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Hydrogeochemical Characterization and Groundwater Quality of Jamshedpur Urban Agglomeration in Precambrian Terrain, Eastern India

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ABSTRACT

Systematic and comprehensive analysis with integration of geochemical methods, multivariate statistical analysis, and quality for drinking and irrigation uses were carried out on forty-two groundwater samples to elucidate the regional factors and processes influencing the geochemical composition of groundwater. Groundwater geochemistry revealed that the abundance of Ca^{2+} and Na^{+} was contributed by weathering of carbonate and sodium bearing minerals, while higher HCO_3^- and Cl^- resulted from dissolution of carbonic and salt deposits. The rock weathering is the dominant mechanism controlling the major ion chemistry of groundwater as well as anthropogenic activities. The dominant hydrogeochemical facies of groundwater was Ca-Mg-SO_4 and Ca-Mg-Cl. About 33% of the groundwater samples have negative values of chloro-alkaline index revealing chloro-alkaline disequilibrium and the reaction as a cation–anion exchange reaction, while in 67% of the samples, the values are positive, indicating a base–exchange reaction. The saturation index reveals the presence of calcareous nodules, containing a mixture of calcite. The suitability for domestic uses as per BIS 2012 and WHO 2009 for drinking water reaveals that high concentrations of EC, TDS, SO_4^{2-}, Cl^- and F^- makes it unsuitable for drinking and domestic uses. Quality assessment for irrigation uses suggest that the groundwater is of excellent to good category, which can be used for irrigation without any serious hazards. Higher salinity and magnesium hazard values at some sites restrict the suitability of groundwater for irrigation.

INTRODUCTION

In developing country like India, groundwater is considered as a major source of water for domestic supply and it is the most important and reliable source of freshwater. Less than 1% of all waters on earth is for human consumption, and this resource is not only being overexploited but also seriously degraded due to anthropogenic activities involving huge disposal of pollutants in water bodies which make it unfit for sustenance of life (Ramachandra and Solanki, 2007). Groundwater quality in an area is a function of physico-chemical parameters that are greatly influenced by natural processes such as intermixing of water, water chemistry in recharge area, flowpath, rock-water interaction, climatic conditions along with geological formations and anthro-pogenic activities (L-Ruiz et al., 2015). Water quality plays an important role in promoting agricultural production and standard of human health. A total 90% of rural and 30% of urban Indian population still depend completely on untreated surface or groundwater resources. Urban expansion and population explosion due to industrial development and infrastructure growth in countries like India lead to stress on water resources (Kumar et al., 2017). Environmental neglect by society, since the dawn of the industrial revolution has resulted in severe contamination of water resources (Kumar et al., 2014).

Groundwater is the principal source for drinking in urban agglomeration of eastern India. In recent years demand for water has increased abruptly due to population and industrial activities. Jamshedpur is a major epicenter for industries in eastern India, which has more than 1,200 industries like Tata Steel, Tata Motors, Tata Power, Lafarge Cement, Telcon, BOC Gases, Tata Technologies Ltd., Praxair, TCE, TCS, Timken India, and Tinplate etc. The discharge of anthropogenic waste from industries into streams, nalas and rivers; subsequent leaching of pollutants resulted in degradation of water quality. In recent years groundwater resources are depleting continuously and in some places like Mango, Jugsalai, Birsanagar and Baridih no groundwater will be available for future generation. In Jamshedpur urban regions water table goes down to 6 to 11 meter before monsoon and after monsoon it goes down to 1.8 to 7.9 meter (CGWB 2012). Owing to this people are migrating to safer havens. groundwater peoples are un-grating from town. There is inadequate information available on groundwater chemistry, controlling mechanism of groundwater resource and suitability for drinking and irrigation purposes. In view of the above the present study is aimed to define the chemistry of groundwater in the Jamshedpur urban agglomeration and to assess hydrogeochemical processes that control groundwater composition and its suitability for drinking and irrigation uses which helps in future water resource planning for the area.

STUDY AREA

Jamshedpur urban agglomeration lies in the 22°47' N latitude 86°12' E longitude with average elevation of 135 metres with range from 129 m to 151 m. According to the 2011 census of India, Jamshedpur (East Singhbhum & Seraikela-Kharsawan) district hasa current population of 1,337,131; Jamshedpur urban area is the third largest city in eastern India with total geographical extent of 209 km^2. Jamshedpur is primarily located in a hilly region and surrounded by the Dalma hills running from west to east and covered with dense forests. Jamshedpur is located at the confluence of Kharkai and Subarnarekha rivers. Subarnarekha is the main river of Jamshedpur, which flows from west to south-eastern part of the territory. Drainage pattern is dendritic. Major tributaries which meet Subarnarekha river from west to east are Sapnara nadi, Garra nadi, Dudh nadi, Chakdaha nadi. Kharkai flows from south and joins the Subarnarekha river at a place called Domuhani. The two rivers are the major sources of drinking water and groundwater. The groundwater occurrence and movement is basically controlled by the prevailing morphology and intensity of structural discontinuities. The intensity of joints, fractures, foliation planes are more along anticlinal or synclinal flexures. Therefore, structure is another controlling factor for occurrence and movement of groundwater in the area. The rainfall is the main source of groundwater recharge in the area. The climate of this region

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may be considered as extreme, being extremely hot in summer and moderately cold in winter. The climate of the area is also characterized by a hot dry summer with well-distributed rains in the monsoon season. Annual rainfall is 1200 mm to 1400 mm. During the summer seasons maximum temperature goes up 40°- 45° C whereas in winter it has a minimum of 8°C.

GEOLOGY

The general geology of the study area is a part of Precambrian terrain of the Singhbhum craton (Fig. 1a). Detailed geology and chronostratigraphic succession are given by Ramakrishnan and Vaidyanadhan (2008) and Sarkar and Saha (1977), Saha (1994) respectively. About 83% area is occupied by hard rocks like granite-schists, mica schists, gabbro, etc., and remaining 17% is underlain by soft rocks represented by Tertiary grits and gravels and Quaternary alluvial sediments. It is underlain by folded and fractured Precambrian metasediments, mainly mica schists, quartzite and hornblende schists (Ghosh et al. 2002) and shows dominant vertical fractures (Négrel et al. 2007).

Only facture type aquifers were identified in the study area and groundwater occurs under unconfined condition in the hard rock areas (Négrel et al. 2011).

Field and Laboratory Methods

To understand the hydrogeochemistry facies, groundwater samples were collected from hand pumps in such a way that they represent different geological formations and land use patterns at varying topography of the Jamshedpur urban agglomeration in the pre-monsoon season (May 2016) (Fig. 1b). The spatial variation in the sampling location is due to some locations being restricted by government under different regulations. The information about the age of hand pumps was collected from local people and public Health and Engineering Department (PHED) and the range varied from less than 2 to 10 years, with an average of 4 years. Geographic coordinates and elevation were recorded for each sampling location using handheld global positioning system (Etrex 20 Garmin).

The groundwater samples were obtained from the hand pumps after allowing the water to run for at least 5 minutes to stabilize the variation in electrical conductivity (EC) and temperature. One liter sample was collected in high density polyethylene bottles. After collection of each sample, 100 ml samples was filtered using 0.45μm syringe filter and preserved separately with pure 2 N nitric acid (pH< 2) in the field itself. The bottles after labeling were brought to laboratory for determining the physicochemical analysis as per standard protocol (IS: 10500). In situ measurements for temperature, pH, EC, TDS, salinity, and ORP were carried out in the field using multiparameter analysis kit PCSTestr35 (Eutech Oakton). Bicarbonate was determined by potentiometric titration method (APHA 1995). Major anions (F^-, Cl^-, NO_3^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) were analysed through ion chromatograph (Metrohm 815, Swiss made) using Robotic USB sample Processor XL (6.20.41.800) in recycle mode. To maintain the purity and quality, a known standard was used after every five samples. High purity reagents (Merck) and milli-Q water (Model Milli-Q, Biocel) were used for all the analyses. Analyses were carried out in triplicates to quantify the error. An overall precision was obtained below 5% for all samples. Analytical precision for the measurement of ions was determined by calculating the normalized inorganic charge balance (NICB), which is defined as $[Tz^+ - Tz^- / Tz^+ + Tz^-]$ and represents the fractional difference between the total cations and anions (Edmond et al. 1995; Huh et al. 1998). The saturation index was derived using PHREEQC version 2.

RESULT AND DISCUSSION

Results of analysed hydrogeochemical parameters for the (n=42) groundwater samples in addition to the pH, EC, TDS, salinity and ORP were statistically analyzed and the results is compared to drinking water suitability standard are given in Table 1. The choro-alkaline indices (CAI), sodium adsorption ratio (SAR), %Na, permeability index (PI), Kelley index (KI) and magnesium hazards (MH) of the Jamshedpur township area are given in Table 3.

Groundwater Chemistry

The temperature of the groundwater samples collected during the fieldwork ranged from 25.6°C to 28.7°C. The pH of groundwater

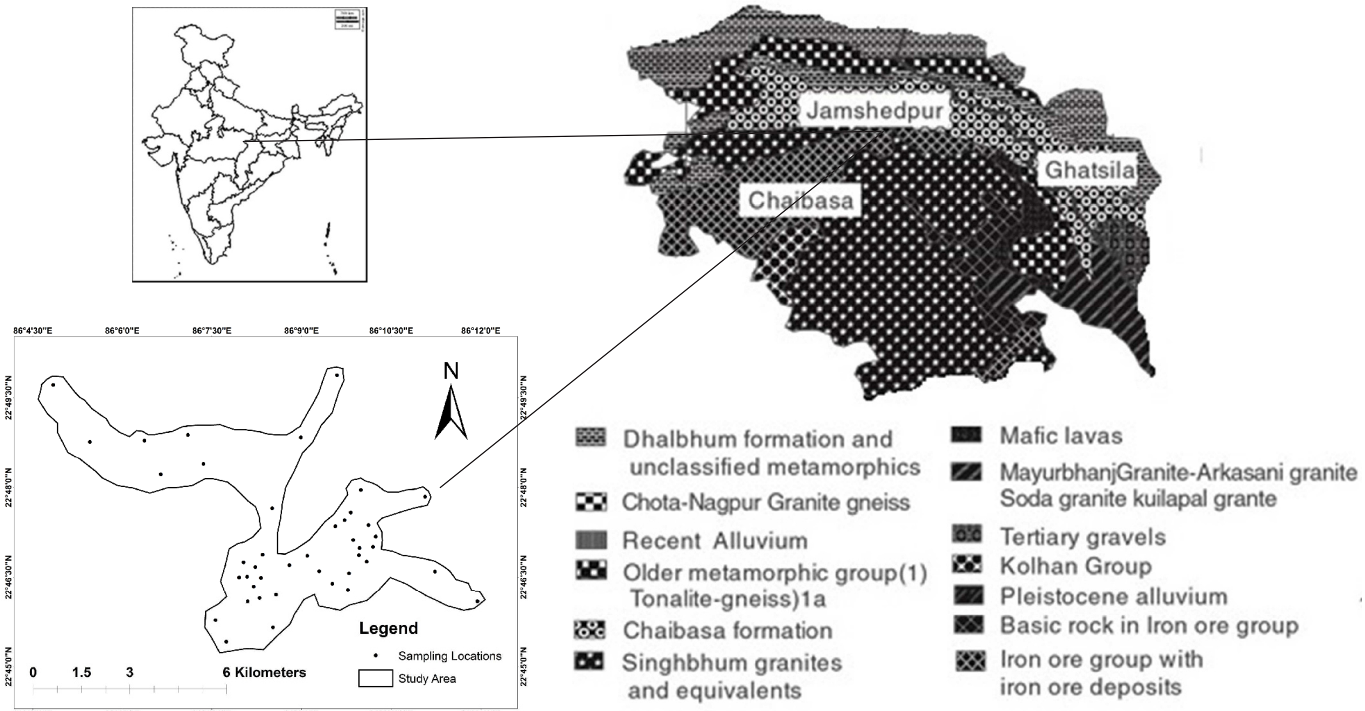

Fig.1. Map showing **(a)** Geology of the study area and **(b)** groundwater sampling locations in the study area.

samples was found slightly acidic to alkaline, and it varies from 6.25 to 7.45 with mean ± S.D. 6.81±0.28. The EC values varied from 271.70 µS/cm to 1364 µS/cm with an average value of 790.93 µS/cm, which is directly related to the ionic concentrations present in the groundwater and its higher values contribute to higher salinity and total dissolved concentration. However, the large variation in EC may be attributed to anthropogenic activity and geochemical processes through rock-water interaction (Chio et al. 2005). TDS concentration varies from 202 mg/l to 989.48 mg/l with an average concentration value of 623.07 mg/l. However, 81% of the groundwater samples have TDS values above the desirable limit 500 mg/l recommended by WHO (2009). Davis and Dewiest (1966) have classified the uses of the groundwater on the basis of TDS range as, up to 500mg/l (desirable for drinking), 500-1000 mg/l (permissible for drinking) and upto 3,000 mg/l (useful for agriculture). According to this classification, only 19% groundwater samples from the entire study area have drinking utility. The salinity concentration in the groundwater samples ranges from 157 mg/l - 776 mg/l with an average of 456 mg/l. The ORP values ranges from 160 mV to 290 mV with an average of 248 mV.

The dominant trend of major cations are $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ for the study area. Calcium is the dominant cation in the groundwater samples of the study area. It varies from 28.59 - 219.79 mg/l with an average of 94.68 mg/l, constituting 52.64% of the total cation (Tz^+). Magnesium is the third dominant cation in study area, which ranges from 4.63 – 126.98 mg/l with an average of 27.10 mg/l, constituting 15.07% of the total cation (Tz^+). Weathering and dissolution of limestone, gypsum, and anhydrite in sedimentary rock and cation exchange processes release Ca^{2+} and Mg^{2+} ions into groundwater. The Na^+ and K^+ ranges from 19.19 – 178.38 mg/l and 1.07 – 20.02 mg/l, constituting 29.78% and 2.51% of the total cation (Tz^+) of the study area. The possible sources of Na^+ in the groundwater are dissolution of rock salts and weathering of sodium bearing mineral. The K^+ ions shows least concentration in groundwater due to relatively less mobility and adsorption during weathering process.

The dominant trend of major anion was $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > F^-$. HCO_3^- was the dominant anion ranging from 113 - 255 mg/l and it accounts for 38.03% of the total anion (Tz^-). The HCO_3^- concentration in groundwater is derived from carbonate weathering as well as dissolution of carbonic acid in the aquifers (Singh et al. 2012). The second dominant anion is Cl^- which varies from 24.01 - 500.17 mg/l. The higher concentration of Cl^- in the study area may be due to natural process of the dissolution of salt deposits, and the irrigation return flow in groundwater. The concentration of SO_4^{2-}, NO_3^-, and F^- was found to be 6.95-295.48 mg/l, 0.11-28.35 mg/l and 0.12 - 2.85 mg/l respectively. Sulphates in the groundwater commonly derived from the oxidative weathering of sulphide bearing minerals, such as pyrite (FeS_2); however, gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$) can also be source of sulphate (Han et al. 2013). The chief sources of nitrate are atmospheric precipitation, application of fertilizers, animals waste and discharges from municipal and domestic sewage (Singh et al. 2013c). The high concentration of fluoride at some locations may be due to weathering of fluoride bearing minerals like muscovite, biotite, fluorite and fluoro-apatite, besides industrial and agricultural sources (Nair et al. 2015).

Hydrogeochemical Classification and Hydrogeochemical Facies

Several factors such as geological structure, mineralogy of rocks, anthropogenic activities and diverse climate condition control groundwater chemistry in the study area. The positive linear relationship for ($Ca^{2+} + Mg^{2+}$) versus Tz^+ indicate major source of Ca^{2+} and Mg^{2+} ions in groundwater, is due to weathering of carbonate minerals (Fig. 2a). The linear relationship of HCO_3^- versus ($Ca^{2+} + Mg^{2+}$) reveals weathering of mineral involved in concomitant production of bicarbonate ions from dissolved carbon dioxide and reactions of minerals in presence of H_2CO_3 (Fig. 2b). The ($Ca^{2+} + Mg^{2+}$) are not only derived from carbonate weathering but also the release of Ca^{2+} and Mg^{2+} by silicate weathering or by reverse ion exchange, which is evident from the relationship between ($HCO_3^- + SO_4^{2-}$) versus (Ca^{2+}/ Mg^{2+}) (Fig. 2c). The Gibbs diagram was plotted by using TDS concentrations versus weight ratios of $Na^+/(Na^+ + Ca^{2+})$ for cations and the weight ratios of $Cl^-/(Cl^- + HCO_3^-)$ for anions (Fig. 3). The Gibbs diagram shows that rock weathering is the dominant mechanism controlling the major ion chemistry of groundwater and anthropogenic activities in the area. The Piper (1944) diagram is very useful in determining relationship of different dissolved constituents and classification of water on the basis of its chemical characteristics. Piper diagram revels that 40% of the groundwater samples fall into non-dominant class. About 45% of the samples fall in Ca field indicating that the calcium may be from the weathering and dissolution of calcium bearing sedimentary rocks. In the Mg field about 10% of the samples plot and 5% in the Na/K field. In anionic triangle majority of the samples (52%) falls in Cl field which suggest that major source of chloride may be from the domestic sewage. About 40% of the samples fall in the no dominate type whereas 5% of the sample fall be in sulphate field (Fig. 4). In all the groundwater samples, alkaline earth metals ($Ca^{2+} + Mg^{2+}$) exceed alkali metal cation ($Na^+ + K^+$) whereas dominance of strong acids ($SO_4^{2-} + Cl^-$) over weak acids. About 50% of the samples fall in the field of Ca-Mg-SO_4 type which shows non-carbonate hardness of groundwater. About 44% of the samples fall in the field of Ca-Mg-Cl type reveals mixed nature of groundwater having none of cation-anion pairs dominate the chemical composition. About 4% of the

Table 1 Summary of physicochemical parameters analysed in groundwater samples (n=42) collected around Jamshedpur Urban Agglomeration

Parameter(s)	Min.	Max.	Avg.	S.D.	CV (%)	WHO (2009)	BIS (2012)
pH	6.25	7.45	6.81	0.28	4.11	6.5 - 8.0	6.5 - 9.5
EC (µS/cm)	271.70	1364	790.93	253.69	32.07	1500	-
TDS (mg/l)	202	987.48	623.07	203.76	32.70	1000	500
Salinity (mg/l)	157	776	456	120.75	26.48	-	-
ORP (mV)	160	290	248	28.96	11.68	-	-
Na^+ (mg/l)	19.19	178.38	53.57	26.43	49.34	200	-
Ca^{2+} (mg/l)	28.59	219.79	94.68	52.87	55.84	200	200
K^+ (mg/l)	1.07	20.02	4.52	4.02	88.81	30	-
Mg^{2+} (mg/l)	4.63	126.98	27.10	20.09	74.12	150	100
F^- (mg/l)	0.12	2.85	0.60	0.52	87.10	1.5	1.5
Cl^- (mg/l)	24.01	500.17	162.31	94.57	58.26	250	1000
SO_4^{2-} (mg/l)	6.54	295.48	98.49	66.62	67.65	250	400
NO_3^- (mg/l)	0.11	28.35	7.61	7.15	94	50	45
HCO_3^- (mg/l)	113	255	165.04	37.36	22.64	300	600

samples fall in the Ca-Mg-HCO_3 type which suggest that the groundwater is having carbonate hardness. About 2% of the samples in the Na-Cl type reveals the mixed character of groundwater. Based on the dominance of different cations and anions in the groundwater, two hydrogeochemical water types can be defined as Ca-Mg-SO_4 and Ca-Mg-Cl.

Hydrogeochemical Processes and Stoichiometric Relations

The chemical quality of groundwater depends on some important controlling factors like infiltrating rainwater, geological structure and mineralogical composition of aquifer, duration of water–rock interaction, dissolution and precipitation of mineral species and seawater and anthropogenic influences (Singh et al. 2008). The ratio between dissolved ions are shown in Table 2. The ratio $(Ca^{2+}+Mg^{2+})/Tz^+$ ranges from 0.32 to 0.87. About 4% of the groundwater samples show a ratio less than 0.5 which may suggest the contribution of alkalis to Tz^+. The ratio $(Na^++K^+)/Tz^+$ varies from 0.13 to 0.68. Out of 42 groundwater samples only 2 samples have a ratio value greater than 0.5 which indicates that the contribution of cation via silicate weathering. Another source of major cation in groundwater can be weathering of calcium minerals (Krishna et al. 2009). Higher value of Ca^{2+} / Mg^{2+} indicate that the study area is enriched with calcium ion whereas values less than 1 indicate enrichment of magnesium ion. The Na-Cl relationship has often been used to identify the reasons of salinity in groundwater (Magaritz et al. 1981; Sami 1992). The ratio $(HCO_3^- + SO_4^-)/Tz^-$ varies from 0.29 to 0.88 which shows bicarbonate and sulphate ions are the major contributors in Tz^-. The Cl^-/Tz^- ratio ranges from 0.11 to 0.69. The ionic ratio $(HCO_3^- + SO_4^-)/Tz^-$ is greater than the ratio Cl^-/Tz^- in all the groundwater samples. The Na^+/Cl^- ratio varied from 0.14 to 3.86. About 26% of the groundwater samples have values greater than 1 which reflects a release of Na^+ from weathering while 74% of the samples have values less than 1, suggesting that the reduction of sodium concentration may be due to ion exchange processes. The HCO_3^- /Na^+ ratio has mean value of 1.45 which reaveals that carbonate weathering occurs at most of the locations while some locations have values less than 1 which indicates silicate weathering. The variation of ratio of Na^+/ (Na^++Cl^-) along locations suggesting that that ion exchange process has occurred in the study area. The SO_4^-/Na^+ ratio mean value is 1.05 shows the dominance of sulphate in the study area. The ratio Ca^{2+}/Na^+ ranges from 0.21 to 6.25 having mean value 2.38 which indicate that majority of groundwater samples is enriched with Ca^{2+} which is also supported by Ca^{2+}/Mg^{2+} ratio. The ratio Mg^{2+}/Na^+ varies from 0.28 to 3.13 which suggest that the contribution of magnesium ion from minerals.

Chloro-alkaline Indices (CAI)

The ion exchange between the groundwater and its host environment during residence or in movement processes are the important controlling factors for water chemistry of the region. The ion exchange process can be understood by chloro-alkaline indices, also known as Schoeller index (Schoeller 1977) and expressed as

$$CAI\text{-}I = Cl^- \rightarrow (Na^+ + K^+) / Cl^-$$
$$CAI\text{-}II = Cl^- \rightarrow (Na^+ + K^+) / SO_4^{2-} + HCO_3^- + NO_3^-$$

Table 2. Stoichiometric relation between the observed solutes in the groundwater samples of Jamshedpur Urban Agglomeration

Parameter(s)	Min.	Max.	Avg.	S.D.	CV (%)
$(Ca^{2+}+Mg^{2+})/Tz^+$	0.32	0.87	0.73	0.11	15.17
$(Na^++K^+)/Tz^+$	0.13	0.68	0.27	0.11	40.42
Ca^{2+} / Mg^{2+}	0.19	16.59	3.93	3.74	94.99
$(HCO_3^-+SO_4^-)/Tz^-$	0.29	0.88	0.54	0.13	24.39
Cl^-/Tz^-	0.11	0.69	0.45	0.13	29.68
Na^+/Cl^-	0.14	3.86	0.89	0.85	96.19
HCO_3^-/Na^+	0.26	3.50	1.45	0.67	45.94
$Na^+/(Na^++Cl^-)$	0.12	0.79	0.38	0.19	49.92
SO_4^{2-}/Na^+	0.07	3.09	1.07	0.76	70.80
Ca^{2+}/Na^+	0.21	6.25	2.38	1.36	57.17
Mg^{2+}/Na^+	0.28	3.13	1.06	0.72	68.19

In the present case, about 33% of the groundwater samples have negative values indicating chloro-alkaline disequilibrium and the reaction as a cation–anion exchange reaction. In 67% of the samples, the values are positive, indicating a base–exchange reaction (Table 2).

Statistical Analysis

Principal component analysis (PCA) of the normalized data was done by SPSS 21 statistical package. The Bartlett's Sphericity test was carried out on the correlation matrix, which showed a^{-2} (calculated = 1056) greater than the critical value a^{-2} (crit = 458) [degree of freedom 410 and p value <0.0001 with significant level 0.05]. These values show that PCA can successfully achieve a significant reduction of the dimensionality of original data (Helena et al. 2000). Table 4 shows initial principal component (PC), its Eigen values and percent of variance contributed in each PC using Varimox rotation with Kaiser Normalization and rotated factor solutions. Based on initial eigen values and extraction sum of square loading, the first six PCs have eigen values > 1 and are able to explain 78.194 % of the total variance. The 19.315 % of variance is explained by PC1 followed by PC2 (14.563%), PC3 (12.230%), PC4 (11.672%), PC5 (10.965%) and PC6 (9.449%). The factor analysis of physicochemical parameters indicates six factors (Table 4). The total variability accounted for six factors was 78.194 %. Based on rotation sum of square loadings, PC loadings which had values greater than 0.5 were considered for interpretation of factor analysis (Mazlum et al. 1999).

Factor 1 has eigen value 2.318 and it explains 19.315 % of total variance. High loadings of Cl^-, SO_4^{2-} are observed in factor 1 which indicate a common source for of Cl^-, and SO_4^{2-} i.e., from anthropogenic or industrial activities (Gautam et al. 2015). High loading of SO_4^{2-} (+0.821) may be due to copper (sulphide) mining activities in the

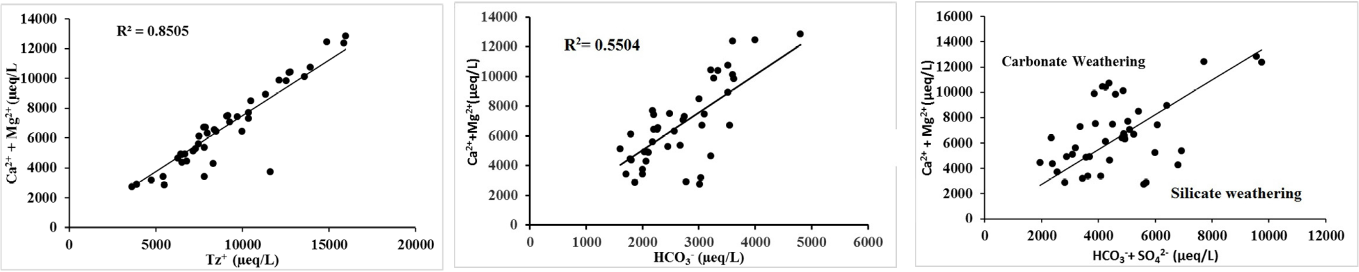

Fig.2. Sactter diagram of groundwater between **(a)** Ca^{2+} + Mg^{2+} vs. Tz^+ **(b)** HCO_3^- vs. Ca^{2+} + Mg^{2+} **(c)** carbonate weathering vs. silicate weathering process realtion between $(HCO_3^- + SO_4^{2-})$ vs $(Ca^{2+} + Mg^{2+})$.

Table 3. Saturation Index and water quality for irrigation uses in the groundwater samples of Jamshedpur Urban Agglomeration

ID	Saturation Index									Irrigation purposes						
	Aragonite	Calcite	CO_2(g)	Dolomite	Fluorite	Halite	N_2(g)	NH_3(g)	O_2(g)	CAI-1	CAI-2	SAR	%Na	PI	KI	MH
1	-0.61	-0.46	-1	-1.29	-2.07	-6.85	-0.74	-28.92	-41.27	0.64	0.63	0.64	17.56	17.67	0.21	24.24
2	-0.65	-0.51	-1.24	-1.17	-2.58	-6.75	-0.21	-29.13	-40.63	0.70	0.74	0.70	20.30	20.45	0.25	34.44
3	-0.52	-0.38	-1.26	-0.88	-1.43	-7.07	-0.56	-29.46	-40.43	-1.20	-0.48	0.90	29.39	29.30	0.40	35.53
4	-1.22	-1.07	-0.62	-2.01	-2.38	-7.32	-0.62	-28.17	-42.19	-0.02	-0.01	0.96	32.39	32.84	0.46	50.16
5	0.19	0.34	-1.63	-0.41	-0.67	-7.18	-0.42	-30.83	-38.51	0.67	0.39	0.55	13.48	13.89	0.15	5.69
6	-0.48	-0.33	-1.57	-0.68	-1.5	-6.84	-0.45	-30.27	-39.27	0.62	0.70	0.82	25.61	26.07	0.34	41.45
7	-0.65	-0.51	-0.93	-1.4	-1.34	-7.15	-0.23	-28.81	-41.07	-0.21	-0.08	0.93	32.52	31.05	0.43	23.34
8	-1.24	-1.1	-1.19	-2.09	-1.44	-6.98	-0.2	-28.83	-41.03	0.85	0.98	0.78	23.86	24.59	0.30	48.15
9	-0.32	-0.17	-1.45	-1.08	-1.77	-7.38	-0.53	-30.01	-39.67	-1.81	-0.22	0.92	30.76	30.50	0.43	12.05
10	-0.42	-0.28	-1.6	-0.59	-2.16	-6.53	-0.59	-30.19	-39.47	0.72	0.96	0.69	23.50	19.74	0.24	40.23
11	-0.05	0.09	-1.56	-0.55	-1.93	-6.58	-0.41	-30.04	-39.55	0.57	0.52	0.61	16.20	16.16	0.19	11.89
12	-0.29	-0.15	-1.71	0.57	-1.92	-6.88	-0.2	-30.93	-38.23	-0.76	-0.15	0.73	21.72	21.62	0.27	84.28
13	-0.47	-0.33	-1.49	-0.68	-0.88	-6.17	-0.52	-30.28	-39.31	0.52	0.54	1.35	48.08	48.28	0.91	41.21
14	0.47	0.61	-2.05	0.4	-1.41	-5.36	-0.33	-31.62	-37.39	-0.24	-0.14	0.72	21.48	21.17	0.26	9.97
15	-1.02	-0.88	-1.43	-1.18	-2.58	-6.84	-0.41	-29.62	-40.11	0.53	0.61	0.79	24.35	24.61	0.32	73.63
16	-0.77	-0.62	-1.47	-1.33	-0.33	-6.36	-0.44	-29.85	-39.83	0.14	0.18	1.53	56.11	54.43	1.16	37.68
17	0.14	0.28	-1.74	-0.18	-1.14	-6.6	-1.07	-31.48	-38.07	0.76	1.06	0.82	25.91	25.99	0.33	11.71
18	-0.21	-0.06	-1.28	-0.62	-1.79	-7	-0.19	-29.42	-40.23	-0.02	-0.01	0.65	17.97	17.68	0.21	19.01
19	-0.6	-0.46	-1.5	-0.77	-2.01	-6.4	-0.5	-29.81	-39.91	0.66	1.01	0.81	25.48	25.05	0.33	50.33
20	-0.16	-0.01	-1.37	-0.25	-1.94	-6.6	-0.54	-30.02	-39.67	0.57	0.49	0.71	20.93	20.63	0.25	30.69
21	-0.12	0.03	-1.92	-0.3	-2.02	-6.83	-1.45	-31.37	-38.47	0.64	0.89	0.65	17.79	17.75	0.21	24.62
22	-0.32	-0.18	-1.68	-0.45	-2.48	-6.66	0.04	-30.18	-39.07	0.70	0.81	0.73	21.42	21.48	0.26	36.85
23	-1.05	-0.91	-1.03	-2.12	-1.74	-7.41	-1.69	-28.85	-41.99	-1.20	-0.55	0.78	23.94	23.93	0.31	26.87
24	-0.88	-0.73	-1.62	-1.21	-2.14	-6.48	-0.92	-30.33	-39.51	-2.90	-2.28	2.04	67.73	67.88	2.08	57.30
25	-0.2	-0.05	-1.36	-1.16	-0.61	-7.11	-0.98	-30.12	-39.83	0.67	0.46	0.57	14.29	14.62	0.16	6.09
26	-0.83	-0.69	-1.22	-1.3	-1.33	-6.66	-0.56	-29.28	-40.67	0.62	0.81	0.87	28.06	28.40	0.38	46.95
27	-0.08	0.06	-1.8	-0.22	-1.25	-1.51	0.07	-30.79	-38.23	-2.39	-0.50	0.96	33.92	32.20	0.46	24.87
28	-0.52	-0.38	-1.89	-0.61	-1.36	-6.89	0.06	-30.83	-38.19	0.85	1.00	0.80	24.94	25.58	0.32	51.06
29	-0.77	-0.63	-1.13	-2.06	-1.98	-6.26	0.27	-28.5	-41.15	0.86	1.88	0.85	27.42	27.24	0.36	10.25
30	-0.55	-0.41	-1.01	-1.03	-2.52	-6.44	-0.67	-29.15	-40.91	0.35	0.30	1.00	35.59	33.94	0.50	30.98
31	-0.3	-0.15	-1.08	-0.93	-1.75	-6.37	-0.88	-29.2	-40.99	0.57	0.52	0.68	19.34	19.27	0.23	14.75
32	-0.76	-0.61	-1.56	-0.76	-17.85	-6.83	-2.14	-30.91	-39.55	0.74	0.83	0.66	18.33	18.55	0.22	68.20
33	-0.74	-0.6	-1.06	-1.52	-1.43	-6.76	-1.29	-29.58	-40.75	0.52	0.36	1.07	36.84	37.50	0.57	25.95
34	-0.19	-1.65	-1.65	-0.8	-2.27	-6.72	0.12	-29.81	-39.51	-0.24	-0.19	0.81	25.44	24.96	0.33	12.43
35	-0.8	-0.65	-1.57	-0.81	-2.74	-6.99	0.17	-29.87	-39.39	0.53	0.47	0.77	23.41	23.82	0.30	69.94
36	-0.8	-0.65	-1.57	-0.81	-2.74	-6.99	0.17	-29.87	-39.39	0.14	0.14	1.27	47.10	45.61	0.81	26.24
37	-0.55	-0.41	-1.47	-1.61	-1.21	-6.68	0.24	-29.36	-40.03	0.76	1.26	0.78	24.31	24.24	0.31	10.76
38	-0.56	-0.42	-0.87	-1.32	-1.77	-6.99	-0.89	-28.63	-41.75	-0.02	-0.01	0.65	18.21	17.92	0.21	19.33
39	-0.54	-0.39	-1.36	-0.73	-2.9	-6.55	-0.27	-29.58	-40.07	0.66	0.82	0.77	23.72	23.45	0.30	45.78
40	-0.76	-0.61	-1.27	-1.53	-2.04	-6.57	-0.4	-28.87	-41.11	0.71	1.13	0.67	18.86	18.53	0.22	26.95
41	-0.11	0.03	-1.45	-0.24	-2.2	-6.97	-2.07	-30.81	-39.63	-0.86	-0.40	0.76	22.84	22.62	0.29	26.85
42	-0.57	-0.42	-1.18	-1.3	-2.5	-7.04	-0.4	-28.86	-41.11	-0.09	-0.06	0.66	18.39	18.27	0.22	20.44

study area. High loading of Cl^- (+0.760) is due to release of effluents from large number of industrial effluents.

The factor 2 accounts for 14.563% of the total variance with Eigen value 1.748. It is mainly associated with high loadings of Ca^{2+}, EC and TDS indicating alkaline condition favors dissolution of calcium in the groundwater. The higher loading Ca^{2+} is might be due to carbonate weathering (Naaz et al. 2016). This factor also shows that the geogenic parameters determine the calcium ion of the groundwater that favors substitution reaction (Handa 1975; Apambire et al. 1997).

The factor 3 accounts for 12.230% of the total variance with Eigen value 1.468. It shows high loadings of only K^+ (+0.675) and Na^+ (+0.790) indicating independent geogenic source of dissolved potassium in groundwater and possible sources of Na^+ in groundwater are dissolution of rock salts and weathering of sodium bearing minerals.

The factor 4 accounts for 11.672% of the total variance is mainly associated with high loadings of F^- indicating alkaline condition

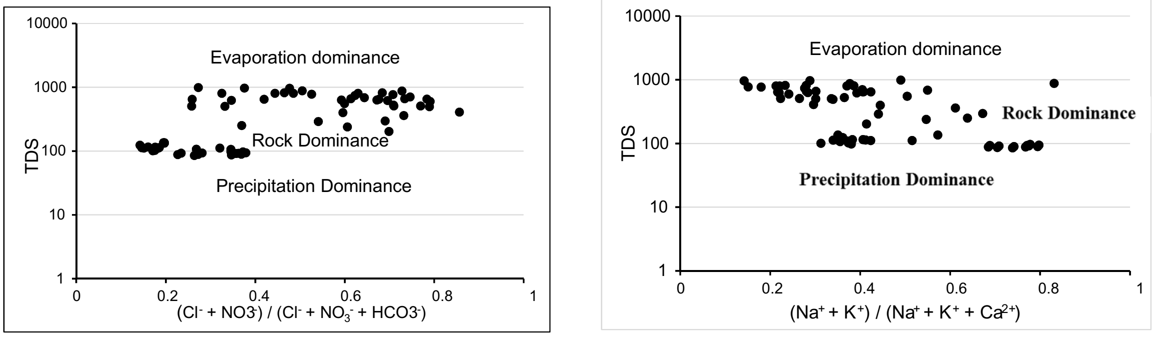

Fig.3. Gibbs diagram showing the mechanism controlling the geochemistry of groundwater in Jamshedpur Township area.

Table 4. Factor loadings for significant principal components (Eigen value >1).

Parameters (s)	Component					
	F1	F2	F3	F4	F5	F6
pH	.044	-.059	.068	-.066	-.080	**.920**
EC	-.710	**.540**	-.148	.147	-.075	.074
TDS	-.654	**.559**	-.282	.108	.090	.129
Na	-.136	.072	**.790**	-.222	-.070	.124
Ca	.042	**.865**	.122	.094	.081	-.055
K	.236	-.092	**.675**	.307	.057	-.023
Mg	.172	-.193	.080	-.867	.084	.136
F	.033	-.559	.250	**.567**	.145	.303
Cl	**.760**	.109	-.182	.211	-.302	-.019
SO4	**.821**	.110	.012	-.275	.149	.244
NO3	.158	.013	-.366	.124	-.606	.272
HCO3	.030	.063	-.171	.038	**.879**	.042
Eigen Value	2.318	1.748	1.468	1.401	1.316	1.134
% of variance	19.315	14.563	12.230	11.672	10.965	9.449
Cumulative %	19.315	33.879	46.109	57.781	68.745	78.194

favors dissolution of fluoride in the groundwater. The higher alkalinity of the groundwater favor the leaching and dissolution of $F^{''}$ from fluorite, fluorapatite and silicates (Selvakumar et al. 2017). This factor also shows that the geogenic parameters determine the alkalinity of the groundwater that favors substitution of fluoride for hydroxyl ion on clay surfaces at high pH (Jacintha et al. 2016; Hamzah et al. 2017). At high pH, OH^- could displace F^- ions and resulted in desorption of F^- into the aqueous phase or limited the F^- sorption capacity (Jacks et al. 2005).

The factor 5 accounts for 10.965 % of the total variance is mainly associated with high loading of HCO_3^- (0.879) is mainly due to carbonate weathering as well as dissolution of carbonic acid in the aquifers (Singh, 2017).

The factor 6 accounts for 9.449 % of the total variance is mainly associated with high loading of pH (0.920) is mainly due to substitution/displacement reaction between cation/anion in the groundwater.

Saturation Index

Saturation index (SI) is defined as the logarithm of the ratio of ion activity product (IAP) to the mineral equilibrium constant at a given temperature and expressed as

$$SI = \log (IAP/Ksp)$$

Where IAP is the ion activity product and Ksp is the solubility product of the mineral.

The computed SI values for Argonite vary from -1.24 to 0.47 reveals that it is formed by biological and physical processes, including precipitation freshwater environments. The SI of dolomite is ranged from -2.12 to 0.57 explains the presence of calcareous minerals in the study area. The saturation index (SI) express the intensity of soluble minerals and it is quantitatively described as the deviation of water from equilibrium with respect to dissolved minerals. The SI equals to zero if the water is exactly saturated with the dissolved mineral (equilibrium state); while positive values of SI indicate over-saturation (precipitation state), and negative ones indicate under-saturation (dissolution state). The computed SI values for CaF_2 and $CaCO_3$ vary from -1.65 to 0.61 and -2.12 to 0.57, respectively. The SI for $CaCO_3$ versus the SI for CaF_2 indicates variation of the relationship between $CaCO_3$ and CaF_2 saturation indexes (Fig.5). These variations are as follows: (1) only 45% groundwater locations are approaching equilibrium with respect to under-sutured $CaCO_3$ and CaF_2, (2) only 30% sampling locations are under-saturated with respect to both $CaCO_3$ and CaF_2 (3) 16% sampling locations are approaching equilibrium with respect to over-saturated $CaCO_3$ and under-statured CaF_2, (4) all sampling locations are under-statured with respect to CaF_2, and (5) overall 76 % and 16 % sampling locations are over-saturated and

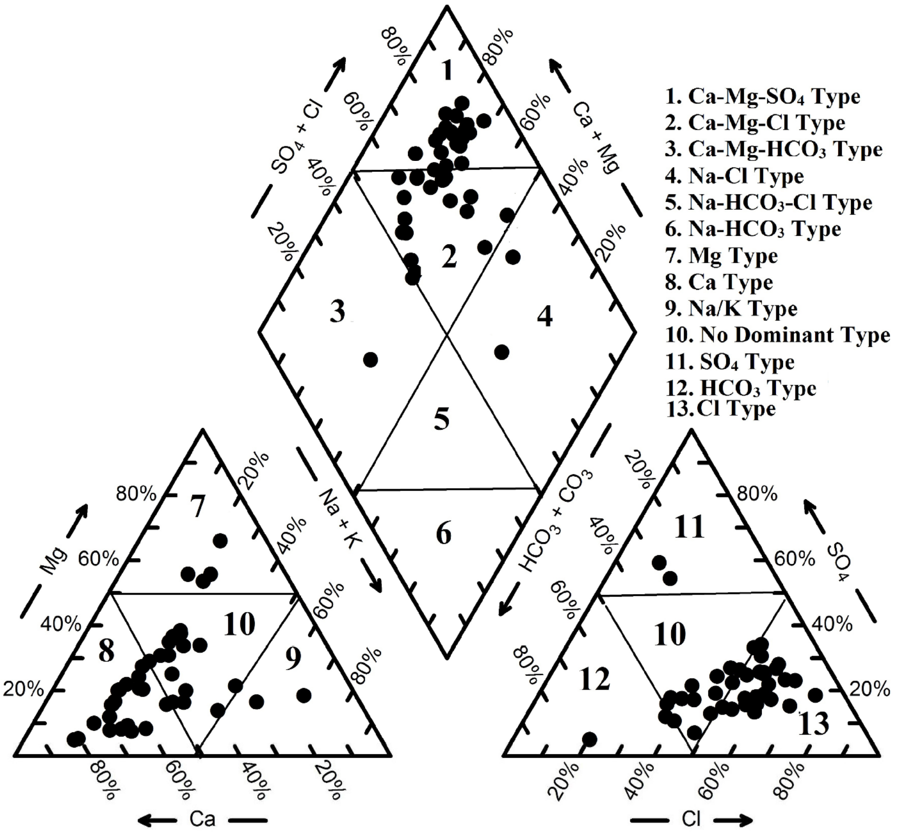

Fig.4. Piper diagram showing water type in the study area.

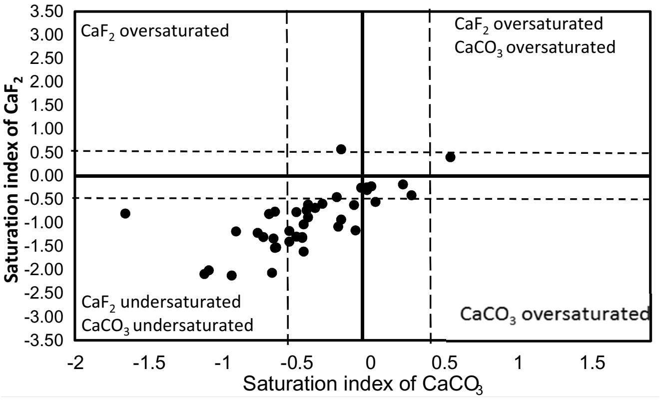

Fig.5. Plot of calcite saturation index (SI_c) versus fluorite saturation index (SI_F).

under-saturated, respectively with $CaCO_3$ and CaF_2. The super-saturation of carbonate phases may result from gypsum dissolution after the water was already saturated with respect to carbonate minerals. Such supersaturation could lead to the precipitation of Ca and/or Ca–Mg carbonate. This explains the presence of calcareous nodules, which contain a mixture of calcite in the study area.

Potability of Groundwater for Drinking and Domestic Uses

The physical and chemical parameters of the analytical results of groundwater were compared with the standard guideline values recommended by the World Health Organization (WHO 2009) and Bureau of Indian Standards (BIS 2012) for drinking and public health (Table 1). The pH of the groundwater samples (6.2–7.4) are within the safe limit of 6.5–8.5, prescribed for drinking water. The EC values (271 µS/cm -1364 µS/cm) of the groundwater samples within maximum permissible limit recommend by WHO 2009. The TDS exceeded the desirable limit (500 mg/l) in 81% of the samples and only 19% of groundwater samples are within limits. The value of dissolved sodium ion (17 mg/l – 178 mg/l) in the groundwater are below maximum permissible limit i.e., 200mg/l. The Ca^{2+} in the groundwater varies from 28 mg/l to 219 mg/l; 98% of the samples are safe for drinking purposes according to BIS 2012 and WHO 2009. Only 2% of the samples are beyond the safe limit for uses i.e., 200mg/l. For K^+ all the samples are within limits. 98% of groundwater samples are within desirable limit and only 2% of the samples are within the maximum permissible limit. Fluoride is an essential element for maintaining normal development of teeth and bones. However, higher F^- concentration causes dental and skeletal fluorosis such as mottling of teeth, deformation of ligaments and bending of spinal chord (Tiwari and Singh 2014). Concentrations of F^- are within limit of 98% of the samples only 2% of the groundwater samples fall beyond the maximum permissible limit. Concentration of Cl^- is higher than the recommended level of 250 mg/l in 12 % of the groundwater samples. Excessive NO_3^- in drinking water can cause a number of disorders including methaemoglobinaemia in infants, gastric cancer, goitre, birth malformations and hypertensions (Majumdar and Gupta, 2000). The concentration of nitrate are within desirable limits according BIS 2012. Concentration of sulphate in 3% of the groundwater samples exceeds the recommended level of 250 mg/l, restricting direct use for drinking and domestic uses. Higher concentration of sulphate in drinking water is associated with respiratory problems (Subba-Rao 1993). High SO_4^{2-} concentration may have a laxative effect with excess of Mg^{2+} in water. Groundwater with 200–400 mg/l sulphate has a bitter taste and those with 1000 mg/l or more can have laxative effect. The recommended limit for HCO_3^- in drinking water is 300 mg/l (WHO 2009). Concentrations of HCO_3^- in the groundwater of Jamshedpur township is less than that recommended limit.

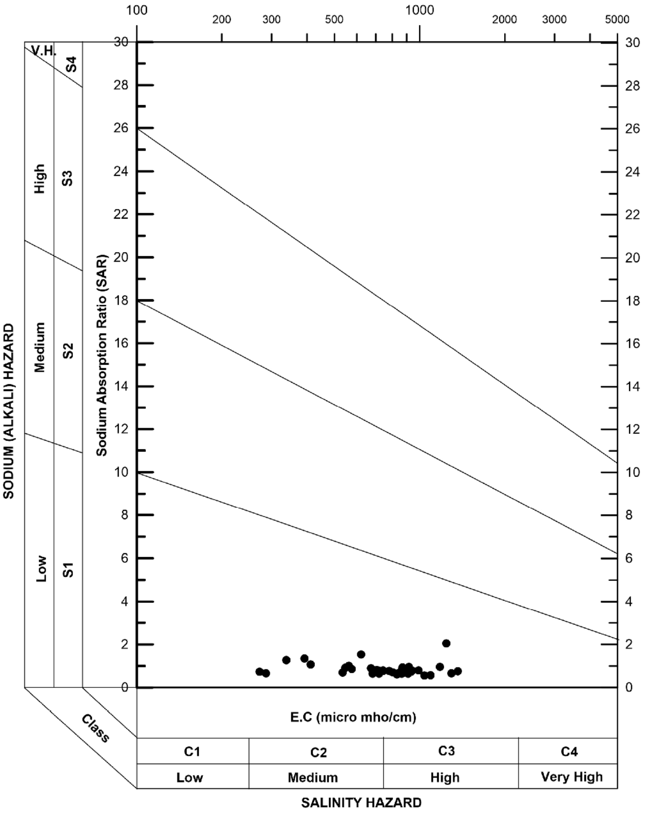

Fig.6. US Salinity diagram for classification of irrigation waters (after Richards, 1954).

Suitability for Irrigation Uses

The water quality evaluation in the area of study is carried out to determine their suitability for agriculture purposes. Total salt concentration (EC), sodium adsorption ratio (SAR), percentage sodium (%Na), permeability index (PI), Kelley index (KI) and magnesium hazard (MH) are the important parameters which are widely used in assessing the suitability of water for irrigation uses (Ayers and Westcot, 1985).

The US Salinity Laboratory (USSL 1954) proposed a diagram for studying the suitability of groundwater for irrigation purposes based electrical conductivity and sodium adsorption ratio. In this diagram, irrigation water are classified as low (EC = < 250 µS/cm), medium (EC=250-750 µS/cm), high (EC=750-2250 µS/cm) and very high (EC=2250-5000 µS/cm), salinity classes. The sodium or alkali hazard expressed in terms of SAR and estimated by the following formula

$$SAR = Na/\ [(Ca+Mg)/2]^{0.5}$$

where concentration in meq/l

On the basis of SAR value, water are classified into low (SAR<6), medium (SAR 6-12), high (SAR 12-18) and very high (SAR>18) alkali water. The calculated value of SAR in the study area ranges from 0.55 to 2.04 with mean value of 0.84 (Table 3).

The plot of data on US salinity diagram in which EC is taken as salinity hazard and SAR as alkalinity hazard shows that 38% of the samples fall in C2S1 categories indicating good to permissible quality of water for irrigation uses (Fig. 6). Due to low sodium and medium salinity, water of C2S1 class can be used for irrigation purpose on almost all soil with little danger of sodium problem. About 62 % of the samples fall in the categories C3S1, indicating high salinity and low alkali water. High salinity water (C3) cannot be used on soils with without special salinity control measures. Such water can be used to irrigate salt-tolerant and semi-tolerant crop under favorable drainage conditions.

Percent sodium (%Na) is widely used for evaluation the suitability of water quality for irrigation (Wilcox 1955). High percentage of Na^+ with respect to (Ca^{2+}, Mg^{2+}, Na^+) in irrigation water, causes deflocculating and impairing of soil permeability (Panigrahy et al. 2014). The Indian Standard (BIS 2012) recommends a maximum sodium percentage (%Na) of 60% for irrigation water. When the concentration of sodium is high in irrigation water, sodium ions tend to be adsorbed by clay particles, displacing Mg^{2+} and Ca^{2+} (Raju et al. 2009). The percentage sodium (%Na) can be determined by the following formula:

$$\%Na = Na + K / (Ca + Mg + Na + K) \times 100$$

where concentration is in meq/l.

The percent sodium in the study area ranged from 13 to 67% (average 26%). The plot of analytical data on the Wilcox diagram relating EC and %Na show that water samples fall in all classes. About 42% of the water samples are excellent to good and 58% good to permissible quality, which may be used for irrigation purposes without any hazard (Fig. 7).

Permeability index (PI) is another parameter for assessing the suitability of water for irrigation uses. PI can be determined by the following formula:

$$PI = (Na^+ – HCO_3) / (Ca + Mg + Na) \times 100$$

where concentration is in meq/l.

Doneen (1964) classified irrigation water in three PI classes. Class-I and class-II water types are suitable for irrigation with 75 % or more of maximum permeability, while class-III type of water, with 25 % of maximum permeability, are unsuitable for irrigation.

On this basis, 55% of the water samples fall in class-I and 35 % in class-II in the Doneen's chart implying that the water is of good quality for irrigation purposes with 75 % or more of maximum permeability (Table 3).

Kelley index (KI) and magnesium hazard (MH) are also used in classification of water for irrigation. The KI and MH can be determined by the following formulas:

$$KI = Na^+ / (Ca^{2+} + Mg^{2+})$$
$$MH = Mg / (Ca + Mg) \times 100$$

Water with >1.0 Kelley's ratio indicates an excess level of sodium and is unsuitable for irrigation (Kelley 1946). Water with Kelley's ration of <1.0 is only considered suitable for irrigation. The Jamshedpur township 0.15 to 2.08 with mean value of 0.36, thus 95% of groundwater samples are suitable for irrigation uses based on the KI values. A magnesium ratio > 50% is considered as harmful and unsuitable for irrigation (Szabolcs and Darab, 1964; Sreedevi, 2004). The groundwater had MH values 6% to 84% with mean of 32%. Since 14% of the groundwater samples have MH value >50% which it make it unsuitable for irrigation.

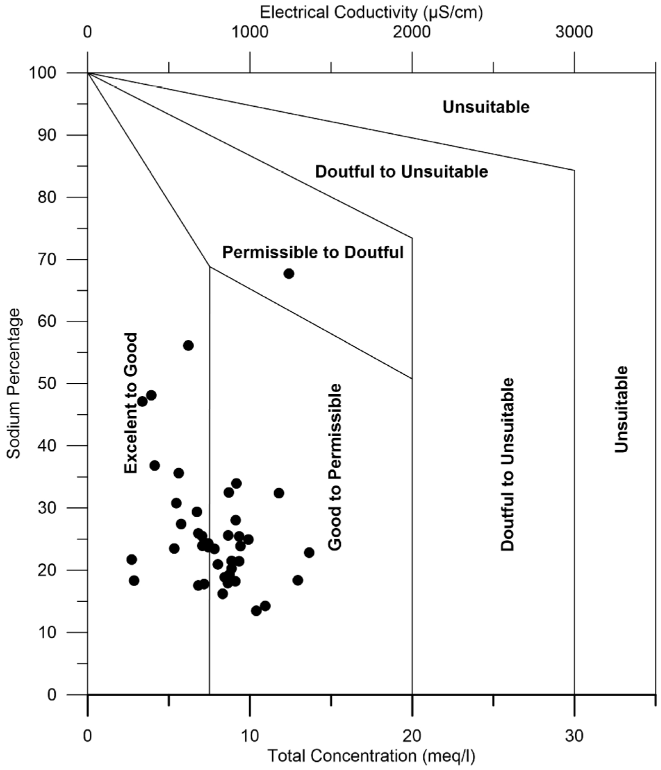

Fig.7. Plot of Sodium percent versus electrical conductivity (after Wilcox, 1955).

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