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An application of Water Quality Index (WQI) and multivariate statistics to evaluate the water quality around Maddhapara Granite Mining Industrial Area, Dinajpur, Bangladesh

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Abstract

Background: Pure water is an absolutely necessary component of the earth not only for life but also for sustainable socio-economic development of today's civilization. The aim of this study was to analysis the quality of water resources and to investigate the influences of mining activities on water quality around the Maddhapara Granite Mining area, Dinajpur, Bangladesh.

Result: 31 samples from surface and groundwater were collected from this selected area to assess their hydrochemistry, suitability, and their possible sources of contamination. Consequently, in the case of physico-chemical analysis, the 24 parameters such as P^H, Electrical Conductivity, TDS, TH, Ca^{2+}, Mg^{2+}, K^+, Cd^{2+}, Cr^{3+}, Cl^-, SO_4^{2-}, PO_4^{3-}, NH_4^+, NO_3^-, HCO_3^- etc. were analyzed in laboratory. Multivariate statistical methods were adopted for determining the water quality and their sources of contamination. The Gibbs ratio plot suggests that most of the samples fall in the rock dominance fields and some are in the precipitation dominance field. Cluster analysis confirms that three main groups of water samples where cluster I includes 70.97% of water samples, cluster II and cluster III includes rest 22.58 and 6.45% of the water samples respectively. Factor Analysis/Principal Component Analysis (FA/PCA) illustrates five factors extracted which explain 75.89% of the total variance.

Conclusion: The collective results of multivariate analysis and Water Quality Index implies that most of the areas around the mining area are dominated by the good to excellent quality water for different purposes. In addition, the results of this research will then be helpful to estimate the major sources of contamination in different areas within the framework of activities intending to improve the quality of water.

Keywords: Maddhapara Granite Mine, Hydrochemistry, Multivariate statistical methods, Water Quality Index, Contamination sources, Water quality for various uses

Background

Mining is one of the major anthropogenic activities which are liable for deteriorating the quality of water, soil as well as the environmental ecosystem not only in the surrounding area but also can far away with the help of river and stream flow. Anthropogenic activities can adversely affect water quality by introducing contaminants, such as metals and metalloids, and by enhancing natural processes, such as acid drainage generation (Gomshei and Allen 2000; Zhu and Anderson 2002; Edraki et al. 2005; Ribeiro et al. 2014). The availability of good quality water is vital for life, wellbeing, food and socio-economic development of mankind and it is generally obtained from two principal natural sources: surface water such as fresh water lakes, rivers, streams etc. and ground water such as borehole water and well water (McMurry and Fay 2004; Mendie 2005; Boateng et al. 2016). However, poor contaminated water can be threaten to health, more over to the subsistence

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of the biotic integrity and therefore hinders the ecosystem services and functions of aquatic ecosystems. On the other hand, water is necessary and an unavoidable element for domestic and industrial purposes because of its numerous physical and chemical both quantitative and qualitative characteristics. Maddhapara Granite Mining has been running since 2007 by adopting room and pillar sublevel stopping method in order to extract of hard rock commercially which are predominantly composed of diorite, quartz diorite and granite. However, rock storage as well as rock pilling is very ubiquitous features around the mine area. Surface waters are more vulnerable to pollution due to their easy accessibility for disposal of wastewaters (Singh et al. 2004; Bu et al. 2009; Hossain et al. 2010; Howladar 2013; Howladar et al. 2013, 2014). Prevention and control of the surface water pollution must rely on the reliable information of water quality and identification of pollutant sources (Simeonov et al. 2003; Shrestha and Kazama 2007; Bu et al. 2009; Howladar et al. 2017; Howladar 2017). Groundwater moves through pore-spaces within rocks and reacts with minerals that make up the rocks in the course of migration (Amadi et al. 2012; Boateng et al. 2016). Groundwater quality in any locality takes after the chemical composition of the aquifer through which it migrates in accordance with the hydrological cycle and flow direction (Offodile 1983; Amadi et al. 2010; Boateng et al. 2016). The aim of this study is to evaluate the hydrochemical characteristics, water quality, contamination as well as sources of contamination of ground and surface water around Maddhapara Granite Mining Industrial Area, Northwest Bangladesh.

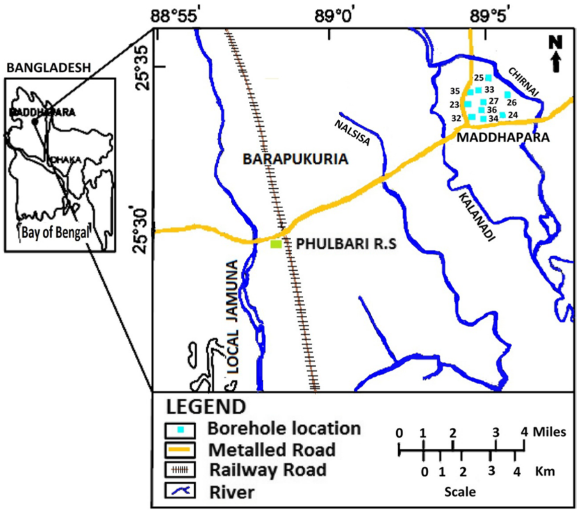

Fig. 1 Location map of Maddhapara Hardrock Mining Project (MHRMP) area (NAMNAM 2000)

Location and geographic environment of the study area

Location and climatic characteristics of study area

The Maddhapara Granite Mine area lies within Latitudes 25° 33′ 15″ N to 25° 34′ 13″ N and Longitude 89° 3′ 30″ E to 89° 4′ 53″ E (Fig. 1). Maddhapara is located in Parbottipur upazila of Dinajpur district of the northern part of Bangladesh. Maddhapara Granite Mine area is 330 km away from the capital city, Dhaka of Bangladesh. Bangladesh has a tropical monsoon climate characterized by variations in rainfall, high temperatures, and high humidity. The climate of the study area is described by considering hot season in summer, moderate season in monsoon and cool season in winter. The temperature and humidity records in the recent years are plotted in Fig. 2a, b, respectively.

Geology of study area

Bangladesh is divided into two main tectonic divisions namely (1) The Precambrian Indian Platform (Northwest part) and (2) The basin or geosyncline (south-east part) based on the basic structural or tectonic framework. A north-east to south-east aligned about 25 km wide zone separates the Precambrian Platform from the Basin part. Again, the Precambrian Indian platform is subdivided into (1) Rangpur Saddle, and (2) Bogra shelf; whereas the basin or geosyncline is subdivided into (1) Bengal for deep and (2) folded belt. Maddhapara hardrock mining area is located in the Rangpur Saddle. The distinguish features of this area are that it's sedimentary cover is very thin and basement lies at shallow depth. The Dome shaped Maddhapara Hard Rock Mining (MHRM) area is located in the Barind Tract of Pleistocene era, drained by Jamuna and Jamuneswari river in the west and east sides respectively. Two rivers named Kalanadi and Chirnai flow from west to south-east and north to south-east directions respectively and meet with Jamuneswari river separately. Due to the tectonic activity during the Permo-Carboniferous (about 300 million years ago), the subsurface features of the Maddhapara mine area is highly fractured and fault controlled. At shallow depth (128 m) a basement high is located at Maddhapara. This high is limited on the east by a Northwest-Southeast trending fault. The Basement rock of the Maddhapara is below the layers of alluvium soil (0–0.5 m), Madhupur Clay (0.5–6 m), Dupitila Formation (6–120 m), Tura Formation (120–141 m, Gondwana Group (160–259.6 m). Basement is of the Archean era and subdivided into the kaolinized granodiorite, the weathered granodiorite and the fresh granodiorite. Dykes of micro-granodiorite, fine grained silicified whitish granite and pegmatite is thinly inserted in the basement. According to the Geological survey of Bangladesh, the age of granodiorite in

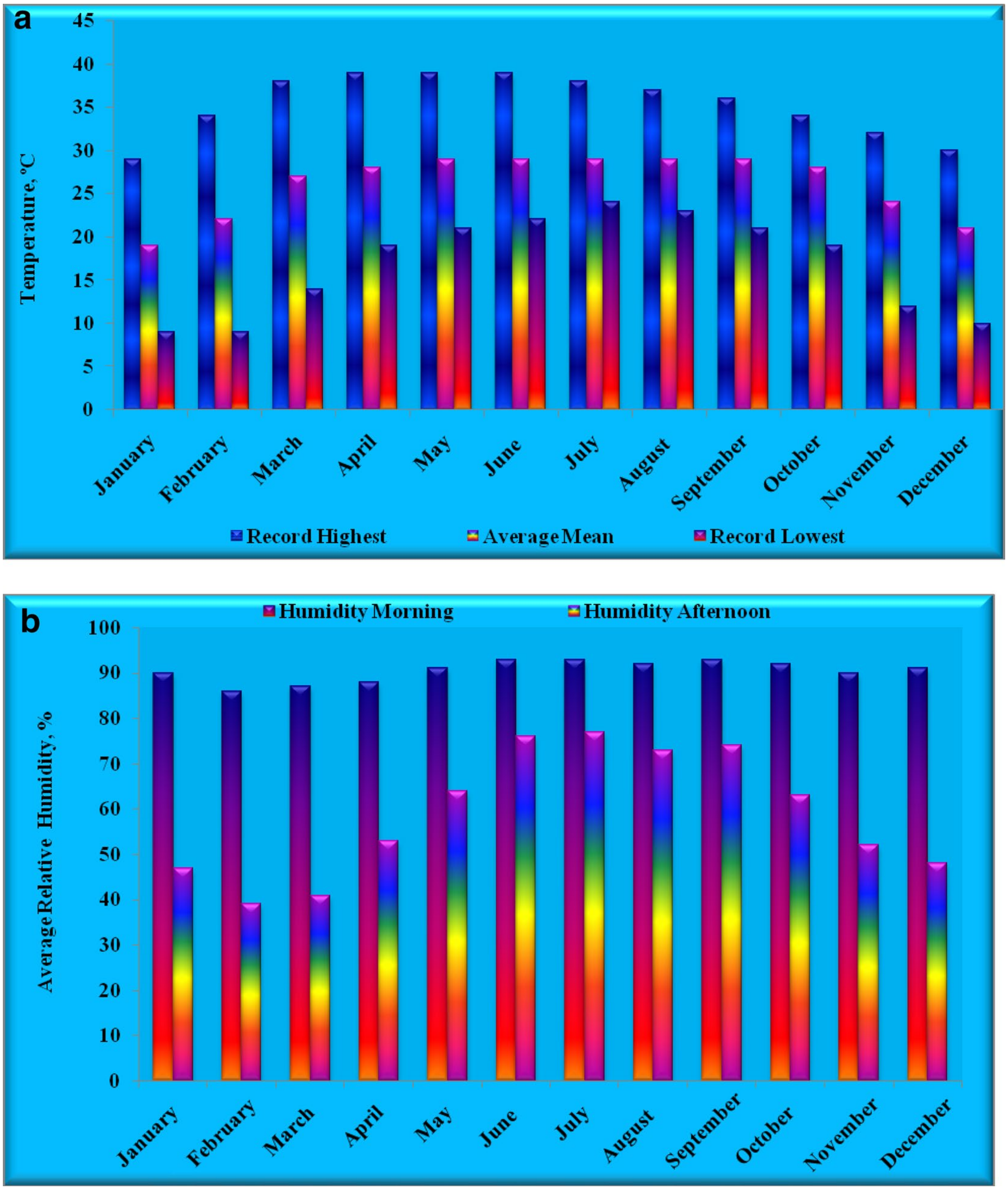

Fig. 2 **a** Column diagram of monthly recorded highest, lowest and average temperature. **b** Column diagram of monthly recorded average relative humidity % in morning and in afternoon

the hardrock deposit is the Archean Era. The Geological cross section across the MHRM boreholes is shown in Fig. 3.

Hydrology of study area

There are two aquifer systems (Fig. 4) in the Maddhapara Granite Mining area (i) Porous aquifer or Upper aquifer and (ii) Fissure aquifer or Lower aquifer. The Porous aquifer comprises Dupi Tila, Tura Sandstone and Gondwana formations (Fig. 4). The Dupitila formation consists of yellowish brown fine to medium grained sands and coarse grained pebbly sands in places. The Tura formation comprises a fine to medium sands and in places pebbles. Gondwana formation is composed of well-rounded fine to medium grained feldspathic sandstone and pebbles in places. Thus this all form an overburden aquifer. The fissure aquifer is composed of the Archean weathered green granodiorite and fresh rocks with numerous fractures,

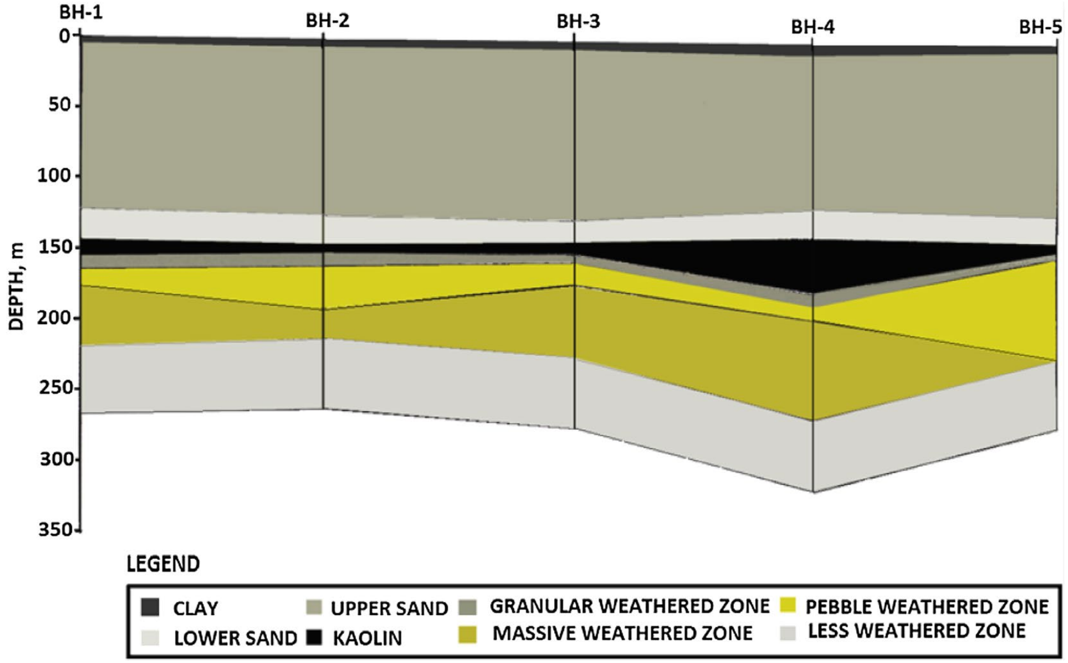

Fig. 3 Geological cross section across the MHRMP boreholes [Modified after Rahman (1987)]

joints, fissures. The white clay separates the two aquifers. The upper aquifer is about 125 m thick, which lies below ground level in most of the area. The flow of water in the confined basement aquifer takes place principally through interconnected fractures. The development of the mine is retarded due to flooding of underground mine area, which is drained out regularly for uninterrupted development of the mine. The Precambrian crystalline basement occurs at a depth of about 130 m below ground level (Bashar et al. 2008).

Methods

Field investigation and samples collection

All thirty-one surface and groundwater samples were collected from different spots of the study area. Plastic bottles with proper washed have been used for collecting the water samples.

Latitude and Longitude of the sample collecting spots were recorded with the help of GPS reading. The collected water samples were marked by MRS-1 to MRS-18 wherein MRS-2, MRS-3, MRS-5 and MRS-11 were collected from surface water and remaining were collected from underground water. Again, other water samples were noted by MDS-19 to MDS-31 wherein MDS-24, MDS-26 and MDS-30 were collected from surface water and rest were collected from underground water. The location of the samples collecting spots around the mine area are shown in Fig. 5.

Laboratory analysis

Different parameters of water samples were analyzed carefully in the Central Chemical Research Laboratory of Water Treatment Plant, Barapukuria Coal based Thermal Power Plant and Bangladesh Power Development Board (BPDB), Dinajpur. Demineralized water was used throughout the analysis wherever applicable. The electrical conductivity (EC), P^H, Total Dissolved solids (TDS) and temperature (T) of all the samples were measured by portable digital meter in the field. Sodium (Na^+) and potassium (K^+) were measured using flame photometer (Model No. PEP 7 and PEP 7/C). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were determined titrimetrically using standard EDTA solution. Chloride (Cl^-) was determined by ion selective electrode method (Cole-Parmer iodine electrode, model no. 27502-13). It was also cross checked by volumetric analysis of the water samples. Bicarbonate (HCO_3^-) concentrations of the water was determined by potentiometric titration method. Sulphate (SO_4^{2-}), orthophosphate (PO_4^{3-}), and dissolved silica (as SiO_2) analyses of the water samples were carried out using UV–visible spectrophotometer. Nitrate (NO_3^-) was measured by using ion selective electrode methods (Cole-Parmer Iodine Electrode, model no. 27502-19). High purity analytical reagents were used throughout the study, and chemical standards for each element when necessary were prepared separately. As^{3+} was test by using the Hach EZ Arsenic test kit (calt. no. 28228-00). However

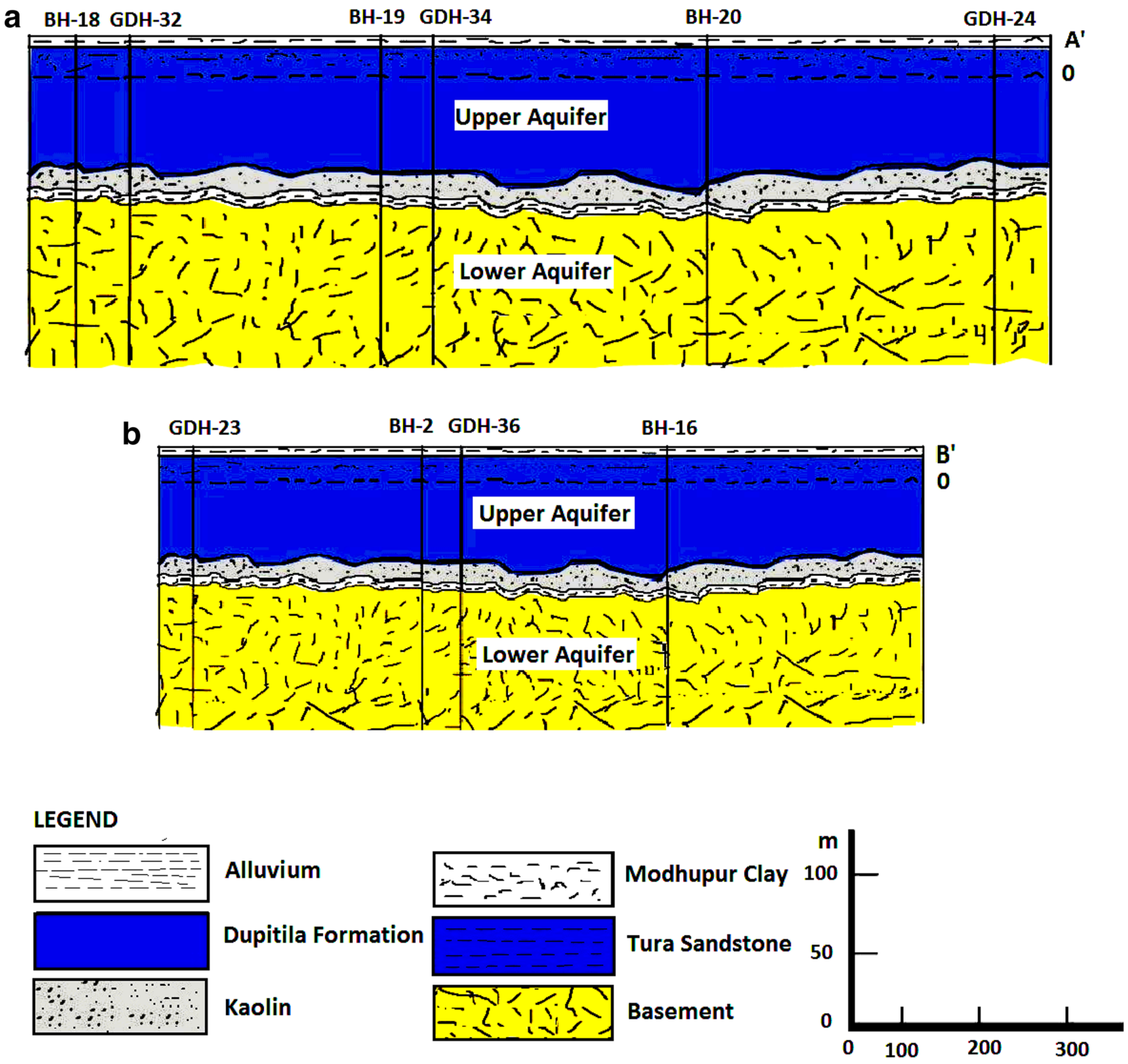

Fig. 4 Hydrogeological cross section of the Maddhapara Mine area [Modified after Bashar et al. (2008)]

the similar physical and analytical procedure was previously reported by many researcher such as Howladar et al. (2013, 2014); Howladar and Rahman (2016); Martinello et al. (2014); Ramos et al. (2015); Rodriguez-Iruretagiiena et al. (2015); Sanchís et al. (2013); Tezza et al. (2015) and so on.

Water Quality Index (WQI)

The Water Quality Index (WQI) analysis provides a comprehensive picture of the quality of surface and ground water for most domestic uses. WQI is defined as a rating that reflects the composite influence of different water quality parameters (Sahu and Sikdar 2008). It is an important parameter for assessing groundwater quality and its suitability for drinking purposes (Tiwari and Mishra 1985; Singh 1992; Subba 1997; Mishra and Patel 2001; Naik and Purohit 2001; Avvannavar and Shrihari 2008; Pawar et al. 2014; Boateng et al. 2016).

Water Quality Index (WQI) is a single value expression that numerically summarizes multiple water quality parameters. It is calculated from the point of view that a lower value of it signifies less deviation from the recommended values of parameters included and more good quality water for human consumption or vice versa. In order to calculate the WQI in this study, 12 physicochemical parameters have been considered. Relative weight (w_i) is assigned with respect to their perceived effects on primary health and relative importance in the overall water quality. The parameters which have major impacts on water quality (viz., TDS, Cl^-, SO_4^{2-}, NO_3^- are assigned to the highest weight of 5 and

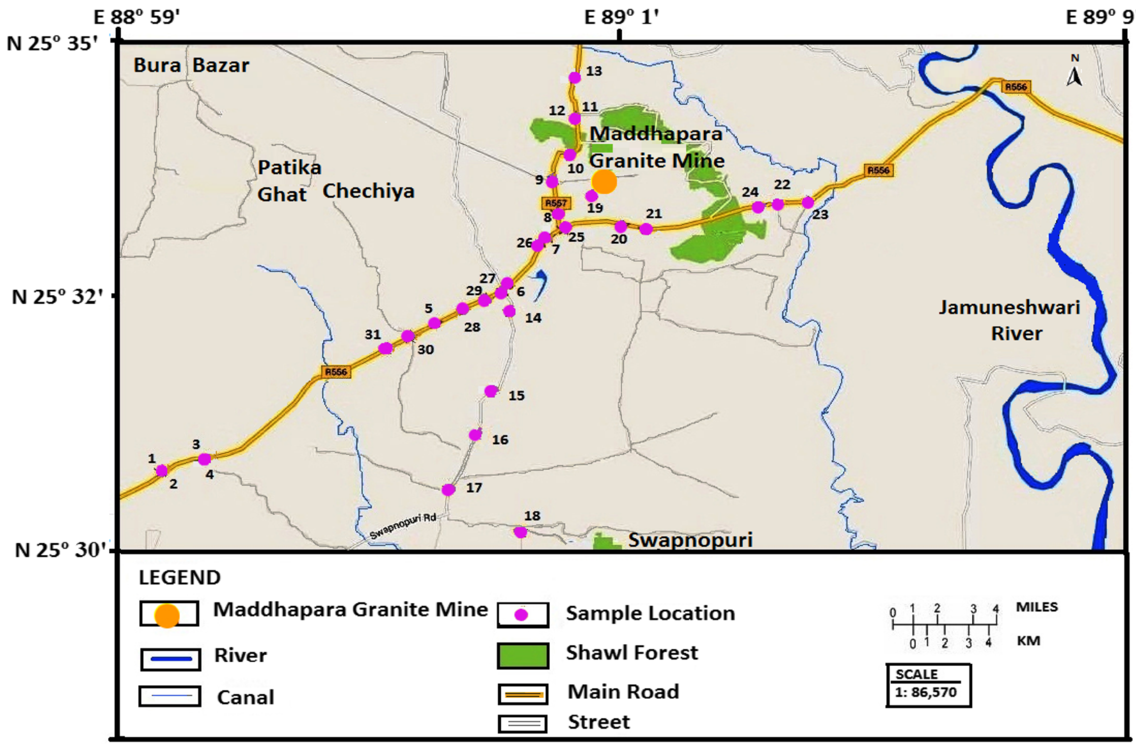

Fig. 5 Location map of the samples

a minimum of 1 is assigned to parameters which are considered of less impacts (viz., HCO_3^- and PO_4^{3-}) on the water quality. Other parameters such as P^H, EC, TH, Ca^{2+}, Mg^{2+} and K^+ are assigned a weight between 2 and 4 depending on their importance in the overall water quality.

The relative weight is then calculated by using the Eq. (1):

$$W_i = \frac{w_1}{\sum_{i=1}^{n} w_1} \tag{1}$$

where W_i is the relative weight of ith parameter, w_i is the weight of each parameter, and n is the number of parameters. The assigned weight, WHO standard value and calculated relative weight are summarized in Table 1. The quality rating scale for each parameter is calculated by using Eq. (2):

$$q_i = \frac{c_i}{s_i} \times 100 \tag{2}$$

where q_i is the quality rating, C_i is the concentration (mg/L) or value of each parameter and S_i is the World Health Organization standard of respective parameter.

For computing the WQI, sub-index (SI) is calculated for each parameter using Eq. (3) and the WQI is then calculated by Eq. (4).

Table 1 Relative weight of some physicochemical parameters and WHO water quality standards

Parameters	WHO standards (2011)	Weight (w_i)	Relative weight $W_i = \frac{w_1}{\sum_{i=1}^{n} w_1}$
EC	500	4	0.097560976
TDS	500	5	0.121951220
TH	100	3	0.073170732
Ca^{2+}	75	3	0.073170732
Mg^{2+}	50	3	0.073170732
K^+	10	2	0.048780488
Cl^-	250	5	0.121951220
HCO_3^-	500	1	0.024390244
SO_4^{2-}	250	5	0.121951220
NO_3^-	45	5	0.121951220
PO_4^{3-}	0.5	1	0.024390244
p^H	6.5–8.5	4	0.097560976
		$\sum w_i = 41$	$\sum W_i = 1.00$

$$SI_i = W_i \times q_i \tag{3}$$

where SI_i is the sub-index of the ith parameter.

$$WQI = \sum SI_i \tag{4}$$

Boateng et al. (2016) have classified the water quality into five categories as excellent, good, poor, very poor, and unsuitable for human consumption based on WQI values as shown in Table 2.

Multivariate statistical analysis

Multivariate statistical analysis is a useful tool for the assessment of the water quality where a lot of variables are responsible for influencing the water quality. The most common statistical analysis that are widely used to identify the dominating components and sources that explain the variations in the water quality and their impacts on water environments are hierarchical cluster analysis, factor analysis/principal component analysis (FA/PCA), correlation matrix analysis. Cluster analysis comprises of multivariate methods which are used to find true groups of data. In clustering, the objects are grouped such that similar objects fall into the same class (Oketola et al. 2013). The main aim of the cluster analysis is to join the homogeneous groups which are most similar to each other considering some of the certain properties. Hierarchical clustering joins the most similar observations and successively the next most similar observations (Oketola et al. 2013). Statistica 8.0 software was used for analyzing the cluster analysis as well as the principal component analysis. Principal component analysis is a powerful technique for pattern recognition that attempts to explain the variance of a large set of inter-correlated variables and transform them into a smaller set of independent (uncorrelated) variables (Bu et al. 2009) which can be computed as:

$$Z_{ij} = a_{i1}X_{1j} + a_{i2}X_{2j} + a_{i3}X_{3j} + \cdots + a_{im}X_{mj} \tag{5}$$

Table 2 Water quality classification for drinking purposes based on the WQI values (Boateng et al. 2016)

Range	Type of water
<50	Excellent
50–100	Good
100.1–200	Poor
200.1–300	Very poor
>300	Unsuitable

Factor analysis (FA) generally helps to reduce and simplify the outcome from the PCA. Hence the FA can be calculated as:

$$Zji = a_{f1}f_{1i} + a_{f2}f_{2i} + a_{f3}f_{3i} + \cdots + a_{fm}f_{mi} + e_{fi} \tag{6}$$

where z, a, i, x, m, j, e and fare component score, factor loading, sample numbers, measured value of variable, total number of variables, other source of variation and the factor score, respectively. However, correlation matrix analysis shows the relation between any two parameters, its strengths and the direction of relationship in which they vary.

Results and discussions

Physicochemical characteristics of water samples

The physicochemical parameter analysis is the preliminary study by which the nature, quality and types of water can be identified. The summary of the values, average, variations, median of physicochemical parameters such as P^H, Electrical Conductivity (EC), turbidity, total alkalinity (TA), total hardness (TH), total dissolved solids (TDS) and soluble silica are tabulated in Table 3.

The P^H value of the water samples ranged from 5.3 to 9.02 with an average value of 7.49. The permissible limit of the pH for drinking water is 6.5–8.5 (WHO 2011). The P^H levels of the most of the samples were found within the permissible limit for drinking purposes. The P^H values lower than the 6.5 are considered as too acidic and unsuitable for drinking purposes. The lowest value of P^H was recorded in surface water (MRS-5) which was open to the agricultural land near the mine area. Again, the P^H values of water samples greater than 8.5 are too alkaline and are not suitable for human consumption. The highest value was recorded in groundwater (MDS-31). The electrical conductivity (EC) is the ability of water to pass electric current through it which is related to the concentration of the ionized substances dissolved in water and an indication of the salinity of water. The EC value in water samples ranged between 41 and 587 μS/cm with

Table 3 Statistical analysis of physicochemical parameters in water around the study area

	Min.	Max.	Mean	Median	Std. deviation	Variance	WHO (2011)
P^H	5.3	9.02	7.49	7.46	0.71	0.51	6.5–8.5
EC	41	587	147.2	112.4	113.65	12,915.95	500
Turbidity	3	45	10.74	7.00	10.69	114.33	<5
TA	5	88	29	19	22.19	492.4	–
TH	2.5	87.5	22.74	15.5	20.44	417.81	100
TDS	24	382	103.9	84.3	74.05	5483.33	500
Soluble silica	11.9	53.8	28.82	32	9.9	98.08	–

an average value of 147.2 μS/cm. A lower EC value signifies less concentration of the dissolved ions and organic matters and vice versa. The lowest value of 41 μS/cm was recorded in surface water sample (MRS-5) and the highest value of 587 μS/cm was recorded in the groundwater samples (MRS-14). The recommended value of EC for drinking water purposes is 500 μS/cm. Turbidity is a measure of the water cloudiness or haziness of water caused by large numbers of individual particles that are generally invisible to the naked eye. The turbidity of water was recorded between 3 NTU and 45 NTU with an average value of 10.74 NTU. The WHO (2011) recommends the turbidity of water should not exceed five NTU. Total alkalinity (TA) is a measure of water's resistances to change in P^H. It is the amount of alkali in the form of bi-carbonates, carbonates and hydroxides present in the water. The TA was varied in the water samples from 5 to 88 mg/L (as $CaCO_3$) with an average of 29.64 mg/L (as $CaCO_3$). The suggested alkalinity in our drinking water is 20–200 mg/L. Water with low alkalinity can be corrosive and can irritate the eyes. Water with high alkalinity has a soda like taste, can dry out skin and can cause scaling on fixtures and throughout water distribution system. The hardness of water is due to the presence of the calcium and magnesium ions containing minerals that are naturally present in the water. Hard water is formed when water is got mixed with the limestone and chalk which are highly enriched with calcium and magnesium carbonates and bi-carbonates. The Total Hardness (TH) values in the water samples ranged from 2.5 to 87.5 mg/L with an average of 22.74 mg/L (as $CaCO_3$). The maximum permissible limit of TH for drinking water is 500 mg/L and the most desirable limit is 100 mg/L as per the WHO International standards (2011). Total dissolved solids (TDS) is a measure of the inorganic salts and small amounts of the organic matter present in solution in water. So, it is related to the conductivity of the water because of effect of dissolved ions though their relation is not constant. Total dissolved solids in water samples ranged from 24 to 382 mg/L with an average of 100.9 mg/L. According to WHO (1996), the presence of dissolved solids in water may affect its taste. Moreover, the palatability of drinking water may be classified as excellent (<300 mg/L), good (300–600 mg/L), fair (600–900 mg/L), poor (900–1200 mg/L) and unacceptable (>1200 mg/L). Water with low TDS concentrations, may also be unsuitable for drinking due its flat, insipid taste. The concentration of the soluble silica ranged from 11.9 to 53.84 mg/L with an average of 28.82 mg/L. It is very higher than the natural limit (5–25 mg/L) in that area which strongly supports the dissolution and the weathering effect of the hardrock that are extracted and stock filled in the mine area which contains 50.17–74.7% (by weight) of SiO_2. Though, silica ingested orally is essentially non-toxic with an LD_{50} of 5 g/kg, this result gives a massage that there may also a great amount of silica dust in the air around the mine site which can lead to silicosis, bronchitis or cancer for inhaling with finely divided crystalline silica dust. Silicosis is a serious lung disease caused by the accumulation of silica dust in the lungs (Gbadebo et al. 2013).

Abundances of different ions

Statistical analysis of the concentration of different parameter in water sample around the study area and corresponding WHO recommended value of those different parameters are tabulated in Table 4. Calcium is a major cations found in water which makes water hard. Calcium constitutes our body's bones and teeth and works as a structural elements of our body. The risk of osteoporosis, nephrolithiasis (kidney stones), colorectal cancer, hypertension and stroke, coronary artery disease, insulin resistance and obesity increases because of inadequate intake of calcium. The WHO guideline value of Ca^{2+} for drinking purpose is 75 mg/L. The concentration Ca^{2+} in the water samples ranged from 1.3 to 55 mg/L with an average of 15.06 mg/L. The results show that all samples were within the guideline value. The second most abundant inorganic ion that present in water is magnesium. The concentration of Mg^{2+} in the water samples varied from 1 to 41 mg/L with an average value of 10.56 mg/L. The WHO recommended value for Mg^{2+} concentration is 50 mg/L. All samples were found within the WHO (2011) permissible limits for calcium and magnesium. Both calcium and magnesium ions generally originate from the carbonate minerals, such as calcite and dolomite. The concentration of Na^+ in the water ranged from 2.1 to 53 mg/L with an average value of 14.34 mg/L. It is an essential element for human body for keeping body in proper working conditions. Sodium helps in maintaining blood pressure, controlling fluid levels, as well as keeping normal nerve and muscle functions. The spatial variation of the sodium ion concentration indicates localized weathering of feldspar (plagioclase bearing) rocks present in the granite rocks and may also due to the over exploitation of groundwater because of mining and basic consumption needs. EQS (2004) suggests a desirable sodium concentration of 100 mg/L in water for drinking purposes. Potassium (K^+) concentration in water samples varied from 0.4 to 12.2 mg/L with a mean of 3.1 mg/L which had exceeded the WHO (2011) recommended potassium ion concentration in water of 10 mg/L. The increased level of potassium may be due to both the dissolution and weathering of the K-feldspars and clay minerals from the aquifer matrix as the granite rock in the mine area that is extracted is highly rich

Table 4 Statistical analysis of the ion concentration in water around the study area, Dinajpur

Ions	Min.	Max.	Mean	Median	Std. deviation	Variance	WHO (2011)
Ca^{2+}	1.3	55	15.06	10	14.01	196.4	75
Mg^{2+}	1	41	10.56	5.75	10.16	103.24	50
Na^{+}	2.1	53	14.34	13.8	10.58	111.97	–
K^{+}	0.4	12.2	3.1	2.7	2.53	6.41	10
Fe^{3+}	0.09	0.92	0.34	0.24	0.23	0.05	–
As^{3+}	0	0.0017	0.001	0.0011	0.0005	0	<0.01
Cd^{2+}	0.0008	0.0042	0.002	0.002	0.001	0	0.05
Zn^{2+}	0.08	0.32	0.15	0.13	0.06	0	3
Cr^{3+}	0	0.015	0.0023	0.002	0.003	0.002	<0.05
SO_4^{2+}	0.08	10	0.86	0.34	1.86	3.44	250
PO_4^{3-}	0.08	2.3	0.48	0.34	0.5	0.25	2.5
HCO_3^{-}	5	87.5	28.31	19	20.94	438.51	500
NO_3^{-}	0.07	0.71	0.35	0.33	0.16	0.03	45
Cl^{-}	0.71	73.84	9.79	4.26	14.4	207.48	250
NH_4^{+}	0.22	1.07	0.7	0.7	0.24	0.06	35
CO_3^{2-}	4.3	18	9.35	8.95	3	9.03	–

with feldspar minerals. Iron ion concentration in water samples in the form of Fe^{3+} varied from 0.09 mg/L to a maximum of 0.92 mg/L with a mean concentration of 0.34 mg/L. It is essential for human body as it is needed in the transmission of oxygen in blood. However, excess iron in water can cause yellow, red, or brown strains on laundry, dishes, and plumbing fixtures such as sinks. Arsenic (As^{3+}) is a toxic metalloid, ubiquitous element in the environment and affecting over 150 million people worldwide through consumption of arsenic contaminated potable water (Ahmad and Qadir 2011; Rahman et al. 2009; Srivastava et al. 2015). Arsenic in water for drinking purpose should be below 0.01 mg/L. However, the World Health Organization (WHO) recommended the arsenic concentration in the drinking water should not beyond 0.05 mg/L. Arsenic (As^{3+}) concentration in the water samples varied from 0 to 0.0017 mg/L where the mean concentration was 0.001 mg/L. Cadmium ion (Cd^{2+}) concentration in water varied from 0.001 to 0.004 mg/L with a mean value of 0.002 mg/L. The WHO (2011) guideline value for cadmium concentration in water samples should be less than 0.01. The concentration of zinc (Zn^{2+}) in water was found within the maximum permissible limit of 3 mg/L by the WHO (2011) and ranged from 0.08 to 0.32 mg/L with an average value of 0.15 mg/L. According to WHO (1996), the concentration of chromium (Cr^{3+}) in drinking water should not be acceded over 0.05 mg/L. The concentration of the Cr^{3+} in water samples varied from 0 to 0.015 mg/L with a mean value of 0.0023 mg/L. Sulfates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4{\cdot}7H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) (Greenwood and Earnshaw 1984). These dissolved minerals contribute to the mineral content of both surface and groundwater bodies. Sulfate ion concentration in the water samples varied between 0.08 and 10 mg/L with an average value of 0.86 mg/L. The sulfate concentration (SO_4^{2+}) in the all experimental water samples were within the permissible limits of 250 mg/L (WHO 2011). Higher concentration of sulfate in groundwater may be attributed to contamination of untreated industrial and domestic waste and their effluents (Baruah et al. 2008; Jeevanandam et al. 2008, 2012; Boateng et al. 2016). Higher concentration of SO_4^{2-} may cause gastrointestinal irritation particularly when Mg^{2+} and Na^{+} are also present in drinking water resources (Suthar et al. 2009; Boateng et al. 2016).

According to WHO (2011), the permissible limit of phosphate concentration in drinking water should be below 0.1 mg/L. Phosphate (PO_4^{3-}) concentration in the water samples ranged from 0.08 to 2.3 mg/L with an average value of 0.48 mg/L. Some of the water samples exceeded the permissible limits of phosphate concentration. Most of the people around the mine area use Triple Super Phosphates (TSP) for agricultural purposes. So, the presence of phosphates in water may be due to anthropogenic origin. The concentration of the bi-carbonate ranged from 5 to 87.5 mg/L. Bicarbonate is responsible for the alkalinity of groundwater. The bicarbonates are probably derived from weathering of silicate rocks, dissolution of carbonate precipitates, atmospheric and soil CO_2 gas (Jeong 2001; Subramani et al. 2005; Kumar et al. 2011; Boateng et al. 2016).

The concentration of nitrate ion in water samples ranged from 0.07 to 0.71 mg/L with an average value of 0.35 mg/L were found within the permissible limits. The source of NO_3^- may be from the high infiltration of soil layer and anthropogenic activities. Nitrate may occur as an intermediate product during the nitrification process of ammonia and also may be from the use of ANFO (Ammonium Nitrate Fuel–Oil Mixture) during blasting work in mining activities. The presence of high nitrate concentration in the drinking water may increases the possibility of gastric cancer and some other potential hazards to the pregnant women. The concentration of ammonium ion in the water samples varied from 0.22 to 1.07 mg/L with a mean concentration of 0.7 mg/L. The threshold odor concentration of ammonia in water is approximately 1.5 mg/L. A taste threshold limit of 35 mg/L has been proposed by the WHO (1996). Chloride concentration in the water may result from the evaporation of the chloride bearing minerals which are soluble to the water, encroachment of the saline water to the fresh water zone and different anthropogenic activities. Chloride ion concentration in the experimental samples ranged between 0.71 and 73.84 mg/L with a mean value of 9.73 mg/L. The carbon dioxide that is dissolved by the naturally circulating water appears in chemical analysis principally as carbonate ions. Carbonate ion concentration in the water samples ranged from 4.3 to 18 mg/L with a mean concentration of 9.35 mg/L.

Application of Gibbs plot

Gibbs plot (Fig. 6) is used to interpret the effect of hydrogeochemical processes such as precipitation, rock–water interaction and evaporation on groundwater geochemistry (Boateng et al. 2016). With a view to discerning the source of contamination of water in an area, Gibbs ratio (GR) plot is a useful tool to find the interaction between rock and water. The concentration of dissolved ions in groundwater samples are generally governed by lithology, nature of geochemical reactions and solubility of interaction rocks. The functional sources of dissolved ions can be broadly assessed by plotting the samples, according to the variation in the ratio of $Na^+/(Na^+ + Ca^{2+})$ and $Cl^-/(Cl^- + HCO_3{}^-)$ as a function of TDS (Gibbs 1970).

$$\text{GR-I (for anion)} = \frac{Cl^-}{Cl^- + HCO_3^-} \tag{7}$$

$$\text{GR-II (for cation)} = \frac{Na^+ + K^+}{Na^+ + K^+ + Ca^{2+}} \tag{8}$$

where all ions are represented as meq/L.

Gibbs ratios for the all samples are plotted against TDS (ppm) in Fig. 6 to know whether the groundwater chemistry is due to rock dominance, evaporation dominance or precipitation dominance. From the pot of the Gibbs Ratio plot it is visible that, most of the samples are rock dominated (shown in dash line area) and rest of the samples suggested to be precipitation dominated. This scenario suggests that the evaporation control field increases

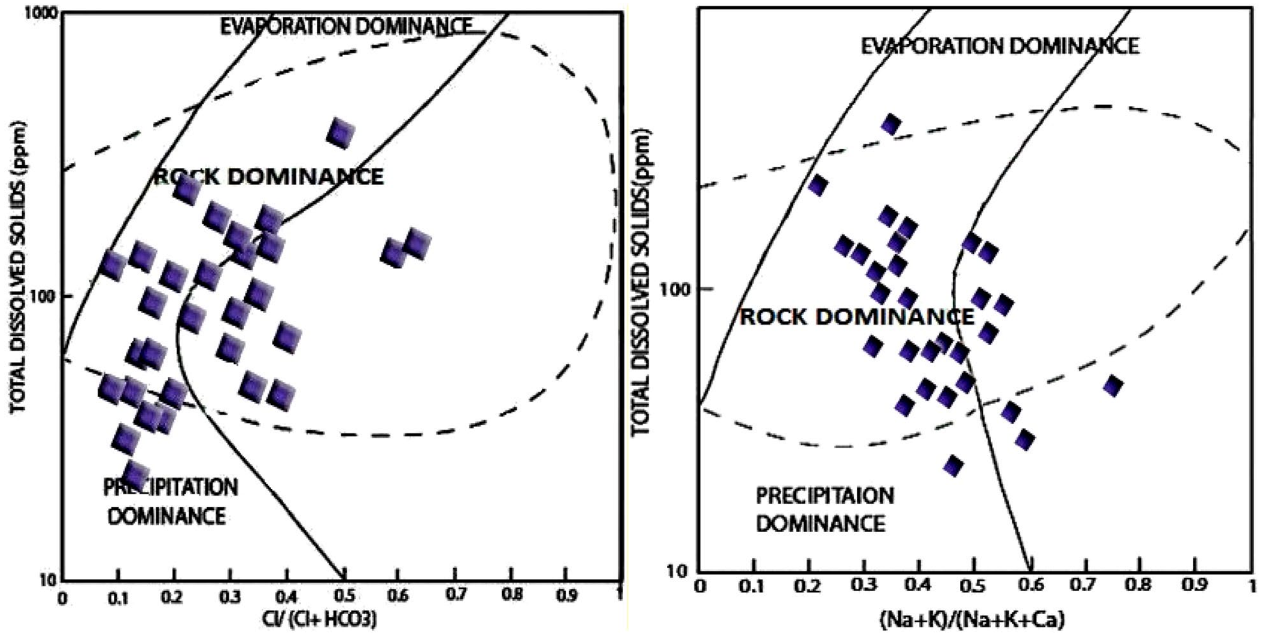

Fig. 6 GR for different samples are plotted alongside their relevant total dissolved solids

salinity by the increasing ions of Na and Cl in relation to increase in TDS and agricultural fertilizers.

Cluster analysis (CA)

Cluster analysis is a group of multivariate technique whose primary aim is to assemble objects based on the characteristics they possesses (Shrestha and Kazama 2007; Oketola et al. 2013). Hierarchical clustering joins the most similar observations. The levels of similarity at which observations are merged are used to construct a dendrogram (Oketola et al. 2013). Cluster analysis is the unsupervised classification of patterns (observations, data items, or feature vectors) into groups (clusters). The Euclidean distance (D^2) is the geometric between two objects and can be calculated by the given formula:

$$D^2 = (Z_{EC1} - Z_{EC2})^2 + (ZH_{TDS1} - Z_{TDS2})^2 + \left(Z_{pH1} - Z_{pH2}\right)^2 + \left(Z_{Ca^{2+}1} - Z_{Ca^{2+}2}\right)^2 + \cdots \tag{9}$$

The dendrogram for cluster analysis of 31 water samples are shown in Fig. 7. It is visible that the cluster analysis grouped the whole samples into three distinct groups of cluster. Cluster groups in the CA are tabulated in Table 5. Cluster I groups 70.97% of total samples into two sub-cluster group A1 and A2 whereas, Cluster II is consisted of 22.58% of samples and finally Cluster-III includes 6.45% of the total samples. In order to find out the similarity of grouped samples, their grouped physical and chemical parameters analysis are shown collectively in Table 6. The P^H in the cluster I is comparatively lower (mean = 7.42) than that of water class of cluster II (mean = 8.38) and cluster III (mean = 8.08). Likely P^H, EC of the cluster I (average = 98.28) is also show the lowest value than the samples grouped in cluster II (average = 274.71) and cluster III (average = 483.5) water samples. Unlike P^H and EC, turbidity in cluster I is the highest than that of cluster II and cluster III. However,

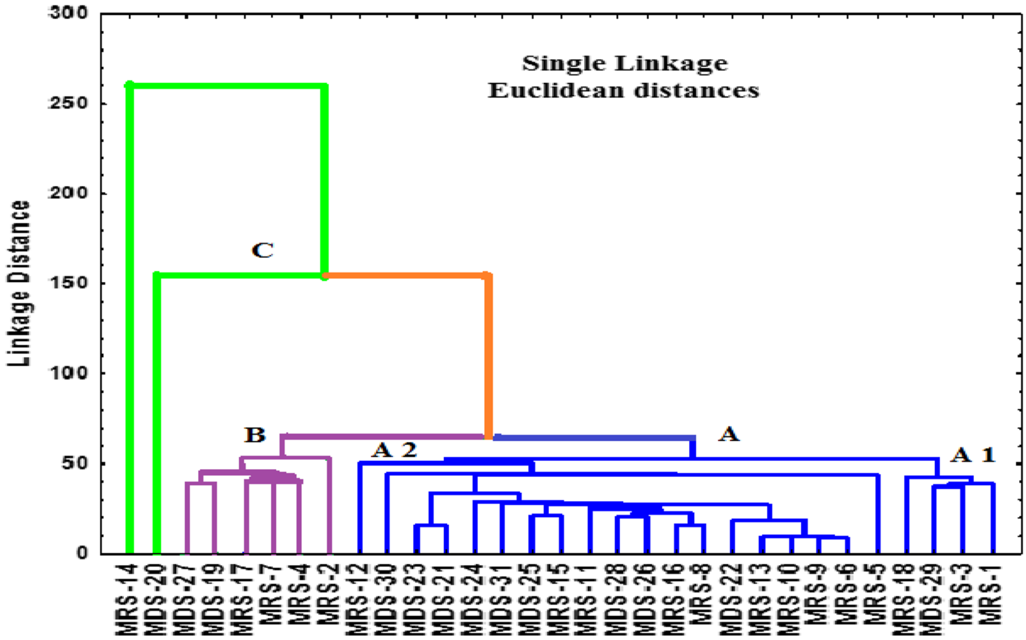

Fig. 7 The dendogram of the cluster analysis

Table 5 Cluster analysis of the water samples

Group	Sample number	Cluster	Sample percentage
A1	MRS-1, MRS-3, MRS-18,29	Cluster I	70.97
A2	MRS-5, MRS-6, MRS-8, MRS-9, MRS-10, MRS-11, MRS-12, MRS-13, MRS-15, MRS-16, MDS-21, MDS-22, MDS-23, MDS-24, MDS-25, MDS-26, MDS-28, MDS-30, MDS-31		
B	MRS-2, MRS-4, MRS-7, MRS-14, MRS-17, MDS-19, MDS-27	Cluster II	22.58
C	MRS-14, MDS-20	Cluster III	6.45

Table 6 Physico-chemical parameters of different clustered groups

	P^H	EC	Turbidity	TA	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	As^{3+}	Cd^{2+}
Cluster I											
Min	5.3	41	3	5	2.5	1.3	1	2.1	0.4	0	0.0008
Max	9.02	194	45	74	43	28	41	53	5.72	0.0017	0.0033
Mean	7.42	98.28	12.26	24.70	15.05	9.78	9.15	11.55	2.05	0.001	0.0018
Cluster II											
Min	6.6	188	4	14	17.5	9.4	5	15.5	3.44	0	0.0009
Max	8.38	587	10	88	87.5	51	36.5	37.9	12.2	0.0016	0.0042
Mean	7.65	274.71	6.71	38.86	41.25	26.7	14.55	22.73	6.18	0.001	0.0027
Cluster III											
Min	8.03	380	4	59	70	51	15	19.7	5.72	0.0011	0.0032
Max	8.13	587	8	88	87.5	55	36.5	37.9	12.2	0.0014	0.0039
Mean	8.08	483.5	6	73.5	78.75	53	25.75	28.8	8.96	0.00125	0.0036

	Fe^{3+}	Zn^{2+}	Cr^{3+}	SO_4^{2-}	PO_4^{3-}	SiO_2	NO_3^-	Cl^-	NH_4^+	TDS	CO_3^{2-}
Cluster I											
Min	0.09	0.08	0	0.08	0.08	11.9	0.07	0.71	0.22	24	4.3
Max	0.92	0.23	0.015	2	0.64	53.84	0.63	15.76	1.07	135.8	13.6
Mean	0.34	0.13	0.002	0.39	0.32	28.25	0.31	4.52	0.68	71.49	8.39
Cluster II											
Min	0.16	0.1	0.0014	0.16	0.27	12.85	0.24	6.39	0.38	141.4	7.85
Max	0.52	0.3	0.005	10	2.3	35.9	0.71	73.84	0.92	382	18
Mean	0.34	0.2	0.002	2.43	1.04	29.51	0.47	26.57	0.70	190.01	11.71
Cluster III											
Min	0.24	0.3	0.0023	0.55	0.37	32.45	0.41	13.49	0.84	247	15
Max	0.52	0.32	0.003	1.52	0.52	37.15	0.45	73.84	1.04	382	18
Mean	0.38	0.31	0.00265	1.035	0.445	34.8	0.43	43.665	0.94	314.5	16.5

hazardous cadmium concentration in the group of cluster III is the highest than that of cluster I and cluster II.

The concentration of the calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), iron (Fe^{3+}), zinc (Zn^{2+}), chromium (Cr^{3+}), Sulfate (SO_4^{2-}), phosphates (PO_4^{3-}), nitrates (NO_3^-), chloride (Cl^-), Ammonia (NH_4^+), TDS and dissolved silica (SiO_2) ions in cluster I is the lowest in average than that of cluster II and cluster III.

Principal component analysis (PCA)

Principal component analysis (PCA) is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. PCA is a powerful tool to find the patterns in the high dimension data although the luxury of graphical representation is not available for analyzing data. The pattern of the data reduces the dimension of the data without much loss of data. In case of water quality analysis, PCA is useful tool to identify the ecological aspects of pollutants on environmental systems. PCs were defined according to the criterion that only factors that account for variance greater than 1 (eigenvalue-one criterion) should be included. The rationale for this is that any component should account for more variance than any single variable in the standardized test score space. In order to evaluate the most significant parameters in the assessment of the water quality, principal component analysis have been carried out upon 24 variables for 31 samples from surface and groundwater for identifying the water pollution sources and water quality around the Maddhapara Granite Hard Rock Mine area. An eigenvalue gives a measure of the significance of the factor and factors with the highest eigenvalues are the most significant. Eigenvalues of 1.0 or greater are considered significant (Shrestha and Kazama 2007). Classification of principal components is thus "strong", "moderate" and "weak", corresponding to absolute loading values of >0.75, 0.75–0.50 and 0.50–0.30, respectively (Liu et al. 2003). The summary of the PCA including the factor loadings, eigenvalues of each PCs, total variance as well as the cumulative variance generated by Statistica 8.0 software where loading was unrotated for 24 parameters are summarized and strong (medium slate blue color), and moderate (chartreuse color) loading values are highlighted in Tables 7 and 8. Table 8 shows that each five factor has eigenvalue greater than 1, whose factor 1 (PC 1) (eigenvalue = 9.557823) is the most significant variables which explains 39.82426% of the total variance. Factor 2 (PC 2) (eigenvalue = 3.060269) is the second significant value that contributes 12.75112% of the total variance. Factor 3 (PC 3) defines 9.62826% of the total variance with eigenvalue of 2.310782. Factor 4 (PC 4) and factor 5 (PC 5) possess eigenvalue of 1.870234 and 1.43581 respectively and define 7.79264 and 5.88992% of the total variance in some respects. Tables 7 and 8 show five factors (PCs) have explained 75.89% of the total variance. The first factor (PC 1) explained 39.82% of the total variance and dominated by the sp. conductivity, total alkalinity, alkalinity (HCO_3^-), calcium, potassium, chloride, TDS and carbonate (highlighted by medium slate blue color) inversely strongly. P^H, sodium and zinc (highlighted by chartreuse color) show a moderate and negative correlation with factor 1 (PC 1) representing chemical components due to the geologic feature in the water environment which satisfy the previous published scientific results by Bu et al. 2009. Nevertheless, the P^H is weakly loaded on F1 (Figs. 8, 9), its negative loading suggests a weak bipolarity of a factor, substantiates the idea of good solubility of limestone at low (acid) P^H conditions. It is concerned with positive association between

Table 7 Summary of the PCA loading for 24 variables

Variables	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
P^H	*−0.505140*	−0.423783	−0.523819	0.281011	0.231837
Sp. conductivity	*−0.973220*	0.078222	0.062930	−0.105619	−0.052161
Turbidity	0.027478	−0.437808	*0.685626*	0.218108	−0.157060
Total alkalinity	*−0.835965*	−0.389071	−0.155823	0.100161	0.047304
Alkalinity (OH)	−0.298613	−0.443572	−0.304156	0.432541	−0.020149
Alkalinity (HCO_3)	*−0.854348*	−0.365501	−0.133041	0.060517	0.052251
Total hardness	*−0.959257*	−0.105187	0.034686	−0.051546	0.055754
Iron	−0.176503	−0.311548	0.125313	0.259103	*−0.703320*
Calcium	*−0.917427*	−0.056955	0.121062	−0.094580	0.070455
Magnesium	−0.458933	−0.356458	−0.138375	0.118694	*−0.520944*
Sodium	*−0.615277*	0.107953	0.049094	0.078692	0.121033
Potassium	*−0.871104*	0.105514	0.060418	−0.269454	−0.140015
Arsenic	−0.014235	0.364144	*−0.699425*	−0.245118	−0.361498
Cadmium	−0.450872	*0.598943*	0.040729	0.214109	0.166345
Zinc	*−0.722452*	0.384863	−0.011331	−0.468652	0.035537
Chromium	−0.029260	0.269727	0.122538	*−0.544966*	−0.284185
Sulfate	−0.302047	*0.583734*	0.107611	0.416829	0.057136
Phosphate	−0.351122	*0.592348*	0.052115	*0.504778*	0.008429
Soluble silica	−0.251729	0.252323	*−0.793143*	0.170839	0.013400
Nitrate	−0.372521	0.430667	0.393509	0.435109	−0.044675
Chloride	*−0.835263*	0.230616	0.155028	0.033166	−0.119517
Ammonia	−0.350977	−0.448496	0.129445	−0.199509	*0.507021*
TDS	*−0.973249*	0.057827	0.065802	−0.112613	−0.037220
Carbonate	*−0.885900*	−0.171159	0.147483	−0.192210	0.008697

Significant factor loadings are in italics

Table 8 Summary of the PCA including the eigenvalues of each PCs, total variance

Factor	Eigen value	%Total variance	Cumulative eigen value	Cumulative %variance
1	9.557823	39.82426	9.55782	39.82426
2	3.060269	12.75112	12.61809	52.57538
3	2.310782	9.62826	14.92887	62.20364
4	1.870234	7.79264	16.79911	69.99628
5	1.413581	5.88992	18.21269	75.88620

Ca^{2+} and HCO$_3^-$ which is thought to indicate the process of carbonate dissolution on certain locations which bear out the previous published scientific results by Terzic et al. (2010).

Factor 2 (PC 2) is moderately and positively dominated by cadmium, sulfate and phosphate (highlighted by chartreuse color) and explained 12.75% of the total variance. It signifies the weathering of rock and anthropogenic

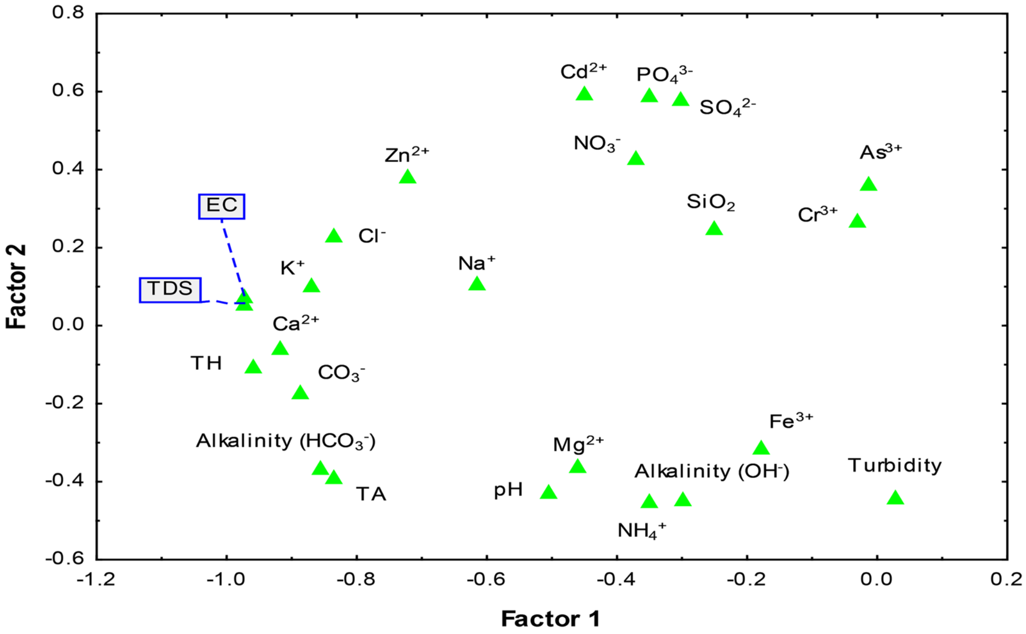

Fig. 8 Factor analysis diagram. Factor loadings: Factor 1 versus Factor 2. Loading: unrotated, extraction: principal components

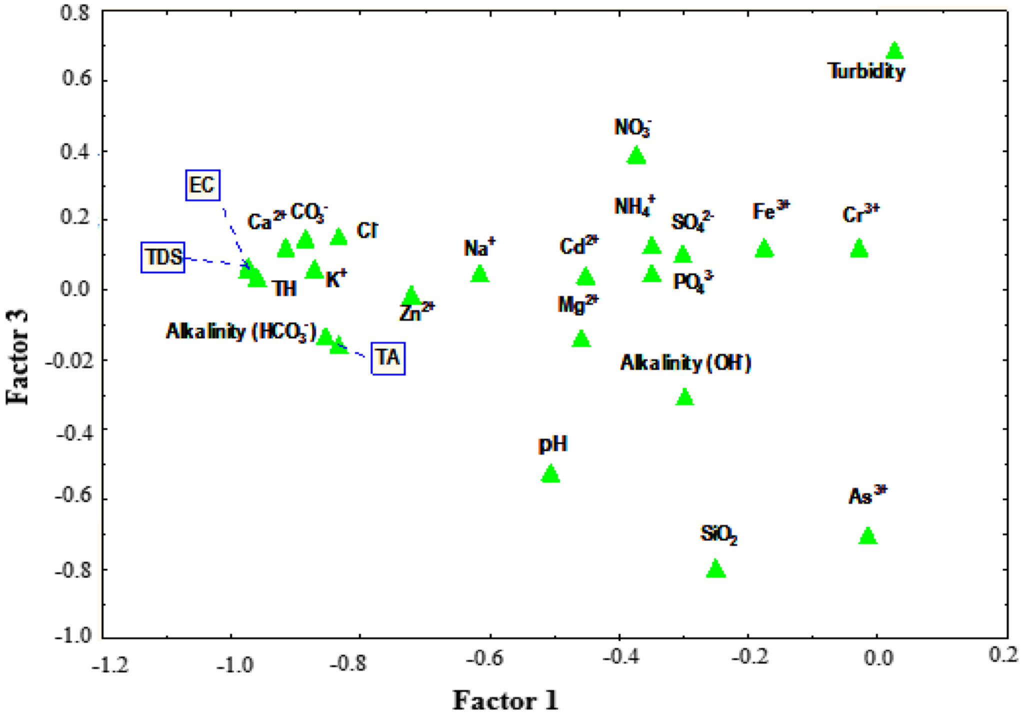

Fig. 9 Factor analysis diagram. Factor loadings: Factor 1 versus Factor 3. Loading: unrotated, extraction: principal components

impacts on the water contaminations. Figure 8 shows the factor 1 vs. factor 2 plot and their level of relationship to each other. Factor (PC 3) is dominated negatively and strongly by the soluble silica and moderately by arsenic. It shows a moderate positive correlation with turbidity. However, factor 3 (PC 3) has explained 9.63% of the total variance. Figure 9 shows the factor 1 vs. factor 3 plot and their level of relationship to each other. It implies the contamination of water by the aquifer and stockpiled rocks and which strongly recommends the weathering and dissolution of granite rocks found in the study area containing 50.17–74.7% by weight of silica and its impacts of the water around the area. Factor 4 (PC 4) shows moderate positive and negative correlation with phosphate and chromium respectively with 7.79% of the total variance. Factor 5 (PC 5) is moderately and hence negatively dominated by the iron (Fe) and magnesium (Mg) and positively with ammonia (NH_3). Factor 4 and factor 5 may direct the anthropogenic effects due to fertilizer uses in the agricultural purposes and one the most important use should be noted in the mining area is the use of ANFO (Ammonium Nitrate Fuel Oil Mixtures) in order to secondary blasting and hence breaking down of the hard rock in the area to be mined (Table 9).

Nitrogen from untreated or partially treated wastewater discharges and manure may be either organic or ammonium form, while nitrogen from chemical fertilizers will typically be in ammonium or nitrate form (Canter 1997). Ammonia volatilization is a physicochemical process where ammonium–nitrogen is known to be in equilibrium between the gaseous and hydroxyl forms and it is P^H (with an alkaline P^H favoring the presence of aqueous forms of NH_3 in water, while at acidic or neutral P^H, the ammonium–nitrogen is predominantly in ionic form) and temperature dependent (low temperature ammonium ion predominant, while high temperature ammonia ion present) (Reddy and Patrick 1981; Terzic et al. 2010).

Application of Water Quality Index and the quality of water for various purposes

The Water Quality Index (WQI) is a single value expression that summarizes numerous parameters and provides a measure of water quality. Water quality indices (WQIs) were calculated for the samples using the concentration of 12 parameters such as P^H, EC, TH, TDS, Ca^{2+}, Mg^{2+}, K^+, Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, and PO_4^{3-}. The WQI of the samples ranged from 10.23 to 63.64. According to the calculated value of the WQI, 96.77% of the experimented samples show excellent and 3.23% of the samples fall under good quality type water for drinking purposes. Figure 10 shows the minimum, maximum and the average WQI values for three cluster groups. It shows that the cluster I group is the best quality water among the three groups and there is a visible upward trend along which water quality deteriorates. Moreover the overall status of the quality of water around the mining area has been shown in Fig. 11 which might be helpful to have the proper monitoring program for maintaining sustainable water environ and sound mining operation in the area.

Table 9 Calculated Water Quality Index and their classification of the samples

Sample	WQI	Water type	Sample	WQI	Water type
MRS-1	31.23008	Excellent	MRS-17	42.11095	Excellent
MRS-2	37.06531	Excellent	MRS-18	31.4552	Excellent
MRS-3	28.06065	Excellent	MDS-19	26.77772	Excellent
MRS-4	35.07572	Excellent	MDS-20	44.10005	Excellent
MRS-5	10.23388	Excellent	MDS-21	17.44005	Excellent
MRS-6	14.97247	Excellent	MDS-22	19.51724	Excellent
MRS-7	37.29106	Excellent	MDS-23	19.94317	Excellent
MRS-8	18.25328	Excellent	MDS-24	19.07301	Excellent
MRS-9	16.69171	Excellent	MDS-25	20.80748	Excellent
MRS-10	16.16417	Excellent	MDS-26	19.08683	Excellent
MRS-11	15.65285	Excellent	MDS-27	29.87894	Excellent
MRS-12	15.77154	Excellent	MDS-28	19.37103	Excellent
MRS-13	15.14981	Excellent	MDS-29	29.33892	Excellent
MRS-14	63.64195	Good	MDS-30	25.17631	Excellent
MRS-15	21.79876	Excellent	MDS-31	20.55718	Excellent
MRS-16	18.54043	Excellent			

Summary and conclusion

The water quality around the Maddhapara Granite Mine Area have been evaluated regarding the suitability of water for drinking purposes as well as the identification of the dominating sources of different water quality parameters. Physicochemical analysis of the samples showed the wide variation of P^H values, high turbid water and appreciable amount of soluble silica in the experimented water samples around the mine sites. All other parameters except these were almost in permissible level based on WHO water quality standards. Based on the Total Hardness (TH) and Electrical Conductivity (EC) values the water samples were found soft to moderately hard and fresh water, respectively. Cluster analysis classified the water samples into three groups such as cluster I (70.97%), cluster II (22.58%) and cluster III (6.45%). Water Quality Index analysis revealed that 96.77% of the water samples fell under excellent quality and rest 3.23% of water samples were of good quality types. WQI analyses among the three clustering groups showed that cluster I was of the best quality water and then sequentially cluster II and cluster III. Principal Components Analysis (PCA) expressed that five factors extracted explained 75.89% of the total variance. The results from the PCA

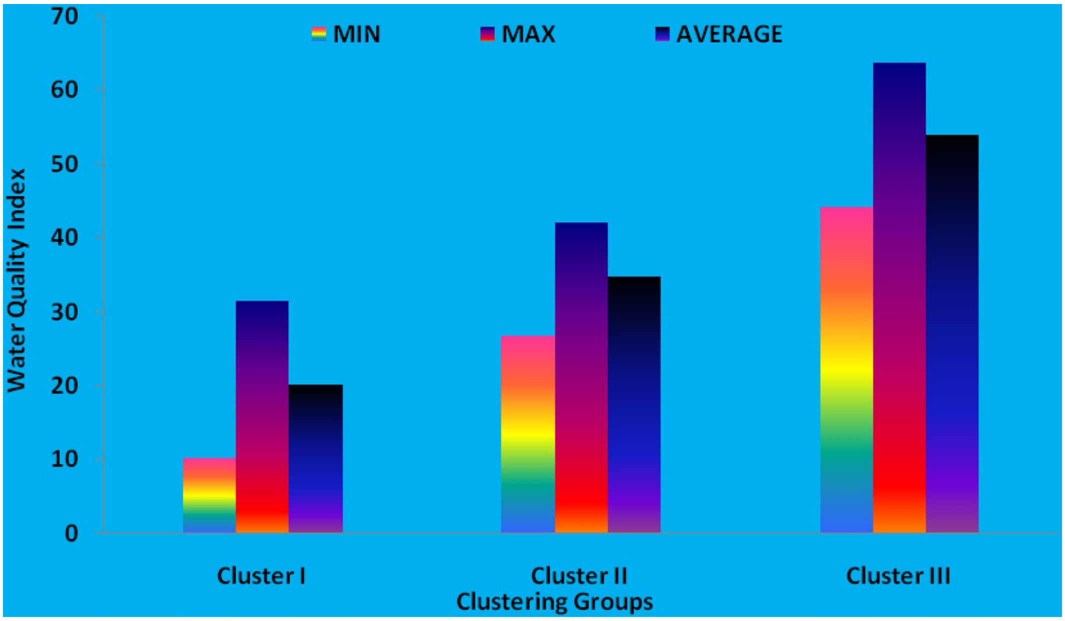

Fig. 10 Comparison of Water Quality Index among the clustering groups with their minimum, maximum, and average values

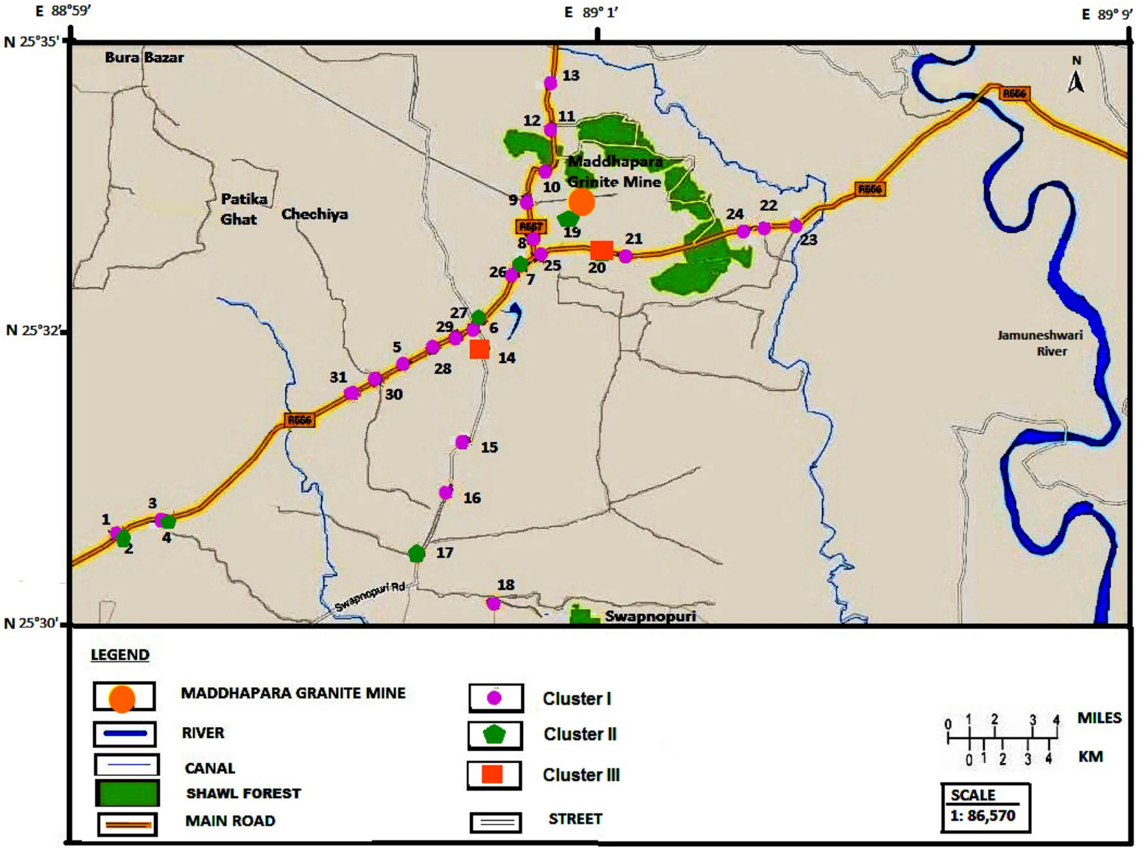

Fig. 11 The status of the quality of water around the mining area. The cluster group I reflects the best quality water of the area

gave a hint that the water quality in mine area is mainly influenced by weathering of rock, mining, dissolution of ions and anthropogenic activities. The Gibbs ratio plot showed that most of the samples were rock dominated and rest of the samples suggested to be precipitation dominated. This study provides a qualitative measure of the water quality around the Maddhapara Granite Mine area, Dinajpur, which suggests the necessity of the remedial actions to the contaminated sources in order to keep the water safe and reliable for present and future consumption. The main innovative things of this research work is that sample locations have been plotted on map based on Cluster Analysis (CA) and Water Quality Index (WQI) which ultimately help us to understand the water quality in surrounding area. Moreover, it will be helpful in monitoring activities and for further water quality management to prevent the pollution.

Authors' contributions

MFH contributed to conception, design, and acquisition of data, data analysis and interpretation of data. AAN participated to acquisition of data, data analysis and interpretation of data as well as involved in drafting the primary manuscript. MOF made a contribution to drafting, checking graphs and revising the manuscript critically to fulfill the reviewer comments as well as maintaining the scientific merits with syntactic correctness for final submission of the manuscript. All authors read and approved the final manuscript.

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Competing interests

The authors declare that they have no competing interests.

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