

Assessment of major ionic compositions and anthropogenic influences in the rainwater over a coal mining environment of Damodar River basin, India

Kumar Mahato, M.^{1*}, Kumar Singh, P.¹, Kumar Singh, A.² and Kumar Tiwari, A.¹

1. Department of Environmental Science & Engineering, Indian School of Mines, Dhanbad-826004, Jharkhand, India
2. Environmental Management Group, CSIR-Central Institute of Mining and Fuel Research, Dhanbad-826015, Jharkhand, India

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ABSTRACT: In the present study, 45 rainwater samples were collected from February to December 2012 on event basis in East Bokaro coal mining environment. Physico-chemical and major ionic compositions of rainwater samples as well as water soluble major ion composition were analyzed to employ principle component analysis for source identification. The average pH value was recorded 6.1 and varied from 5.1 to 6.9 in the collected rainwater samples, indicating slightly acidic to alkaline in nature. The rainwater chemistry of the region showed high contribution of HCO_3^- (32%) followed by SO_4^{2-} (30%), Cl^- (20%), NO_3^- (15%) and F^- (3%) in anionic abundance. In case of major cations, Ca^{2+} (29%) was dominant followed by Mg^{2+} (27%), NH_4^+ (22%), Na^+ (18%) and K^+ (4%). The ratio of Cl^-/Na^+ in the rainwater samples was found to be almost equal to sea water. Higher enrichment of Na^+ and Cl^- concentration may be due to marine contribution. The EFs were found to be high for HCO_3^- , Ca^{2+} , SO_4^{2-} and K^+ indicating sources other than sea; i.e., coal mining and other anthropogenic activities. The principle component analysis for ionic source identification was synthesized into four factors with eigen values cut off at greater than unity and explained about 71.8 % of the total variance. The rainwater quality area is mainly influenced due to mining activities, vehicular pollution and industrialization in the East Bokaro coalfield area.

Keywords: East Bokaro coalfield, enrichment factor, major ion chemistry, principle component analysis, rainwater.

INTRODUCTION

The rainwater compositions play an important role in scavenging soluble ionic components from the atmosphere and helping to understand the relative contributions of different sources of atmospheric pollutants (Akoto et al., 2011; Yang et al., 2011). It has a complex chemical composition that varies from

place to place and season to season. It contains varying amounts of major ions viz. fluoride, chloride, nitrate, bicarbonate sulfate, sodium, ammonia, potassium, magnesium, and calcium (Hutchinson, 1957). Rainwater contains some constituents of local origin, and some that have been transported by winds from elsewhere (Eriksson, 1952). Rainwater acquires dissolved cations and anions from the dissolution of gaseous and particulate

* Corresponding author Email: catchmukesh8317@gmail.com

material present in the atmosphere which could be of natural or anthropogenic origin. The cations such as Ca^{2+} , Mg^{2+} and anions such as HCO_3^- are derived from the soil dust present in the atmosphere whereas SO_4^{2-} and NO_3^- can come from anthropogenic sources in addition to natural precursors (Chatterjee and Singh, 2008; Cobbina et al., 2013).

Rainwater is one of the most important ways of removing the gaseous and particulate pollutants from the atmospheric environment (Yanli et al., 2011; Rai, 2014). The chemical composition of rainwater reflects the quality of the air during the occurrence of rainfall (Hideaki et al., 2008; Budhavant et al., 2009). Past studies have shown very high concentration of anthropogenic substances like NO_3^- and SO_4^{2-} in urban or industrial areas compared to other areas (Khare et al., 2004; Tu et al., 2005; Rastogi and Sarin, 2005). Coal combustion, automobile exhaust, and industrial emissions represent the dominant anthropogenic sources of heavy metals in rainwater (Cheng et al., 2011; Meena et al., 2014; Gabriel and Henry, 2015). Emission of air pollutants is increasing rapidly in many southeastern Asian countries (Granat et al., 1996; Rodhe et al., 2002), due to fast growth in population and the consequent upward trend in agricultural production, industrialization, mining, energy consumption, transport, housing, etc. Thus, rainwater is a serious risk to the environment, such as vegetation, soil, forestry, water bodies and corrosion of building materials.

A number of studies have been carried out on the various aspects of atmospheric chemistry over several parts of India (Saxena et al., 1991, 1996; Kumar et al., 1993, 2002; Ravichandran and Padmanabhamurty, 1994; Kulshrestha et al., 1995; Jain et al., 2000; Parashar et al., 2001; Balachandran and Khilare, 2001; Naik et al., 2002; Das et al., 2005; Ahirakwem, 2012). However, studies related to rainwater in the coal mining areas are scarce. The purpose of the present study is to assess the major ion chemistry of

rainwater in India's richest coal mining area and to assess the constituents in the rainwater and their sources through statistical means. The study will indicate the intensity of the pollution in the coal mining area and thus will be useful for implementing emission-reduction policies in the study area.

MATERIALS AND METHODS

Study area

The study was carried out in East Bokaro Coalfield of Damodar river basin, located in the Bokaro district of Jharkhand State. Major pollution generating activities are associated with many working and abandoned coal mines, thermal power plants, explosive industry and coal washery in these regions. Besides these mining and industrial sources, ever increasing transportation sector contributes significantly to air quality deterioration by means of elevated particulate matter, CO_2 , NO_x and unburnt hydrocarbons (Singh and Mondal, 2008). The coalfield occupies an area of about 237 sq. km and lies between Latitudes $23^\circ 45' \text{N}$ to $23^\circ 50' \text{N}$ latitude and $85^\circ 30' \text{E}$ to $86^\circ 03' \text{E}$ longitude. The coalfield is drained by three prominent rivers viz. the Bokaro River in the Central part, the Konar River in the Eastern and the Damodar River in the Southern. The climate of the study area is humid and sub tropical. The area is under the influence of South West Monsoon with most of the rainfall occurring in June to September.

Sampling of rainwater

The location of Lahariatanr village, 1.5 Km away from Bokaro Thermal Power Station was chosen on the account of the presence of mining, industrial and other human activities in close vicinity which contribute heavily to the atmospheric load of pollutants. Forty five events of rainwater samples were collected from the site during February to May, June to September and October to December considering the pre-monsoon, monsoon and post-monsoon seasons, respectively, in the year 2012. The

rainwater sampling location is shown in Figure 1. Samples were collected using polythene funnel of 20 cm diameter, fitted onto two-liter capacity polythene bottles. The collection gadget was placed about 15 m above the ground level. The bottles as well as funnel were washed daily with distilled water during morning and evening to avoid dry deposition. Collected samples

were then stored in 500 ml polythene bottles, which were cleaned by double distilled water. Suspended sediments were separated from the water samples in the laboratory by using 0.45 μm Millipore membrane filters. Filtered samples were kept in pre-washed high-density polyethylene bottles and were stored in refrigerator at about 4°C.

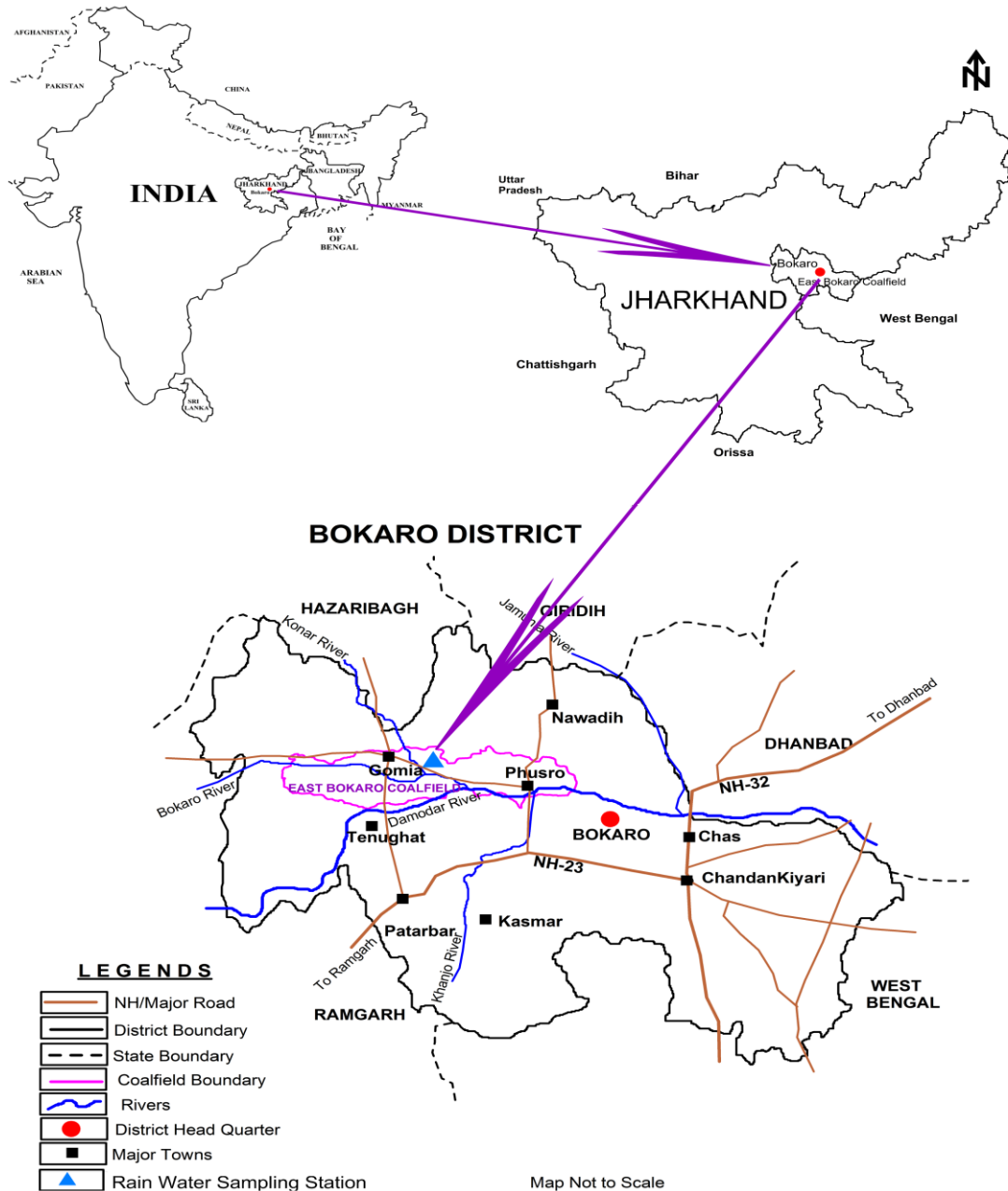


Fig. 1. Sampling location map of study area

Chemical analysis of rainwater

Analysis of rainwater samples was done as per Standard Methods (APHA, 1995) for water quality parameters. The pH and electrical conductivity were measured as immediately as possible. The pH was measured with a digital pH meter using reference and glass electrodes standardized at pH 4.0, 7.0 and 10.0. Conductivity was measured with a digital conductivity meter calibrated against a reference (0.5 M) KCl solution of analytical grade. Samples were kept in a refrigerator at 4°C until the completion of all the analyses. Bicarbonate was estimated using titrimetric method. Major anions (F⁻, Cl⁻, NO₃⁻ and SO₄²⁻) and major cations (Na⁺, NH₄⁺, K⁺, Ca²⁺ and Mg²⁺) were estimated by Ion Chromatograph DIONEX (DX-120) using anion (AS12A/AG12) and cation (CS12A/CG12) columns coupled to a self-regenerating suppressor (ASRS) and (CSRS) in recycle mode respectively.

Quality control

For assessing the accuracy of results, the

rainwater quality data were plotted on an anion cation balance control chart depicted in Figure 2. The principle of electrical neutrality requires that the equivalent weight of positively charged ions (cations) equal that of the negatively charged ions (anions). Because major ions usually represent most of the dissolved ions in rainwater, equivalent amounts of major cations and anions are typically found. In an accurate analysis, the sum of the milliequivalents of major cations and anions should be nearly equal. The anion-cation balance method presented here to determine the reliability of major ion analyses of rainwater assumes that major ions comprise most of the total dissolved solids in a rainwater sample, and requires that all major ion concentrations be measured. % charge difference were found < 10% for rainwater. The percentage charge difference is calculated with the following formula:

$$\% \text{ difference} = 100 \cdot \left(\frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \right)$$

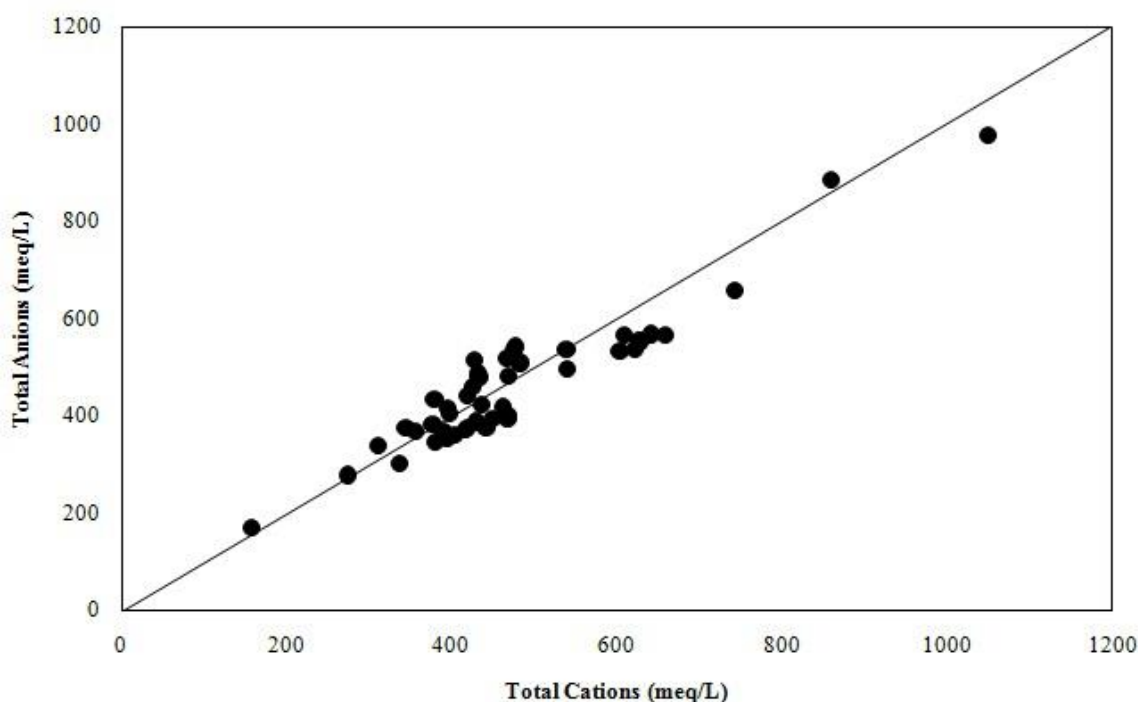


Fig. 2. Anion-cation control plot

RESULTS AND DISCUSSION

Normal annual rainfall in the study area
 The normal annual rainfall (1976–2012) for the study area is collected from Indian Meteorological Department. The annual normal rainfall for the study area is 1366 mm. There is a marked variation in the annual rainfall from year to year. In the thirty-five-year period from 1976- 2012 (with two gaps: 1978 & 1993), the highest

annual rainfall occurred in the year 2001, when it amounted to 2543.8 mm. The annual rainfall variation of the last 35 years of the study area is shown in Figure 3. The monthly variation in rainfall in the study area for the year 2012 is depicted in Figure 4. The bulk of the rainfall occurred during June to September (monsoon period) as anticipated.

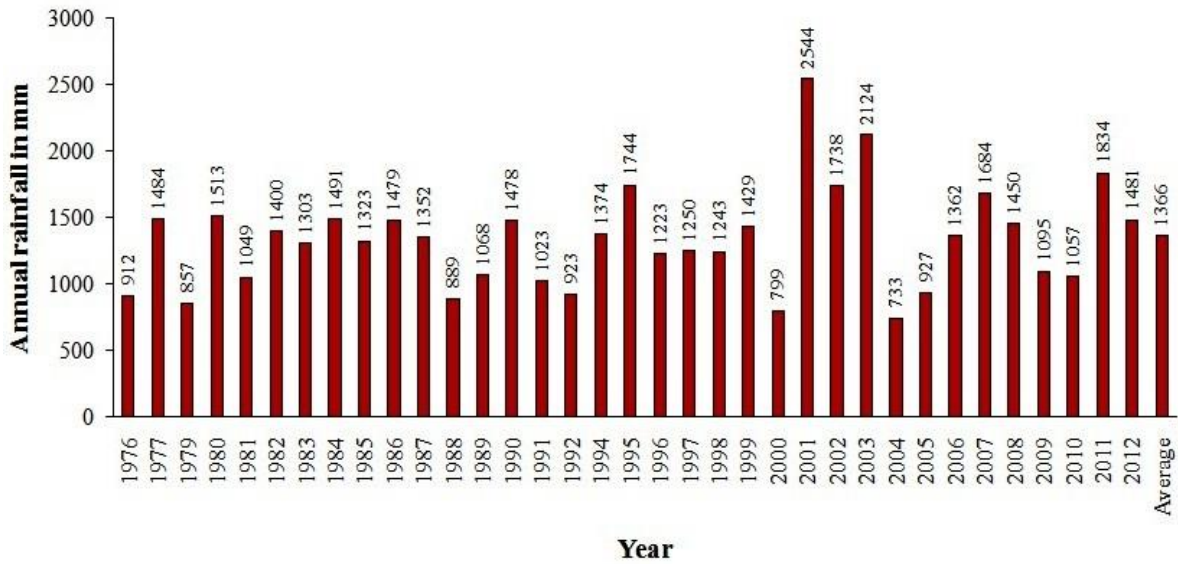


Fig. 3. Normal annual rainfall in mm of the last 35 years

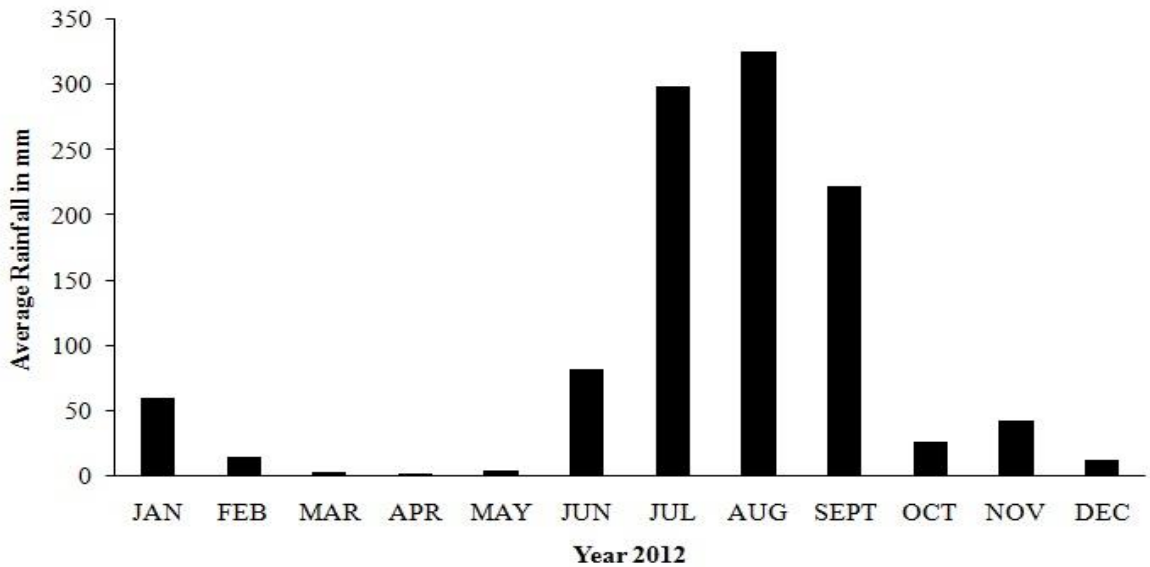


Fig. 4. Average monthly rainfall of the year 2012

Major ionic compositions of rainwater

Analytical results of physico-chemical parameters in rainwater of East Bokaro coalfield area are shown in Table 1. The major ionic composition of rain events contains diverse chemical constituents depending on the amount of rainfall, direction of rain front and period between the rainfall events (Granat, 1972). The average pH value in rainwater was 6.1 and

varied from 5.1 to 6.9, indicating that rainwater samples were alkaline in nature as compared to the reference level of 5.6 (Charlson and Rodhe, 1982). This could be due to the influence of soil dust particles, which are suspended in atmosphere in coarse mode. The frequency distribution of pH showed that the maximum frequency is in the range of 6.1– 6.5 during the study period as depicted in Figure 5.

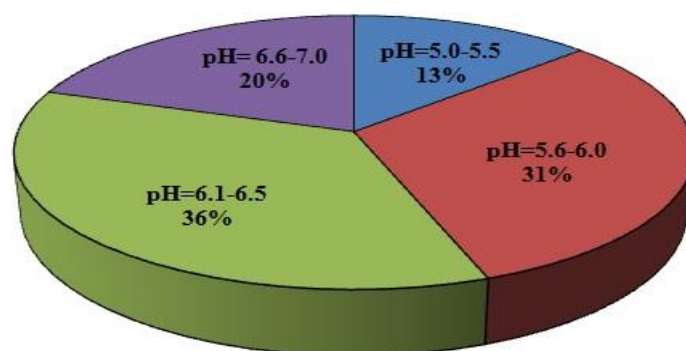


Fig. 5. Frequency distribution of pH of rainwater of the study area

The Electrical Conductivity of collected rainwater sample varied between 17.1 $\mu\text{S}/\text{cm}$ to 105.2 $\mu\text{S}/\text{cm}$ with a mean of 59 $\mu\text{S}/\text{cm}$. EC of rainwater is mainly contributed by water-soluble ions, the value being related to the total sum of anions and cations in the rainwater. Low precipitation conductivity is an indicator of good atmospheric environmental quality. The Total dissolved solids (TDS) varied from 11 mg/L to 72.1 mg/L with an average of 32.7 mg/L.

The F^- in rainwater may be derived from the weathering of soil and phosphates fertilizers used in agricultural field and unburnt carbon in atmosphere released from thermal power plants. The F^- concentration in rainwater samples was found between 8.4 $\mu\text{eq}/\text{L}$ and 35.3 $\mu\text{eq}/\text{L}$ and average concentration value was 14 $\mu\text{eq}/\text{L}$. The Cl^- content varied between 6.5 $\mu\text{eq}/\text{L}$ to 266.9 $\mu\text{eq}/\text{L}$ in the rainwater samples. The NO_3^- concentration varied

from 10.2 $\mu\text{eq}/\text{L}$ to 180 $\mu\text{eq}/\text{L}$ during the study period. The sources of NO_3^- in rainwater include application of fertilizers, burning of coal, industrial emissions and mining activities. The SO_4^{2-} concentration ranged between 36.9 $\mu\text{eq}/\text{L}$ to 490.5 $\mu\text{eq}/\text{L}$ in the rainwater samples. The HCO_3^- concentration in the rainwater varied from 44.6 $\mu\text{eq}/\text{L}$ to 406.5 $\mu\text{eq}/\text{L}$. The source of HCO_3^- may be the exchange of atmospheric CO_2 with water. The carbon-dioxide entering the system changes to HCO_3^- .

The Na^+ concentration in the water samples was found between 22.6 $\mu\text{eq}/\text{L}$ to 167.8 $\mu\text{eq}/\text{L}$. NH_4^+ varied between 6.1 $\mu\text{eq}/\text{L}$ to 213.9 $\mu\text{eq}/\text{L}$ while the range of K^+ in the water samples was 2.8 $\mu\text{eq}/\text{L}$ to 39.4 $\mu\text{eq}/\text{L}$. The Ca^{2+} concentration ranged from 59.4 $\mu\text{eq}/\text{L}$ to 511.5 $\mu\text{eq}/\text{L}$ in the rainwater samples. The total hardness of CaCO_3 ranged from 4.8 $\mu\text{eq}/\text{L}$ to 35.6 $\mu\text{eq}/\text{L}$.

Table 1. Major ionic compositions in rain water of East Bokaro Coalfield (N=45 Samples)

S No.	Rainfall Events	pH	EC	TDS	TH	F	Cl	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
1	16.02.2012	5.9	61	31	13.3	14.2	165.5	137.7	116.6	48.7	30.0	114.8	120.9	107.0	22.2
2	14.03.2012	6.2	60	32	11.2	8.4	51.9	151.6	170.7	78.9	107.2	142.7	80.6	75.7	10.5
3	04.04.2012	5.7	48	26	7.7	16.8	107.12	79.7	53.5	122.6	125.3	92.8	62.8	38.5	25.8
4	25.04.2012	5.2	40	30	11.6	5.2	183.4	62.3	93.7	94.2	188.9	144.7	86.4	52.2	9.4
5	03.05.2012	5.3	46	25	10.9	9.4	78.4	44.6	99.9	111.9	81.8	130.2	88.5	49.7	24.6
6	09.05.2012	6.1	56	30	12.4	9.4	54.2	169.7	139.9	56.9	53.3	176.6	68.3	83.0	5.6
7	26.05.2012	6.3	58	30	16.5	14.7	45.7	150.0	156.6	52.3	48.3	244.0	85.6	39.6	23.8
8	07.05.2012	5.4	62	32	8.1	9.4	20.6	204.9	136.8	77.4	148.3	91.8	70.7	79.6	2.8
9	16.06.2012	5.7	59	35	10.3	8.4	6.5	255.7	71.2	125.8	57.6	131.7	74.9	123.9	5.9
10	18.06.2012	6.8	52	30	9.2	8.9	244.6	209.8	135.3	18.7	6.1	91.3	92.1	167.8	13.2
11	20.06.2012	5.2	38	20	7.0	8.4	31.8	145.9	74.3	13.5	49.4	87.3	53.5	75.2	11.1
12	22.06.2012	6.0	47	28	14.3	20.0	27.9	97.9	143.7	107.3	45.0	183.1	102.0	63.0	9.8
13	28.06.2012	5.7	56	29	12.3	8.9	10.2	143.3	246.5	10.2	48.9	161.2	84.7	58.7	19.9
14	05.07.2012	5.8	59	35	19.7	23.6	30.2	149.5	179.1	92.9	21.7	160.2	234.5	90.0	27.4
15	08.07.2012	6.3	54	28	11.6	10.0	28.4	172.1	164.5	28.7	28.3	73.4	161.2	77.8	19.7
16	09.07.2012	6.4	50	29	14.4	8.9	47.6	95.1	103.7	139.5	30.7	175.1	118.5	80.0	10.1
17	10.07.2012	6.7	71	41	14.3	8.9	206.2	208.5	120.8	108.7	103.3	143.2	145.6	127.0	13.6
18	11.07.2012	6.7	75	41	14.6	9.5	66.8	190.2	81.2	94.0	142.8	133.7	157.9	118.7	13.3
19	15.07.2012	5.9	64	35	13.2	9.4	161.6	147.2	153.9	67.6	101.7	150.7	107.8	82.2	9.5
20	17.07.2012	6.1	72	39	14.3	14.7	44.5	153.3	156.2	57.9	140.6	140.7	140.7	90.4	18.6
21	19.07.2012	6.3	75	40	14.9	25.2	168.4	210.8	98.3	106.0	65.6	153.7	144.8	122.6	11.0
22	20.07.2012	6.2	74	43	15.1	8.4	185.3	179.7	176.3	108.1	171.1	118.3	183.4	85.2	6.9
23	22.07.2012	5.8	69	40	13.7	8.9	42.6	193.4	123.9	53.1	169.4	122.3	152.2	63.5	28.6
24	24.07.2012	6.2	57	30	11.3	8.4	134.8	155.7	101.4	31.3	151.7	113.3	112.7	86.5	21.5
25	25.07.2012	5.8	54	27	11.3	20.0	109.1	167.2	36.9	45.8	103.9	80.8	143.1	95.5	10.0
26	26.07.2012	5.1	18	11	4.8	8.9	32.4	59.7	43.7	13.4	37.2	63.4	32.6	29.1	7.2
27	28.07.2012	6.2	37	21	10.1	23.6	103.5	93.1	47.9	42.4	45.6	59.4	142.3	81.3	9.0
28	30.07.2012	5.9	48	24	10.1	13.2	82.6	107.2	124.7	29.0	70.0	72.4	130.0	74.8	19.7
29	01.08.2012	6.4	58	33	12.4	8.9	108.3	146.4	174.9	28.4	151.1	146.2	105.3	81.7	32.1
30	05.08.2012	6.8	105	72	35.7	31.0	87.4	406.5	490.5	33.2	159.4	511.5	200.7	80.9	22.8
31	06.08.2012	5.6	98	61	22.6	9.4	210.0	331.1	360.2	48.1	213.9	204.6	260.8	165.2	39.4
32	13.08.2012	6.9	70	36	11.0	20.5	209.9	177.9	122.8	57.6	181.7	78.3	139.8	128.7	6.4
33	16.08.2012	5.7	58	32	11.9	9.4	55.5	154.9	132.6	80.5	131.7	82.3	155.5	86.2	22.9
34	17.08.2012	6.8	61	31	10.2	14.7	57.8	143.6	152.4	67.9	105.0	86.8	117.9	92.2	18.9
35	21.08.2012	6.6	53	30	10.4	9.4	105.2	110.7	121.6	94.5	61.7	104.3	104.5	78.7	25.1
36	27.08.2012	5.9	55	31	20.7	8.4	92.5	140.0	101.8	85.0	52.8	267.4	146.4	39.6	8.2
37	03.09.2012	6.4	73	40	10.2	20.5	178.2	157.4	177.0	95.2	160.6	93.8	113.5	109.6	25.0
38	05.09.2012	6.2	59	29	11.2	8.4	117.3	98.0	141.2	60.3	165.0	98.3	125.9	64.3	6.1
39	06.09.2012	6.4	50	25	8.8	20.0	86.0	63.4	162.4	62.4	105.6	61.9	114.3	58.3	14.6
40	13.09.2012	5.8	57	31	9.3	8.9	83.7	147.0	149.9	79.0	152.8	70.4	110.2	45.5	7.7
41	14.09.2012	6.3	34	22	10.9	28.9	29.6	52.5	172.8	52.7	50.9	152.2	65.1	22.6	8.9
42	19.09.2012	5.3	49	27	9.6	10.0	48.8	80.3	141.6	96.3	62.8	96.3	96.2	112.6	13.8
43	05.11.2012	6.7	67	35	14.9	19.4	88.8	168.0	45.6	154.8	175.0	148.2	148.9	50.4	18.6
44	06.11.2012	6.3	97	49	18.1	16.8	33.1	164.7	178.4	180.0	157.2	178.1	185.9	113.5	21.2
45	11.12.2012	6.8	48	27	9.2	11.0	64.3	132.8	118.7	62.9	54.9	97.3	94.6	116.1	4.3
	Minimum	5.1	18	11	4.80	5.3	6.5	44.5	36.8	10.1	6.1	59.3	32.5	22.6	2.8
	Maximum	6.9	105	72	35.6	31.0	244.5	406.5	490.5	179.9	213.8	511.5	260.8	167.8	39.4
	Average	6.1	59	33	12.7	13.3	91.7	151.3	139.9	72.7	100.3	134.0	121.4	83.6	15.7
	Standard Deviation	0.48	16.08	10.10	4.9	6.32	62.5	67.4	77.3	38.6	55.7	74.1	45.9	32.5	8.5

Note: *All units in µeq/L, except pH, EC. The unit of EC (µS.cm⁻¹)

Comparison with other studies

Table 2 compared the chemical compositions in rainwater over a coal mining environment to some other selected

Indian sites of mining and industrial areas. It can be seen from the table that the concentrations of the major ionic compositions are in accordance to other

studies except NO_3^- and NH_4^+ (Rastogi and Sarin, 2006). The higher ionic compositions at present study sites may be attributed to anthropogenic emission from open cast mining activities, thermal power plants, coal washery besides coal burning and mine fires (Singh and Mondal, 2008).

Percentage contribution of ionic species

The proportion of anions in the rainwater samples are shown in Figure 6. Among the major anions; HCO_3^- was dominant as it

constituted 32% of the total anions on an average. SO_4^{2-} is the second dominant anion, representing on an average 30% of the total anions. The Cl^- and NO_3^- were less dominant ions and contributed 20% and 15% to the total anions, respectively. F^- was the least dominant anion and comprised of 3% of the total anions. The order of anions abundance in the rainwater was found to be as follows $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^- > \text{F}^-$.

gTable 2. Major ion chemistry of rain water over East Bokaro Coalfield and comparison with some other selected mining/ industrial sites of India (Concentrations are in $\mu\text{eq/L}$, except pH)

Site	Site Descriptions	pH	F^-	Cl^-	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	References
East Bokaro Coalfield	Mining/Industrial	6.1	13.3	91.7	72.7	139.9	134.0	121.4	83.6	15.7	100.3	Present Study
Dhanbad & Bokaro	Mining/Industrial	5.7	18.4	29.1	5.4	74.0	99.9	23.6	23.3	11.1	28.0	Singh & Mondal. 2008
Dyalbagh (Agra)	Urban/Industrial	7.0	17.6	31.8	22.8	36.4	56.1	45.6	18.4	7.6	40.1	Kumar et al. 2002
Kalyan	Urban/Industrial	5.4	-	134.0	66.0	110.0	130.0	48.0	147.0	6.0	14.0	Naik et al. 2002
Colaba	Urban/Industrial	6.4	-	171.0	34.0	52.0	155.0	59.0	179.0	6.0	12.0	Naik et al. 2002
Goa	Mining/Coastal	6.3	-	113.4	5.5	27.4	41.5	24.5	97.2	2.5	5.5	Parashar et al. 2001
Bangalore	Urban/Industrial	4.8	-	59.2	26.5	88.8	89.6	12.9	54.9	15.0	28.8	Shivashankara et al. 1999
Korba	Mining/sub-urban	4.8	12.2	31.8	25.1	213.0	182.9	42.8	20.7	3.7	15.3	Chandrawanshi et al. 1997
Chembur	Industrial/Urban	4.8	-	140.1	-	421.0	175.0	57.0	96.0	28.0	117.0	Khemani et al. 1989
Kalyan	Urban/Industrial	5.7	6.0	112.0	31.0	108.0	93.0	39.0	103.0	26.0	21.0	Khemani et al. 1989

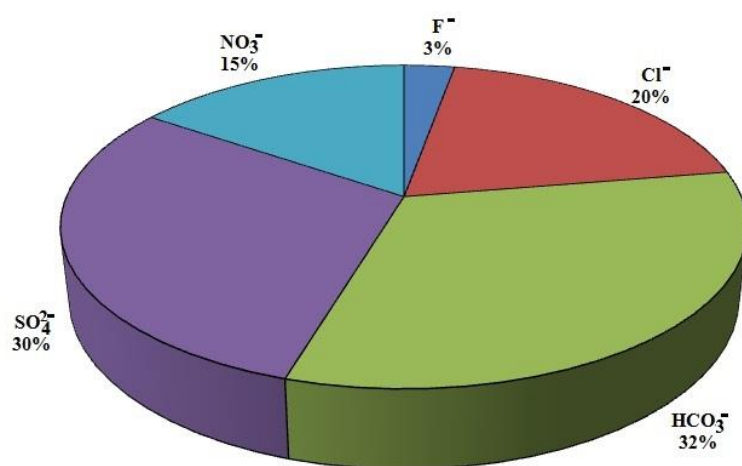


Fig. 6. Percentage contribution of major anions in rainwater at East Bokaro coalfield

In the major cationic chemistry, Ca^{2+} was the dominant ion representing on an average 29% of total cations (Fig. 7). Mg^{2+} , NH_4^+ and Na^+ ions were of secondary importance, representing on average 27%, 22% and 18% of total cations, respectively. K^+ was the least dominant cation representing only 4% of the total cations. The order of cation abundance was $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$.

Marine contribution

The ratio of Cl^-/Na^+ in the rainwater sample was found to be ranged between

0.05 and 3.51, which is almost equal to that of sea water. The average ratio of $\text{HCO}_3^-/\text{Na}^+$ (1.93), $\text{SO}_4^{2-}/\text{Na}^+$ (1.92), $\text{Ca}^{2+}/\text{Na}^+$ (1.95), $\text{Mg}^{2+}/\text{Na}^+$ (1.60), K^+/Na^+ (0.22) were found to be higher than that of sea water as shown in Table 3. The excess of Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} in rainwater is attributed to non marine source such as coal mining dust and other anthropogenic sources. Compound containing Ca^{2+} , Mg^{2+} and K^+ are added to the atmosphere by soil erosion and open cast mining, in the form of their carbonate salt (Ali et al., 2004).

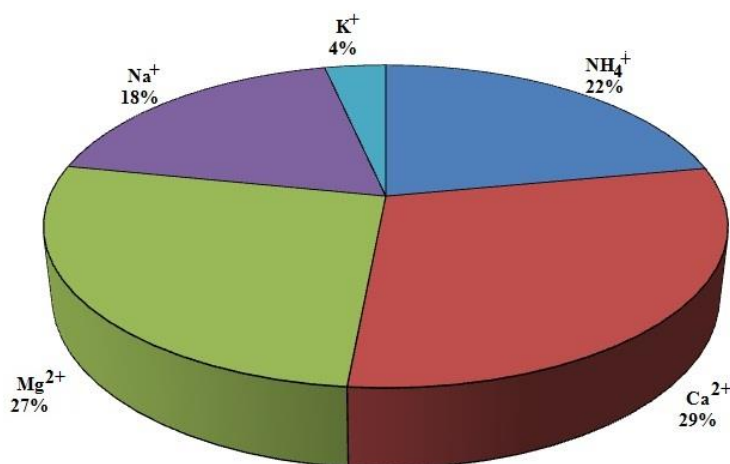


Fig. 7. Percentage contribution of major cations in rainwater at East Bokaro coalfield.

Table 3. Comparison of sea water ratios with rainwater ratios with respect to Na^+ and Enrichment factors

	Cl^-/Na^+	$\text{HCO}_3^-/\text{Na}^+$	$\text{SO}_4^{2-}/\text{Na}^+$	$\text{Ca}^{2+}/\text{Na}^+$	$\text{Mg}^{2+}/\text{Na}^+$	K^+/Na^+
Sea water Ratio	1.60	0.007	0.15	0.064	0.29	0.025
Rainwater Ratio	1.30	1.93	1.92	1.95	1.60	0.22
Rainwater Range	0.05-3.51	0.71-5.03	0.39-7.64	0.54-6.76	0.55-3.70	0.04-0.67
Enrichment Factor (EF)	0.72	142.47	7.47	51.13	1.24	6.01

Enrichment factors (EF) are normally applied to identify the origin of an element in precipitation (Zhang et al., 2006). This calculation is based on the elemental ratio found between ions collected in the rainwater, as compared to a similar ratio for a reference material. Commonly, Na^+ is taken as the best reference element and seawater as the reference source since it is assumed to be of purely marine origin. The

EFs were calculated for Cl^- , HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and K^+ and by using Equation (1).

$$\text{EF} = \frac{[\text{X} / \text{Na}^+]_{\text{rainwater}}}{[\text{X} / \text{Na}^+]_{\text{seawater}}} \tag{1}$$

where X is the concentration of the ion of interest. All the ionic concentrations were taken in $\mu\text{eq/L}$. The EFs were found to be

high for HCO_3^- , Ca^{2+} , SO_4^{2-} and K^+ indicating other than sea sources; i.e., anthropogenic contribution. Higher enrichment of Na^+ and Cl^- may be due to marine contribution.

Acidic and neutralization potentials

The difference between acidic potential (AP) and alkaline or neutralization potential (NP) is one of the useful indicators of chemical nature of the rainwater. Acid potential is the sum of NO_3^- and non sea salt SO_4^{2-} and neutralization potential is the sum of NH_4^+ , Ca^{2+} , Mg^{2+} and K^+ . The variation in AP/NP ratio is less than one indicating the neutralization potential which dominates the acidic potential. This ratio varied from 0.049 to 0.357. The pH has shown an inverse relationship with AP/NP. This result confirmed that the major neutralization occurred due to the major contribution of Ca^+ and NH_4^+ , which is contributed by soil dust in the atmosphere. The elevated pH values might be due to interference by dust particles leading to the neutralization of acidity of rainwater (Tiwari et al., 2015). Indian atmosphere

has a high dust load almost throughout the year, which acts as acid neutralizer and contributes significant fraction of alkaline salts to the rainwater.

Identification of chemical sources

To determine the sources of different anions and cations in the rainwater and their potential linkages, the major ionic component relationships were calculated and depicted in Table 4. A number of significant correlations were obtained in the study like pH with EC TDS and Na; EC and TDS with, TH, Cl^- , HCO_3^- , SO_4^{2-} , NH_4^+ , Ca^{2+} , Mg^{2+} , Na^+ and K^+ ; TH with F^- , HCO_3^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} and K^+ ; Cl^- with NH_4^+ and Mg^{2+} ; HCO_3^- with SO_4^{2-} , Ca^{2+} , Mg^{2+} and Na^+ ; SO_4^{2-} with Ca^{2+} , Mg^{2+} and K^+ ; NH_4^+ with Mg^{2+} ; Ca^{2+} with Mg^{2+} ; Mg^{2+} with Na^+ and K^+ . Overall the divergent results indicated that the significant correlation was not always correlated with the common sources. In other words, the single correlation analysis is not enough for the metal source identification; it should be conducted together with other analysis tools.

Table 4. Pearson correlation matrix between major ions in the rainwater of East Bokaro coalfield

	pH	EC	TDS	TH	F ⁻	Cl ⁻	HCO ₃ ⁻	SO ₄ ²⁻	NO ₃ ²⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺
pH	1.000	0.376*	0.332*	0.260	0.134	0.213	0.280	0.188	0.087	0.069	0.186	0.268	0.320*	0.008
EC		1.000	0.950**	0.709**	0.066	0.488**	0.788**	0.616**	0.270	0.577**	0.520**	0.696**	0.510**	0.371*
TDS			1.000	0.822**	0.179	0.420**	0.834**	0.734**	0.210	0.556**	0.666**	0.712**	0.466**	0.378*
TH				1.000	0.304*	0.186	0.664**	0.722**	0.115	0.228	0.901**	0.704**	0.145	0.348*
F⁻					1.000	0.125	-0.011	0.166	0.107	0.115	0.293	0.171	-0.137	0.002
Cl⁻						1.000	0.125	-0.049	0.212	0.574**	0.001	0.378*	0.238	0.169
HCO₃⁻							1.000	0.611**	-0.086	0.319*	0.562**	0.538**	0.554**	0.218
SO₄²⁻								1.000	-0.218	0.264	0.685**	0.469**	0.181	0.395**
NO₃²⁻									1.000	0.200	0.060	0.165	0.037	-0.057
NH₄⁺										1.000	0.094	0.362*	.084	0.219
Ca²⁺											1.000	0.331*	-0.053	0.204
Mg²⁺												1.000	0.413**	0.436**
Na⁺													1.000	0.104
K⁺														1.000

*Correlation significant at the 0.01 level (two tailed)

**Correlation significant at the 0.05 level (two tailed)

Principal component analysis (PCA)

Source identification of different chemical contaminants present in rainwater samples at East Bokaro coalfield was further carried out through Varimax rotated factor analyses (SPSS-20), which are shown in Table 5. The principal component analysis (PCA) has been used for extracting factors governing the major ionic compositions of rainwater and to identify the possible

source of the major ions in rainwater (Seto et al., 2000; Tang et al. 2005; Singh and Mondal, 2008). Factor loadings show that the data synthesized into four factors with Eigen values cut off at greater than unity and explain about 71.8% of the total variance. A more detailed description regarding the sources of different chemical species associated with different factors is given below.

Table 5. Principal component loadings (rotated varimax normalized) for the ionic composition in rain water of East Bokaro Coalfield

Components	Rotation Sums of Squared Factor Loadings			
	PCA-I	PCA-II	PCA-III	PCA-IV
F ⁻	0.657	-0.069	-0.214	0.279
Cl ⁻	-0.147	0.743	0.184	0.031
HCO ₃ ⁻	0.618	0.556	0.234	-0.160
SO ₄ ²⁻	0.735	0.119	0.412	-0.323
NO ₃ ²⁻	0.007	-0.009	0.065	0.921
NH ₄ ⁺	-0.028	0.226	0.751	0.282
Ca ²⁺	0.841	-0.084	0.179	-0.037
Mg ²⁺	0.490	0.439	0.452	0.222
Na ⁺	0.094	0.910	-0.043	-0.029
K ⁺	0.208	-0.016	0.720	-0.163
Eigen values	2.374	1.958	1.629	1.215
% of Variance	23.75	19.58	16.29	12.15
Cumulative %	23.75	43.33	59.62	71.77

PCA- I registered a variance of 23.74% with high loadings for F⁻, HCO₃⁻, SO₄²⁻, Ca²⁺ and Mg²⁺ indicating natural sources, soil and atmospheric dust, resulting from the chemical transformation of SO₂, NO₃⁻ and Cl⁻ on the surface of the alkaline aerosols. PCA-II contributed Cl⁻ and Na⁺ at 19.58% of variance. This indicates the sources of Na⁺ and Cl⁻ may occur in the form of sea salt. PCA-III with 16.29% of variance comprises NH₄⁺ and K⁺, indicating the anthropogenic source and related to the influence of the coal and biomass burning and thermal power plants (Migliavacca et al. 2004; Singh and Mondal, 2008). PCA-IV explained 12.15% of variance of our result and was associated with NO₃⁻. This component seemed to have

arisen from other anthropogenic sources, like agricultural and vehicular pollution.

CONCLUSIONS

The present study of rainwater quality over a coal mining environment revealed that the chemical characteristics are greatly influenced by mining activities. The pH values in most of the samples were alkaline in reference to the value of 5.6. The order of anions abundance in the rainwater was found as follows HCO₃⁻> SO₄²⁻> Cl⁻> NO₃⁻> F⁻ while the cations followed the order of Ca²⁺> Mg²⁺>NH₄⁺>Na⁺> K⁺. The ratio of Cl⁻/Na⁺ in the rainwater sample was found to be between 0.05 and 3.51, which is almost equal to sea water. The comparison of the ratios of ions of rainwater and sea water revealed the excess

of Mg^{2+} , K^+ , Ca^{2+} and SO_4^{2-} in rainwater which was attributed to non marine source such as coal mining dust and other anthropogenic sources. The EFs also indicated anthropogenic contribution and were found to be high for HCO_3^- , Ca^{2+} , SO_4^{2-} and K^+ . Factor loadings show that the data synthesized into four factors with Eigen values >1 and explain about 71.8% of the total variance and the factors constituting geogenic and human induced sources. The variation in AP/NP ratio is less than one indicating the neutralization potential dominating the acidic potential. The study indicates that receiving rainwater in this region is not under threat of acidification under the present scenario; however, it strongly advocates the anthropogenic influence, in particular the mining activities, on the rainwater quality. The study suggests that there is need for regular monitoring of air quality in the study area as well as proper disposal of mine waste. Scrubbers should be installed at industrial/mining areas and waste disposal sites so as to reduce the quantity of gases released from these sources into the atmosphere. There is also the need to reduce the consumption of fossil fuels in the study area. The future scope of this study is to measure dry deposition rate. Dry deposition is the process by which atmospheric trace chemicals are transferred by air motions to the surface of the Earth in the absence of rain.

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