Precambrian	Basement complex			Diorite, granodiorite, quartzdiorite, granite and diorite gneiss	14.32

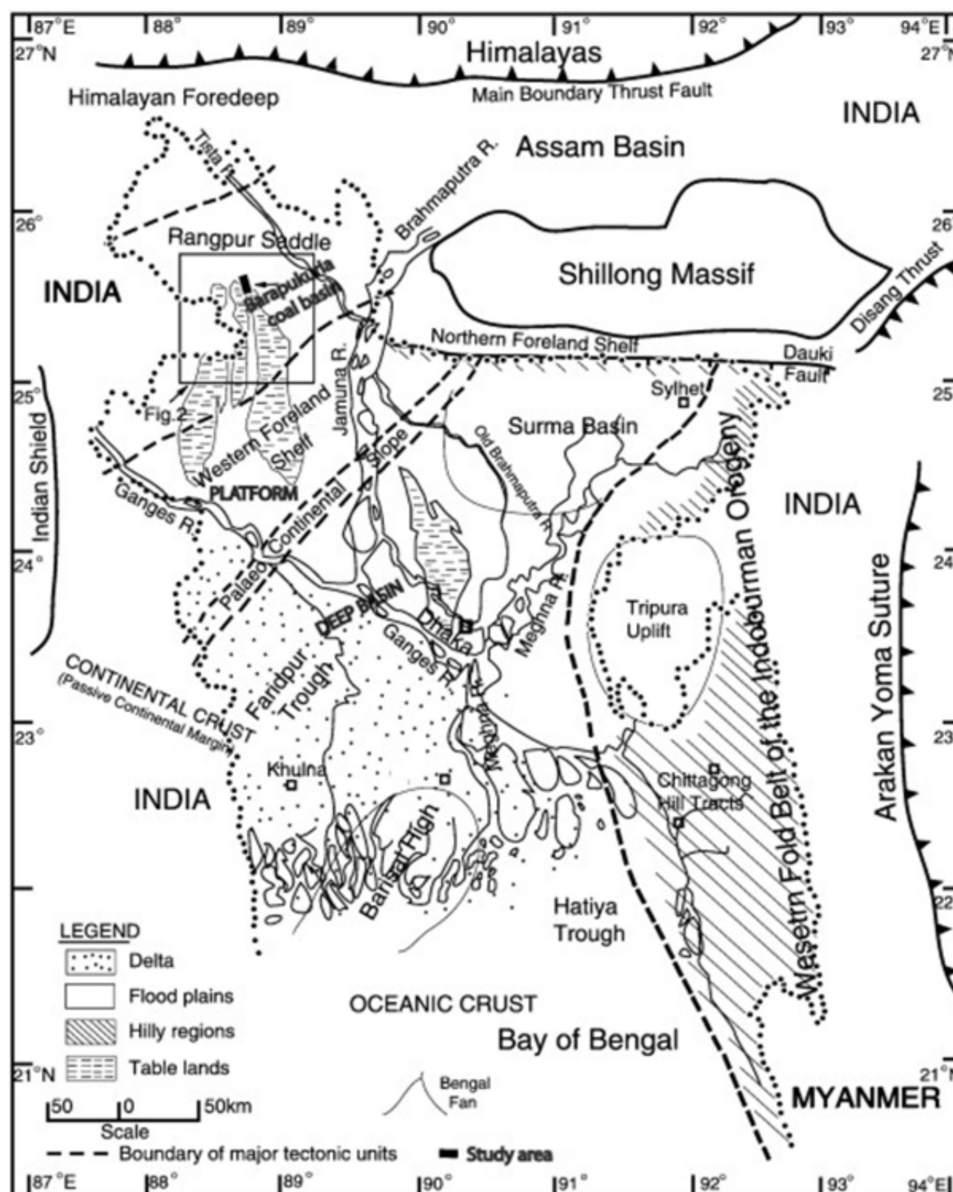


Figure 1: Location of Barapukuria coal mine area, Dinajpur, Bangladesh showing the tectonic elements and physiographic divisions of Bengal Basin (after Farhaduzzaman et al., 2012).

of Barapukuria coal mine. The sampling distance from one station to another was at least about 100 m (Table 2). Soil samples were taken from 0-30 cm depth and rapidly filled in airtight polythene bags. From each location, about 500 g soil sample was collected and the materials were oven dried at 50°C for 24 h. After drying, soil particle size was homogenized by grinding in an agate mortar. Then the samples were sieved (aperture 125 mm) and finally 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.

Collection of Samples for Geochemical Baseline Study

Five (5) fresh soil samples were collected from the study area on the basis of an oral questionnaire to the local people of the area. According to their statement, five sites were selected which fulfill the criteria, such as (i) the soil still is in its original condition; (ii) there is no addition or deletion in the surface soil; (iii) the lands remain fallow for at least last 20 (twenty) years;

Table 2: Description of locations and basic properties of soil samples collected from Barapukuria open coal mine area, Dinajpur, Bangladesh

<i>Sample ID</i>	<i>Location from the mine</i>	<i>Distance from the mine (m)</i>	<i>Land type</i>	<i>pH</i>	<i>EC ($\mu\text{S cm}^{-1}$)</i>	<i>Organic matter (%)</i>
1	North	100	Medium high land	6.92	74	1.49
2	North	200	Medium high land	6.75	30	1.76
3	North	350	Medium high land	6.84	28	1.75
4	North	700	Medium high land	6.92	29	1.64
5	North	850	Medium high land	6.87	20	1.57
6	North	1000	Medium high land	6.94	29	2.51
7	North-east	500	Medium high land	6.87	26	1.76
8	East	100	Medium high land	6.80	120	1.55
9	East	200	Medium high land	6.70	80	2.25
10	East	350	Medium high land	6.90	86	3.05
11	East	500	Medium high land	6.80	59	2.81
12	East	650	Medium high land	6.82	44	2.90
13	East	750	Medium high land	6.80	40	2.74
14	East	900	Medium high land	6.82	43	2.93
15	East	1000	Medium high land	7.09	276	3.05
16	South	100	Medium high land	6.81	135	0.68
17	South	200	Medium high land	6.90	387	2.35
18	South	350	Medium high land	6.89	200	3.22
19	South	500	Medium high land	6.92	51	2.18
20	South	650	High land	6.80	60	2.42
21	South	750	High land	6.78	65	2.43
22	South	850	High land	6.95	42	2.78
23	South	950	High land	6.77	50	1.76
24	South	1050	High land	6.88	70	1.87
25	West	150	Medium high land	7.05	75	1.75
26	West	250	Medium high land	6.89	96	1.85
27	West	400	Medium high land	6.82	78	2.17
28	West	550	Medium high land	6.87	63	2.51
29	West	750	Medium high land	6.88	70	2.32
30	West	850	Medium high land	6.70	120	2.15
31	West	1000	Medium high land	6.77	422	3.26
32	South-west	100	Low land	6.97	450	2.03
33	South-west	200	Low land	6.90	645	3.24
34	South-west	300	Low land	6.96	500	2.78
35	South-west	400	Low land	6.94	610	3.09
36	South-west	500	Low land	6.93	610	3.20
37	South-east	100	Low land	6.92	477	3.02
Mean				6.87	169	2.35
Range				6.70-7.09	20-645	0.68-3.26

and (iv) the soil is not contaminated by the local people. From each location three soil samples were collected upto 60 cm depth and mixed together to get a composite sample. These samples were used to obtain geochemical baseline data. Special attention was given for these samples during processing and analysis to avoid any sorts of contamination.

Determination of Basic Properties of Soil Samples

The pH and electrical conductivity (EC) were measured in 1:2.5 soils to water ratio by using a sensION + PH3 basic benchtop pH meter and sensION + EC5 portable conductivity meter, respectively. Prior to pH determination, the suspension was allowed to stand overnight. The wet oxidation method of Walkley and Black (1934) was used to measure the organic carbon (OC) present in soil samples.

Determination of Heavy Metals Concentration in Soil Samples

Total concentrations of heavy metals (Cu, Zn, Pb, Cd and Cr) in soil samples were determined by using an atomic absorption spectrophotometer (AAS) (Shimadzu, AA7000, Japan). The instrument was equipped with single elements hollow-cathode lamps at the wavelengths of 324.8, 213.9, 283.3, 228.8 and 357.9 nm, respectively, which was operated at maximum sensitivity with an air-acetylene flame. Lamp intensity and bandpass of AAS were used according to the manufacturer's recommendations. Exactly 1.00 g of powdered soil sample was digested with aqua regia (HNO_3 : HCl = 1: 3) to determine total concentration of metal. On the other hand, for the determination of metal up to carbonate bound fraction, exactly 1.00 g of powdered soil sample was taken into 200 mL conical flask followed by the addition of 20 mL of 0.11M acetic acid. Then the content was stirred for 16 hours at room temperature (Rauret et al., 1999). All chemicals and reagents were of analytical reagent grade quality (Merck, Germany).

Mineralogical Study of Soils

Two (2) air-dried, pulverised and sieved soils, regardless of the constituent particle size were used in the mineralogical study. Among these two samples, one was polluted for most of the metals studied (sample # 8), and the other was fresh soil sample (collected for geochemical baseline study). The study was completed using a D8 Advance Bruker AXS (Berlin, Germany) X-ray diffractometer (XRD), and technical specifications required for optimal operation were set

according to the manufacturer's recommendations. The analyzing radiation was Cu K-alpha with wavelength of 1.5406 Å (0.15406 nm). X-ray diffractograms were collected on powder samples within the 2θ range [2° - 70°], with counting for 2s. each 0.02° . The X-ray diffraction was then attached to the advanced diffract plus evaluation software through the computer.

Determination of Geoaccumulation Index (I_{geo})

The geoaccumulation index (I_{geo}) values were calculated for Cu, Zn, Pb, Cd and Cr using formula as introduced by Muller (1969), which is modified as follows for the present study,

$$I_{geo} = \log_2 (Cn/Bn)$$

where Cn is measured concentration of metal in the soil, and Bn is the geochemical baseline for the same element which is directly measured in soils of the present study, and due to this reason, the factor 1.5 introduced by Muller (1969) was omitted from the above equation. According to Muller (1969), there are seven grades or classes of the geoaccumulation index. Class 0 (practically uncontaminated/unpolluted): $I_{geo} < 0$; Class 1 (Uncontaminated to moderately contaminated): $0 < I_{geo} < 1$; Class 2 (moderately contaminated): $1 < I_{geo} < 2$; Class 3 (moderately to strongly contaminated): $2 < I_{geo} < 3$; Class 4 (strongly contaminated): $3 < I_{geo} < 4$; Class 5 (strongly to extremely contaminated): $4 < I_{geo} < 5$; Class 6 (extremely contaminated): $I_{geo} > 5$, which is an open class and comprises all values of the index higher than Class 5.

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 CF and PLI are the quotient obtained as follows:

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

and

$$PLI \text{ for a site} = \sqrt[n]{CF_1 \times CF_2 \dots \times CF_n},$$

where n equals the number of contamination factors and sites, respectively. A number of contamination factors will be calculated for different heavy metals 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. A

zone or area index can also be calculated in exactly the same way such as site pollution index (Tomlinson et al., 1980).

Risk Assessment Code (RAC)

The metals in the soil are bound with different strengths to the different fractions. The risk assessment code (RAC), as proposed by Perin et al. (1985), mainly applies the sum of exchangeable and carbonate bound fractions for assessing the availability of metals in soils. If a soil sample can release in these fractions less than 1% of the total metal it will be considered safe for the environment; 1-10% low risk; 11-30% medium risk; 31-50% high risk and more than 50% of the total metal has to be considered very high risk/dangerous, which can easily enter into the food chain.

Results and Discussion

Basic Properties of Soils

Results on pH, EC and organic matter of soils collected from Barapukuria open coal mine area are presented in Table 2. The pH value around the study area ranged from 6.70-7.09 with an average value as 6.87. The increase in acidity of agricultural soils due to application of coal mine water seems possible for deposition of basic cation in soils from the coal mine water whose basic cation content was considerably high. Maiti and Ghose (2005) reported that the pH vary from 4.9 to 5.3 in a mining dump site, which is located in Central Coalfield Limited's (CCL), North Karanpura, Ranchi, India. The EC value around the study area varied greatly from 20-645 μScm^{-1} and the average value was 169 μScm^{-1} (Table 2). The variation of EC among the sampling sites might be due to the effect of place, slope, soil condition, irrigation, drainage and others. The amount of organic matter among the sampling locations ranged from 0.68 to 3.26% with a mean value

of 2.35%. According to Callesen et al. (2003), the quantitative relationship between soil organic matter and temperature, textural class and precipitation has been documented. In general soil organic carbon pool is increased both due to precipitation and temperature, and the increase with mean annual temperature was more pronounced for coarse-textured soils than for medium-textured soils.

Assessment of Geochemical Baseline of Metals

Environmentally geochemical baseline is the basis for distinguishing anthropogenic from natural influence. Metallic concentration and basic soil properties obtained from collected fresh soil samples are presented in Table 3 and their average value is treated as geochemical baseline data for the study area. The mean total concentration of Cu, Zn, Pb, Cd and Cr in soil samples were 20.40, 32.80, 20.47, 0.12 and 42.69 $\mu\text{g g}^{-1}$, respectively. The geochemical baselines of elements depend on geological background, sample collection, sample grain size and sample treatment (Salminen and Gregorauskiene, 2000; Miko et al., 1999).

Metal Status in Soils of Barapukuria Coal Mine Area

Mining activities are the potential source of metals for surrounding environment of Barapukuria. Total concentrations of different metals along with the mean concentration of geochemical baseline value collected from different locations of Barapukuria open coal mine area are presented in Figure 2. Total concentration of Cu, Zn, Pb, Cd and Cr in soil samples varied from 20.28-49.77, 31.64-72.69, 15.14-32.69, 0.155-0.288 and 40.95-75.82 $\mu\text{g g}^{-1}$, with the mean value of 28.43, 44.83, 20.94, 0.19 and 55.79 $\mu\text{g g}^{-1}$, respectively. Out of 37 sampling stations, all locations had the values higher for Cu and Cd, 34 sites for Zn, 36 stations for Cr and 24 locations for Pb than that of the geochemical

Table 3: Geochemical baseline values of metals and basic properties of fresh soils of Barapukuria open coal mine area, Dinajpur, Bangladesh

Sample ID	Metal concentration ($\mu\text{g g}^{-1} \pm \text{SD}$)					pH	EC ($\mu\text{S cm}^{-1}$)	Organic matter (%)
	Cu	Zn	Pb	Cd	Cr			
1	21.46 \pm 1.4	32.52 \pm 1.6	21.01 \pm 2.1	0.144 \pm 0.02	43.41 \pm 4.1	6.79	76	1.01
2	22.31 \pm 2.2	33.71 \pm 2.3	21.05 \pm 1.6	0.101 \pm 0.01	43.72 \pm 3.8	6.85	23	0.14
3	17.95 \pm 1.2	31.22 \pm 1.3	19.13 \pm 1.8	0.150 \pm 0.02	40.95 \pm 2.0	6.80	20	1.16
4	19.11 \pm 2.1	32.35 \pm 2.6	20.12 \pm 1.6	0.124 \pm 0.01	42.51 \pm 2.2	6.86	16	1.75
5	21.16 \pm 2.0	34.21 \pm 2.8	21.02 \pm 1.2	0.105 \pm 0.01	42.87 \pm 3.4	6.90	18	1.24
Mean	20.40	32.80	20.47	0.124	42.69	6.84	30.6	1.06

baseline value. Mobility and bioavailability of metals are determined primarily by pH and are enhanced under acidic conditions (when $\text{pH} < 4.5$). Other factors controlling mobility of metals in soils include solubility reactions, sorption reactions and redox conditions (Smith, 2007). But the soils of Barapukuria coal mine area had $\text{pH} > 4.5$ (Table 2), so metals present in the study area are not so mobile.

According to Zhai et al. (2009), the strength of contamination of a metal in a coal mining area depends on its concentration in coal, its performance during the combustion of coal and finally its mobility in surface soils. They also stated the Morupule power station in Botswana has experienced of more than 30 years of coal mining and more than 20 years of coal combustion activities and reported that the deposition of outlet fly ash from the coal-fired power plant has increased some heavy metals concentrations in surface soils around the power station. The Barapukuria coal power plant is also a coal-fired power station, which consumed approximately 450 thousand tonnes of coal in a year (BPDB, 2012). High volatile bituminous coal of Barapukuria is mainly formed by: moisture 10%, ash 12.4%, volatile matter 29.2%, fixed carbon 48.4% and total sulphur 0.53% (BCMCL, 2016). So the deposition of outlet fly ash from the power plant may increase metal concentrations to the surrounding soils.

The trace element behaviour is mainly controlled by their vaporization or condensation temperatures during combustion in the coal based power station, and the finer particles of fly ash possess most of the trace elements (Linak and Wendt, 1994). Coal that contained higher concentration of heavy metals, had stronger small particle association during coal combustion and

were less mobile in surface soils, showed stronger contaminations in soils around the plant (Zhai et al., 2009). However, the average metal levels in soils of Barapukuria open coal mine area were relatively lower compared with several other mining areas in the world (Table 4). So it can be inferred from the study results that the soils of the area has not so far polluted yet, but if it is continued, the concentration of metals will increase to unbearable limits, which may create severe impacts on the soil environment as well as to the food chain.

Mineralogical Composition of Soils

Additional independent information on the mineralogical composition of the soil sampling site 8 (polluted for most of the metals studied) and another sample of geochemical baseline was obtained by XRD analysis and the results are presented in Table 5. Quartz has the strongest peak in both the samples at $d = 3.35$ and 4.26 \AA . The next strongest peak was for calcite ($d = 1.82 \text{ \AA}$) in both the samples. Several clay minerals such as micas and illites, chlorites and kaolinite (diffracted peaks at $d = 9.89, 1.54, 14.12, 3.56, 2.28$ and 1.98 \AA) were common in both soils but the peak intensities for site 8 were comparatively stronger than the geochemical baseline sample. Besides this feldspar (anorthite), feldspar/chlorite and bayerite, and iron oxide and hydroxide group minerals, specifically magnetite and goethite were also common in both soil samples. It is apparent from Table 4 that the peak intensity for sampling site 8 was dominant for most of the clay, carbonate and hydroxide minerals. Several study reports stated that the presence of different clay minerals are likely to be the major host of heavy metals in soils (Islam et al., 2000; Sharmin et al., 2010; Zakir et al., 2014; Zakir et al., 2015).

Table 4: Average metal concentrations ($\mu\text{g g}^{-1}$) in collected soil samples of Barapukuria open coal mining area, Dinajpur, Bangladesh compared with other mining areas of the world

<i>Metal</i>	<i>HMA^a</i>	<i>FHCMA^b</i>	<i>PMA^c</i>	<i>LCMG^d</i>	<i>MSS^e</i>	<i>MCC^f</i>	<i>SMS^g</i>	<i>Present study</i>
Cu	11.2	66.1	34.49	110.51	34- 570	35.4	20- 62*	28.43
Zn	28.5	113.8	78.86	107.06	110- 4023	65.0	100- 250*	44.83
Pb	23.7	20.8	29.32	17.86	27- 2847	22.8	60- 90*	20.94
Cd	0.05	0.10	nd	1.56	Trace to 2.4	nd	0.7- 2.0*	0.19
Cr	29.5	85.26	81.61	37.99	nd	125.2	nd	55.79

HMA = Huainan mining area in China; FHCMA = FuXin-Haizhou coal mining area in China; PMA = Panzhihua mining area in China; LCMG = Lignite coal mine at Gujarat, India; MSS = Mining sites soil in South Morocco; MCC = Morupule colliery coalmine in Botswana; SMS = Soils of mining sites in France; nd = not determined and * = With moderate geochemical anomaly.

^a Yao et al. (2010); ^b Xi-Jun et al. (2008); ^c Yanguo et al. (2002); ^d Ladwani et al. (2012); ^e Boularbah et al. (2006); ^f Zhai et al. (2009);

^g Baize and Paquereau (1997).

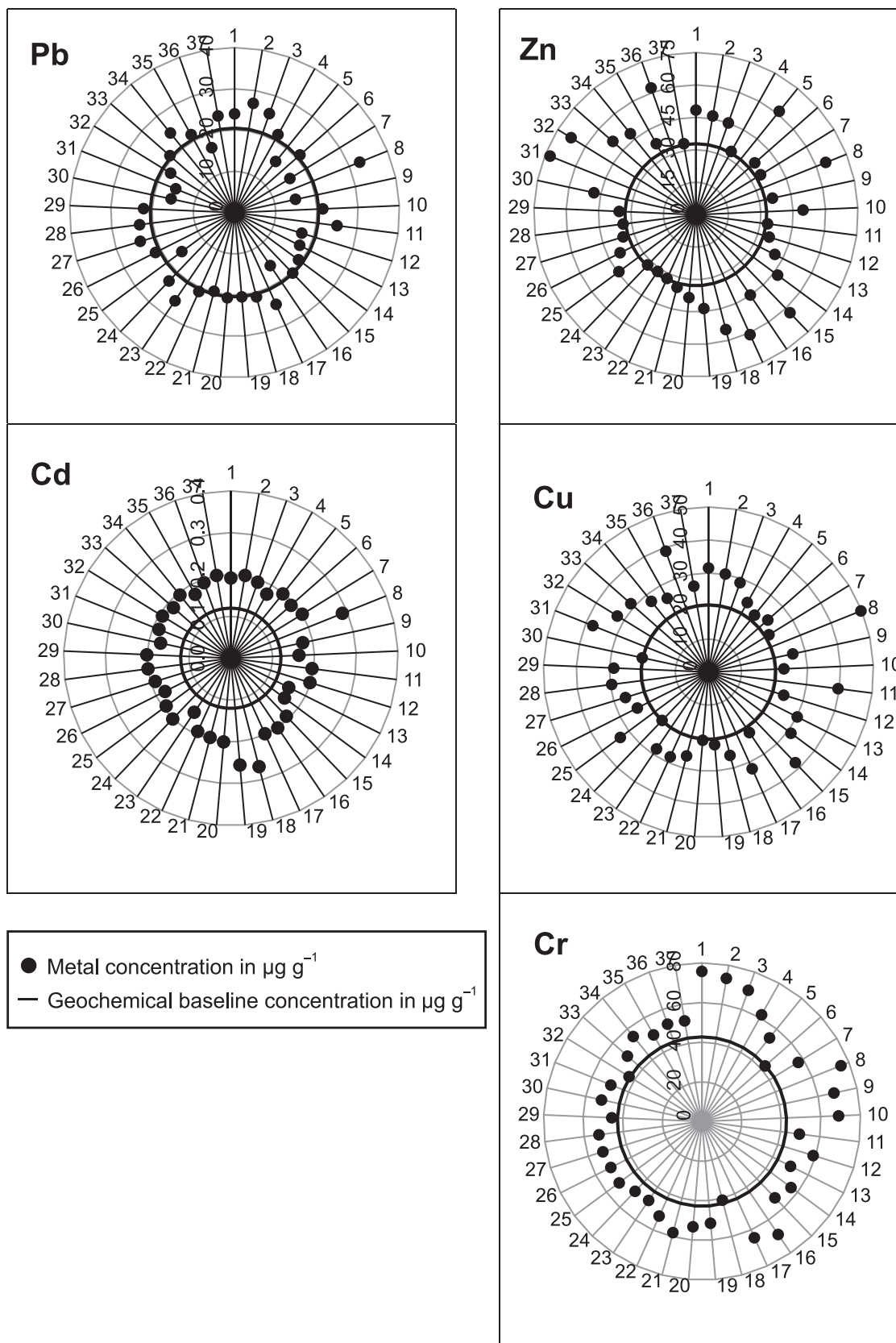


Figure 2: Metal concentrations ($\mu\text{g g}^{-1}$) in soils collected from Barapukuria open coal mine area in Dinajpur, Bangladesh along with geochemical baseline concentration.

Table 5: Mineralogical constituents of soil sampling site 8 (polluted for most of heavy metals studied) and the geochemical baseline

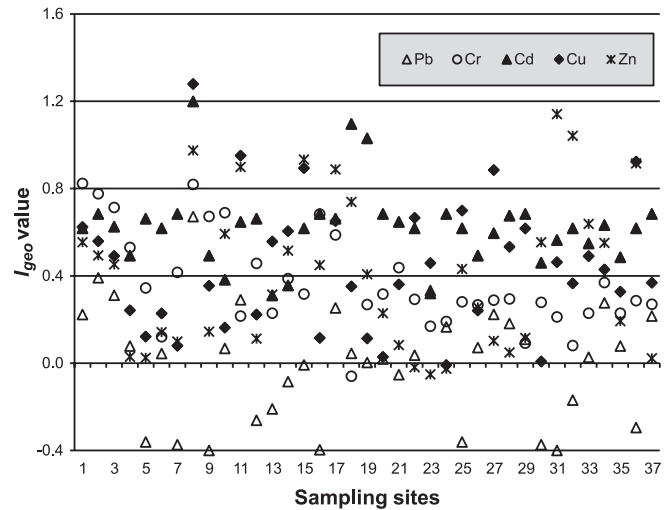
Minerals	Angle (2 θ)	d-value (Å)	Peak intensity (%)	
			Sample ID 8	Geochemical baseline
Quartz	26.59	3.35	100.0	100.0
	20.77	4.26	25.8	19.5
Feldspar	27.45	3.23	4.4	6.8
	24.04	3.67	3.3	4.2
	23.02	3.75	2.6	3.9
	21.18	4.14	–	2.7
Feldspar/ chlorites	31.93	2.82	1.7	2.7
Anorthite	28.54	3.19	3.8	3.9
Micas and illites	8.93	9.89	4.4	0.6
Chamosite	12.37	7.09	2.5	2.0
Chlorites	60.02	1.54	9.3	5.9
	6.21	14.12	1.9	0.1
	24.92	3.56	2.1	–
Biotite/chlorites	19.83	4.46	2.7	3.1
	36.46	2.46	8.5	6.0
Kaolinite	39.51	2.28	8.3	5.3
	45.63	1.98	4.9	2.0
Muscovite	35.08	2.57	2.3	2.7
Goethite	37.08	2.43	8.5	2.4
Bayerite	40.35	2.23	4.9	4.6
Calcite	50.16	1.82	11.9	8.1
Magnetite	35.07	2.53	2.3	2.7

Assessment of Pollution Level

Index of Geoaccumulation (I_{geo})

The geoaccumulation index (I_{geo}) was used to assess metal pollution in soils of Barapukuria open coal mine area in Dinajpur, Bangladesh. The calculated I_{geo} for metals of soils of the study area and their corresponding contamination intensity are illustrated in Figure 3. Out of 37 locations, 92-100% sites showed positive I_{geo} values ($0 < I_{geo} < 2$) and exhibited I_{geo} class 1-2, indicating moderately polluted soil quality for Cu, Zn, Cd and Cr. On the other hand, 59% (22 sites) locations showed positive I_{geo} values ($0 < I_{geo} < 1$) and exhibited I_{geo} class 1, indicating unpolluted to moderately polluted soil quality for Pb. Finally, it can be inferred from the I_{geo} calculation that the soils of Barapukuria open coal mine area are moderately polluted by Cu, Zn, Cd and Cr, and the source of pollution at the study area are

coal mining activities and its use at nearby coal-fired power station.

**Figure 3: Geoaccumulation index (I_{geo}) of metals at different sampling sites of Barapukuria open coal mine area in Dinajpur, Bangladesh.**

Pollution Load Index (PLI)

While computing the contamination factor (CF) for pollution load index (PLI) of soils of the study area, average geochemical baseline value for each metal obtained by this study was considered as background concentration (Figure 4). The concept of a baseline is a fundamental issue to the formation of a PLI (Tomlinson et al., 1980). The PLI values ranged from 1.14 to 1.84 for soil samples collected from 37 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 4 that the PLI for all sampling sites had value higher than 1.0, which indicates progressing worsening of soil quality by several metals at Barapukuria open coal mine area.

Risk Assessment Code (RAC)

The code as applied to the present study revealed that 2.52-17.12, 2.62-40.67, 1.47-17.62 and 4.53-16.10% of total Cu, Zn, Cr and Pb with a mean value of 5.37, 8.25, 9.58 and 6.68%, respectively of the study sites either is adsorb, exchangeable or carbonate bound (Table 6). Hence, overall area comes under the low risk category indicating lower availability from which these metals cannot be easily leached out for the aquatic

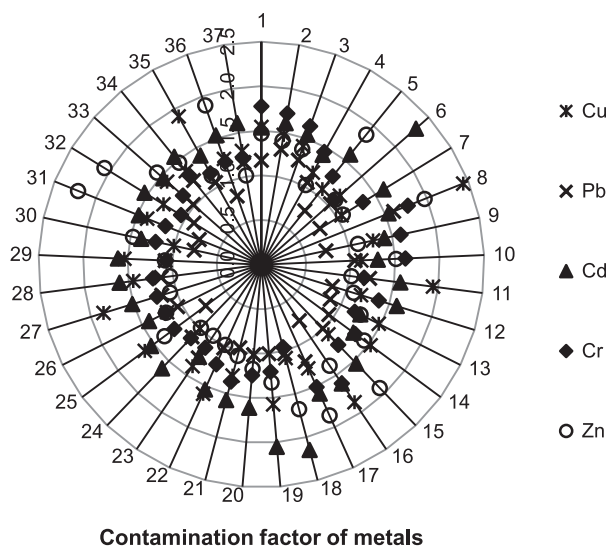


Figure 4: Contamination factor (CF) for each metal at each sampling site along with pollution load index (PLI) of soils in Barapukuria coal mine area in Dinajpur, Bangladesh.

environment. But out of 37 locations, 4 for Pb, 14 for Cr, 5 for Cu and 7 for Zn had >10% of total metal in upto carbonate bound fraction and therefore those sites come under the medium risk category, which can easily enter into the food chain. Due to their inherent toxicity and availability, metals can pose serious problem to the ecosystem and can be remobilized by changes in environmental conditions such as pH, redox potential, salinity etc. (Salomons, 1995). On the other hand, 0% of total Cd was found in the same fraction indicating no risk category or trace amount of availability of this metal to the aquatic environment (Table 5). However, it

can be concluded from the RAC study that the metals investigated are relatively strongly bound to the soils of Barapukuria and are of low risk (<10% of total metal in upto carbonate bound fraction) category for their mobilization.

Table 6: Average metal percentage in upto carbonate bound fraction of soils collected from Barapukuria open coal mine area and risk assessment code (RAC)

Metal	Average percentage of metal in up to carbonate bound fraction		Level of risk on the basis of RAC
	Range	Mean	
Copper (Cu)	2.52-17.12	5.37	Low risk
Zinc (Zn)	2.62-40.67	8.25	Low risk
Chromium (Cr)	1.47-17.62	9.58	Low risk
Lead (Pb)	4.53-16.10	6.68	Low risk
Cadmium (Cd)	0	0	No risk

Conclusion

The present study determined the geochemical baseline and evaluated the heavy metal contents in soils of Barapukuria open coal mine area in Dinajpur, Bangladesh. The mean geochemical baseline concentration of Cu, Zn, Pb, Cd and Cr in soil samples were 20.40, 32.80, 20.47, 0.12 and 42.69 $\mu\text{g g}^{-1}$, respectively. Out of 37 sampling stations, all locations had the values higher for Cu and Cd, 34 sites for Zn, 36 stations for Cr and 24 locations for Pb than that of the geochemical baseline value, which may lead to a potential danger for the environment at the study area. The PLI and I_{geo} calculations indicate that the quality of soils of Barapukuria open coal mine area is deteriorating and are moderately polluted by Cu, Zn, Cd and Cr. The study results also signify that the sources of pollution at the area are coal mining activities and its combustion at nearby coal-fired power station.

Comparing the metal concentration with the other mining areas of the world, it can be concluded that the soils of the study area has not so far polluted yet, but if the activity is continued by ignoring protective measures, the concentration of metals will increase to intolerable limits, which may create severe impacts on the soil environment and finally to the food chain. Although the association of these metals are relatively strongly bound to the soils of the study area and under low risk category for their mobilization after the risk assessment code, it is highly appreciable to monitor

metal concentrations in surface soils routinely in future and accordingly to take necessary initiative by the local authority and government of Bangladesh.

Acknowledgement

This work was partially supported by the Ministry of Science and Information & Communication Technology, Government of the Peoples Republic of Bangladesh under Special Allocation for Science and Technology for the financial year 2010-11; Research Grant no. # 39.009.002.01.00.020.2010/ES-14/1822/1(4).

References

- Agoramoorthy, G., Chen, F.A., Venkatesalu, V. and P.C. Shea (2009). Bioconcentration of heavy metals in selected medicinal plants of India. *Journal of Environmental Biology*, **30**: 175-178.
- Baize, D. and H. Paquereau (1997). Teneurs totales en elements traces dans les sols agricoles de Seine-et-Marne (France). *Etude et Gestion des Sols*, **4(2)**: 77-94.
- BCMCL (Barapukuria Coal Mining Company Limited) (2016). A Company of Petrobangla, Bangladesh. Chowhati, Parbatipur, Dinajpur, Bangladesh. <http://www.bcmcl.org.bd/>. Accessed 24 August 2016.
- Boularbah, A., Schwartz, C., Bitton, G. and J.L. Morel (2006). Heavy metal contamination from mining sites in South Morocco: 1. Use of a biotest to assess metal toxicity of tailings and soils. *Chemosphere*, **63**: 802-810.
- BPDB (Bangladesh Power Development Board) (2012). *Annual Report 2011-12*. Bangladesh Power Development Board, Dhaka, Bangladesh.
- Callesen, I., Liski, J., Raulund-Rasmussen, K., Olsson, M.T., Tau-strand, L., Vesterdal, L. and C.J. Westman (2003). Soil carbon stores in Nordic well-drained forest soils—relationships with climate and texture class. *Global Change Biology*, **9(3)**: 358-370.
- Chaffee, M.A. and R.R. Carlson (1998). Environmental geochemistry in Yellowstone National Park: Distinguishing natural and anthropogenic anomalies. *Yellowstone Science*, **6**: 29.
- Chaffee, M.A., Hoffman, J.D. and R.R. Tidball (1997). Discriminating between natural and anthropogenic anomalies in the surficial environment in Yellowstone National Park, Idaho, Montana, and Wyoming. U.S. Geological Survey Open-File Report 97-496, v. 16.
- Coulthard, T.J. and N.G. Macklin (2003). Modeling long term contamination in river systems from historical metal mining. *Geology*, **31(5)**: 451-454.
- Darnley, A.G. (1997). A global geochemical reference network: The foundation for geochemical baselines. *Journal of Geochemical Exploration*, **60**: 1-5.
- Eppinger, R.G., Briggs, P.H., Brown, Z.A., Crock, J.G., Meier, A., Theodorakos, P.M. and S.A. Wilson (2001). Baseline geochemical data for stream sediment and surface water samples from Panther Creek, the Middle Fork of the Salmon River, and the Main Salmon River from North Fork to Corn Creek, collected prior to the severe wildfires of 2000 in central Idaho. U.S. Geological Survey Open-File Report 01-0161, p. 1-20.
- Fang, W.X., Huang, Z.Y. and P.W. Wu (2003). Contamination of the environmental ecosystems by trace elements from mining activities of Badao bone coal mine in China. *Environmental Geology*, **44**: 373-378.
- Farhaduzzaman, M., Abdullah, W.H. and M.A. Islam (2012). Depositional environment and hydrocarbon source potential of the Permian Gondwana coals from the Barapukuria basin, Northwest Bangladesh. *International Journal of Coal Geology*, **90-91(1)**: 162-179.
- Giller, K.E., Witter, E. and S.P. McGrath (1998). Toxicity of heavy metals to microorganism and microbial processes in agricultural soils: A review. *Soil Biology and Biochemistry*, **30(10-11)**: 1389-1414.
- Islam, M.R., Lahermo, P., Salminen, R., Rojstaczer, S. and V. Peuraniemi (2000). Lake and reservoir water quality affected by metals leaching from tropical soils, Bangladesh. *Environmental Geology*, **39(10)**: 1083-1089.
- Khan, R., Israili, S.H., Ahmad, H. and A. Mohan (2005). Heavy metal pollution assessment in surface water bodies and its suitability for irrigation around the Nayevli lignite mines and associated industrial complex, Tamil Nadu, India. *Mine Water and the Environment*, **24**: 155-161.
- Kurek, E. and J.M. Bollag (2004). Microbial immobilization of cadmium released from CdO in the soil. *Biogeochemistry*, **69(2)**: 227-239.
- Ladwani, K.D., Ladwani, K.D., Manik, V.S. and D.S. Ramteke (2012). Assessment of heavy metal contaminated soil near coal mining area in Gujarat by toxicity characteristics leaching procedure. *International Journal of Life Sciences Biotechnology and Pharma Research*, **1(4)**: 73-80.
- Linak, W.P. and J.O.L. Wendt (1994). Trace metal transformation mechanisms during coal combustion. *Fuel Processing Technology*, **39**: 173-198.
- Maiti, S.K. and M.K. Ghose (2005). Ecological restoration of acidic coal mine overburden dumps—An Indian case study. *Land Contamination and Reclamation*, **13(4)**: 361-369.
- Miko, S., Durn, G. and E. Prohie (1999). Evaluation of terra rossa geochemical baselines from Croatian karst regions. *Journal of Geochemical Exploration*, **66**: 173-182.
- Monni, S., Salemma, M. and N. Millar (2000). The tolerance of *Empetrum nigrum* to copper and nickel. *Environmental Pollution*, **109**: 221-229.
- Muller, G. (1969). Index of geoaccumulation in sediments of the Rhine river. *Geojournal*, **2(3)**: 108-118.
- Naaz, S. and S.N. Pandey (2010). Effects of industrial waste water on heavy metal accumulation, growth and

- biochemical responses of Lettuce (*Lactuca sativa* L.). *Journal of Environmental Biology*, **31**: 273-276.
- Perin, G., Craboledda, L., Lucchese, M., Cirillo, R., Dotta, L., Zanetta, M.L. and A.A. Oro (1985). Heavy metal speciation in the sediments of northern adriatic sea: A new approach for environmental toxicity determination. In: Lakkas T.D. (ed) Heavy metals in the environment. CEP Consultants, Edinburg.
- Pietraszewska, T.M. (2001). Effect of aluminium on plant growth and metabolism. *Acta Biochimica Polonica*, **48(3)**: 673-686.
- Quamruzzaman, C., Mondol, M.A.M., Ahmed, M.T., Kabir, S.M.M. and Z. Ahmed (2014). A proposal of open pit coal mine at the northern part of Barapukuria coalfield, Dinajpur, Bangladesh. *International Journal of Emerging Technology and Advanced Engineering*, **4(3)**: 482-488.
- Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Ph. Quevauviller (1999). Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring*, **1**: 57-61.
- Salminen, R. and T. Tarvainen (1997). The problem of defining geochemical baselines: A case study of selected elements and geological materials in Finland. *Journal of Geochemical Exploration*, **60**: 91-98.
- Salminen, R. and V. Gregorauskiene (2000). Considerations regarding the definition of a geochemical baseline of elements in the surficial materials in areas differing in basic geology. *Applied Geochemistry*, **15**: 647-653.
- Salomons, W. (1995). Environmental impact of metals derived from mining activities: Processes, predictions, prevention. *Journal of Geochemical Exploration*, **52**: 5-23.
- Sharmin, S., Zakir, H.M. and N. Shikazono (2010). Fractionation profile and mobility pattern of trace metals in sediments of Nomi River, Tokyo, Japan. *Journal of Soil Science and Environmental Management*, **1(1)**: 01-14.
- Singh, A.K., Mondal, G.C., Kumar, S., Singh, T.B., Tewary, B.K. and A. Sinha (2008). Major ion chemistry, weathering processes and water quality assessment in upper catchment of Damodar River basin, India. *Environmental Geology*, **54**: 745-758.
- Singh, A.K., Mahato, M.K., Neogi, B. and K.K. Singh (2010). Quality assessment of mine water in the Raniganj coalfield area, India. *Mine Water and the Environment*, **29**: 248-262.
- Smith, K.S. (2007). Strategies to predict metal mobility in surficial mining environments. In: DeGraff J.V. (ed.), Understanding and responding to hazardous substances at mine sites in the western United States: Geological Society of America reviews in engineering geology. Vol. XVII. doi: 10.1130/2007.4017(03).
- Tomlinson, D.C., Wilson, J.G., Harris, C.R. and D.W. Jeffrey (1980). Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. *Helgoland Marine Research*, **33**: 566-575.
- Walkley, A. and I.A. Black (1934). An examination of the Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science*, **37**: 29-38.
- Xi-jun, M., Zhao-hua, L. and C. Jian-long (2008). Ecological risk assessment of open coal mine area. *Environmental Monitoring and Assessment*, **147(1)**: 471-481.
- Yanguo, T., Shijin, N., Xianguo, T., Chengjiang, Z. and M. Yuxiao (2002). Geochemical baseline and trace metal pollution of soil in Panzhihua mining area. *Chinese Journal of Geochemistry*, **21(3)**: 274-281.
- Yanguo, T., Shijun, N., Chengjiang, Z. and L. Yu-chang (2001). Countermeasures to restore environment and rehabilitate ecology in the Panzhihua mining industry base. *Sichuan Environment*, **20**: 31-34.
- Yao, D., Meng, J. and Z. Zhang (2010). Heavy metal pollution and potential ecological risk in reclaimed soils in Huainan mining area. *Journal of Coal Science and Engineering (China)*, **16**: 316-319.
- Zakir, H.M., Islam, M.M., Arafat, M.Y. and S. Sharmin (2013). Hydrogeochemistry and quality assessment of waters of an open coal mine area in a developing country: A case study from Barapukuria, Bangladesh. *International Journal of Geosciences Research*, **1(1)**: 20-44.
- Zakir, H.M., Nahid Sultana and Mousumi Akter (2014). Heavy metal contamination in roadside soils and grasses: A case study from Dhaka city, Bangladesh. *Journal of Chemical, Biological and Physical Sciences*, **4(2)**: 1661-1673.
- Zakir, H.M., Sumi, S.A., Sharmin, S., Mohiuddin, K.M. and S. Kaysar (2015). Heavy metal contamination in surface soils of some industrial areas of Gazipur, Bangladesh. *Journal of Chemical, Biological and Physical Sciences*, **5(2)**: 2191-2206.
- Zaman, Z. (2009). Water management in coal mining project: case study Phulbari. *Coal News of Phulbari – Bangladesh*. <https://phulbarinews.wordpress.com/2009/07/12/water-management-in-coal-mining-project-case-study-phulbari/>. Accessed 20 July, 2016.
- Zhai, M., Totolo, O., Modisi, M.P., Finkelman, R.B., Kelesitse, S.M. and M. Menyatso (2009). Heavy metal distribution in soils near Palapye, Botswana: An evaluation of the environmental impact of coal mining and combustion on soils in a semi-arid region. *Environmental Geochemistry and Health*, **31(6)**: 759-777.