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Statistical Evaluation and Hydrogeochemistry of Groundwater from Western Part of Chandrapur District, Maharashtra with Special Emphasis on Human Health Risk Assessment

M.P. Jaunjalkar and Y.A. Murkute*

Post Graduate Department of Geology, RTM Nagpur University, Law College Square, Nagpur-440001(MS), India
*(*Corresponding author, E-mail: yogmurkute@rediffmail.com)*

Abstract

The groundwater samples were collected from the phreatic aquifers of PG2 watershed of western part Chandrapur district, Maharashtra. The geogenic processes like dissolution of calcium rich minerals are responsible for increase of Ca^{2+} content in groundwater. In the groundwater samples, HCO_3^- and SO_4^{2-} are the prevailing dominant anions. The TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^- as well as Cl^- ions present in basement rocks have been attributed to the geogenic factor through the factor analysis. K^+, SO_4^{2-} as well as NO_3^- correspond to fertilizers and soil amendments used by people to enhance crop production, which is regarded as anthropogenic input. The silicate weathering at water-rock interface is the main process of generation of various solutes in groundwater. The multiple regression analysis expresses the TDS as a linear function of the ions and Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- contribute significantly to the bulk chemical composition of the groundwater from the study area. The health hazard quotient (HQ) for children (4.94%) and adults (7.95%) denotes the intensity of different health risk vulnerable zones at a specific site.

Keywords: Rock-Water Interaction, Silicate Weathering, Statistical Evaluation, Health Risk Assessment, Chandrapur District, Maharashtra

Introduction

Groundwater is the precious natural resource which is also vital for the existence of life; further more it is the only reliable water source in areas of low rainfall also. Groundwater use in India has increased up to 66% in irrigation, and 85% for drinking and domestic purposes. More than 60% of agricultural exercises in India are still dependent on monsoon rain. With the projected increase of population, intern the increased demand of food grain production and hence relying upon drinking/domestic/irrigation water are likely to be doubled by 2050. Consequently, the demands on groundwater are likely to increase, particularly in drought affected areas, specifically dependent only on rainfall. Thus, the groundwater, even though, a replenishable resource, desires sensible and systematic management for the sustainable development. The quality and quantity of groundwater depend on several factors. The movement and storage of groundwater are solely dependent on the geologic factors like voids, interstices in mineral grains, interlocking of grains, stratification, structure and other water-bearing properties of rocks. The geochemical reactions taking place within groundwater, reactions with the rocks and soils, residence time of groundwater with mineral phases, climate and anthropogenic activities control the overall groundwater quality. In past several years, many researchers (Gogulothu *et al.*, 2022) have focused on the geochemical characterization of groundwater using various geo-statistical, geochemical and graphical models. Similarly, the anthropogenic activities responsible for the groundwater contamination from phreatic aquifers tend to be more polluted than deeper confined aquifers. The return flow from irrigation, percolation of insecticides and pesticides as well as the situations of scanty rainfall along with other natural processes affect the groundwater quality (Xu *et al.*, 2018). The groundwater contamination and its threat to human health has now been a major concern of various geochemical, geostatistical and health risk assessment investigations (Wu *et al.*, 2015; Xu *et al.*, 2018; Li *et al.*, 2012, 2018; Murkute, 2022). Similarly groundwater modeling has also been utilized for proper understanding of subsurface contamination (Bhatnagar *et al.*, 2023).

PG2 watershed, which lies on the westernmost tip of Chandrapur District of Maharashtra, gets inadequate supply of fresh water in some parts of watershed or totally deficient in fringe areas. The groundwater which can be abstracted from phreatic aquifers is solely the prime source for drinking, domestic and irrigation utilization from this area. Also, there is inadequate information of the geochemical behavior of groundwater as well as the geogenic and anthropogenic contaminants from this area. Hence, it has been attempted here to comprehend the hydrogeochemical behavior of

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groundwater also by involving statistical evaluation and human health risk assessment from the study area.

Study Area

PG2 watershed (latitude 19º 38' 32": 19º 48' 23" N and longitude 78º 50' 12": 79º 05' 51" E) sprawled over 339.98 km^2, lies 250 km in southwest direction of Nagpur city (Fig. 1). This area experiences the semi-arid climatic conditions, where maximum temperature flares up to 46ºC in summer seasons while it drops down up to 8ºC in winter season (http://imdnagpur.gov.in). The average annual rainfall is 1200 mm in the monsoon season wherein the humidity ranges between 7% in dry seasons to 91% in rainy season.

Geology and Hydrogeology

The Neoprotreozoic Penganaga limestones and limestone-shale units (~ 82%) are the oldest rocks in the study area. These units are well exposed in entire northern and central part of watershed. The dugwells penetrating the Penganga limestone have an average depth between 7 to 18 meters below ground level (mbgl) and have diameters ranging from 2.5 to 5.5 m. These wells have the groundwater discharge of 50 to 300 m^3/ day (GSDA, 2015). The Lower Gondwana Supergroup of rocks (Lr. Permian to Lr. Cretaceous) are disposed on the southern boundary at deeper depth, however these rocks are covered by Deccan Trap basaltic flow (Up. Cretaceous to Lr. Eocene) (Fig.1). At places, intertrappean beds, partially covered by Basaltic flows, are also uncovered. The Deccan basaltic lava-flows exhibit vesicular nature and also disposed with deep weathering as well as well developed joints. The average depth of dugwells in basaltic lava flows ranges from 9 to 21 mbgl and the yield shows greater variation from 75 to 100 m^3/ day (GSDA, 2015). The sand, silt and clays of local Alluvium are noted at north-western side of the study area, particularly in river sections.

Materials and Methods

The 30 dug wells throughout the watershed area were identified and the groundwater samples were collected in pre-monsoon season of 2022 from each well in polyethylene bottles of capacity 1000 ml. The temperature, pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in the field itself by portable-meters. The standard guidelines (BIS, 2022; WHO, 2017) were used for the standard analytical procedures, wherein the calcium (Ca^{2+}), magnesium (Mg^{2+}), chloride (Cl^-), bicarbonate (HCO_3^-) from the groundwater samples were determined by the titration method. The concentrations of sodium (Na^+) and potassium (K^+) were measured by the flame photometer. Sulphate (SO_4^{2-}), nitrate (NO_3^-) and fluoride (F^-) were determined by UV-visible spectrophotometer. The parameters like Total dissolved solids (TDS) and Total Hardness (TH) were evaluated by the mathematical computations. The analytical procedure was maintained by running known standard after every five samples and hence the charge balance error was found to be less than 5%. The concentrations of all ions are presented in Table 1. The bivariate correlation and factor analysis were carried out for all the groundwater samples to appraise statistical evaluation. The Principal Component Analysis (PCA) with varimax rotation option was used in factor analysis (Kaiser, 1958). The factor loadings help to determine the relative contributions of chemical constituents to

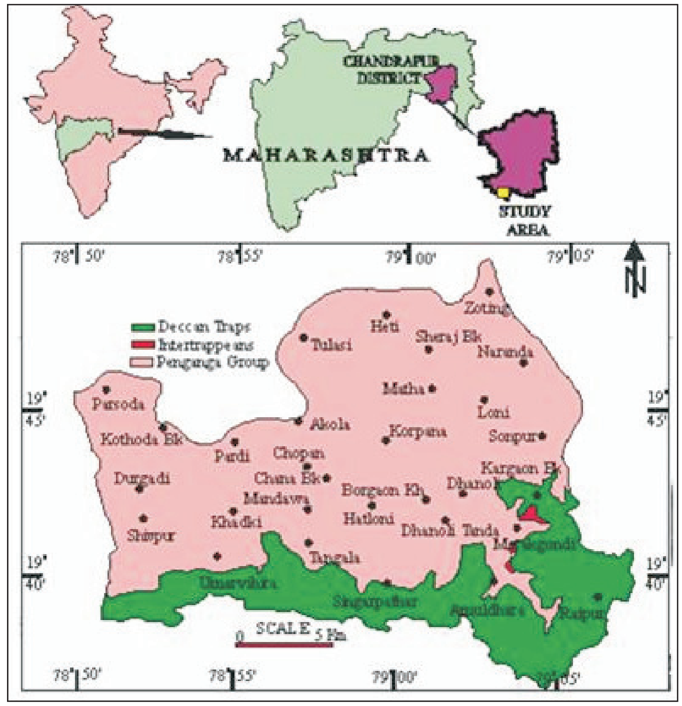

Fig.1. Location and geological map of PG2 Watershed

bulk groundwater chemistry (Najafabadi *et al.*, 2014). Cluster analysis classifies the variables into a set of distinct clusters.

The concentrations of NO_3^- and F^- have been taken for computation of health hazard quotient (HQ) for children and adults (male and female both) (Li *et al.*, 2019; Wu *et al.*, 2020; Subba Rao *et al.*, 2021; Gugulothu *et al.*, 2022) following equations 1 and 2 suggested by USEPA (2014) (Explanations of the abbreviated terms and their values are given in Table 2.)

$$\text{Average Daily Dose (Dd)} = Ci \times Ir \times Ed \times Ef / Bw \times Et \quad \text{(Equation – 1)}$$

$$\text{Health hazard quotient (HQ)} = Dd / Rd \quad \text{(Equation – 2)}$$

Table 1: Analytical data of cations and anions with physical and computed parameters from PG2 watershed (30 samples)

Sr. No.	Parameter	Min	Max	Average	STD	Covariance
1	pH	7.60	8.70	8.14	0.31	3.83
2	EC	897.40	1967.50	1405.77	338.24	24.06
3	TDS	574.34	1259.20	899.69	216.47	24.06
4	TA	134.00	671.00	428.00	167.92	39.23
5	TH	181.04	788.40	436.14	140.59	32.24
6	Ca^{2+}	36.50	160.10	75.88	28.99	38.21
7	Mg^{2+}	21.90	97.87	60.11	18.93	31.49
8	Na^+	14.80	70.70	40.21	12.68	31.54
9	K^+	0.10	5.30	1.61	1.58	98.01
10	HCO_3^-	157.07	670.17	410.08	146.10	35.63
11	Cl^-	49.15	289.65	159.79	73.15	45.78
12	SO_4^{2-}	127.40	656.90	305.65	145.98	47.76
13	NO_3^-	49.50	182.50	135.71	40.15	29.58
14	F^-	0.50	1.90	0.99	0.41	41.54
15	CA-I	0.14	0.96	0.69	0.19	26.92
16	CA-II	0.01	0.43	0.15	0.10	66.48
17	Gibbs Cations	0.16	0.48	0.36	0.06	17.71
18	Gibbs Anions	0.11	0.63	0.29	0.12	42.38

Gibbs Cations: (Na+K)/ (Na+K+Ca), Gibbs Anions: ($Cl/(Cl+HCO_3)$), cation and anion values are presented in mg/l.

Table 2: Health hazard quotient details used in present study

Parameter	Abbre-viation	Children	Adults	Units	Reference
Concentration of ion	Ci	49.50 - 182.50 for NO_3^- 0.5 - 1.9 for F^-		mg/l	Present study
Intake rate (Oral)	Ir	0.78	2	l/day	USEPA (2014)
Exposure duration	Ed	12	67	year	WHO (2017)
Exposure frequency	Ef	365	365	days/year	USEPA (2014)
Average body weight	Bw	15	65	kg	ICMR (2009)
Average exposure time	Et	4380	23360	days	USEPA (2014)
Reference dose	Rd	0.06	0.06	mg/kg/day	USEPA (2014)

Physical Parameters and Ion Concentrations

The temperature of each sample, after the abstraction of groundwater from dug wells was measured, which was found to range from 25 to 28ºC. The water samples have pH values ranging from 7.6 to 8.7, indicating dominantly alkaline nature (Table 1). The values of EC found to grade between 897.4 and 1967.50 µS/cm suggesting involvement of several processes in groundwater system. All the groundwater samples have TDS value (574.3 to 1259.2 mg/l) greater than the 500mg/l, the desirable limit of recommended by WHO (2017), signifying contributions from both geogenic and non-geogenic sources. The range of concentration from 181.04 to 788.4 mg/l of TH as $CaCO_3$ exhibits that 73% all the samples have TH value less the desirable limit of 500 mg/l, as suggested by WHO (2017). The Total alkali (TA) values grade from 134 to 671 mg/l, and almost 49% of groundwater samples show TH values exceeding TA. This clearly indicates that the groundwater from the study area is distinguished by noncarbonated hardness, which cannot be removed easily from the water (Murkute, 2022).

Ca^{2+} and Mg^{2+} vary between 36.5 to 161.1 mg/l and 21.9 to 97.87 mg/l respectively and are well within the safe limit as prescribed by WHO (2017) and BIS (2022). Generally, the geogenic processes like dissolution of calcium rich minerals are responsible for increase of Ca^{2+} content in groundwater and according to Subba Rao and Chaudhary (2019), calcic plagioclases are the main source of Ca^{2+}. Besides the loss of carbon dioxide resulting from change in temperature and pressure conditions, reverse ion exchange as well as precipitation also causes the behavioral change in Ca^{2+} content in groundwater. The probable geogenic sources of Mg^{2+} in aquifers are magnesium bearing minerals and the ion exchange processes (Thivya *et al.*, 2018). Ferromagnesian minerals like mica, pyroxene and amphibole present in basement rocks are the geogenic contributors (Gugulothu *et al.*, 2022). In some of the samples Mg^{2+} content exceeds the Ca^{2+} values as reported above; indicate excess use of fertilizers and pesticides along with Mg rich carbonate rock (dolomite) (Mgbenu and Egbueri, 2019). The $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ is the dominance sequence with Ca^{2+} as dominant cation.

The higher concentration of Na^+ is a threat in human body and may be risky to the patients of cardiac, renal and circulatory diseases (Mor *et al.*, 2006). The weathering of some of the mineral suites or individual minerals like plagioclase feldspar as well as ion exchange processes are responsible for Na^+ content in groundwater and it also acts as an indicator, which eventually suggests the salinity concentration. In addition to such geogenic processes, Na^+ content may also leach out from water by the domestic waste and resultants of the agriculture activities. The concentration of Na^+ in the study area that grades from 14.8 to 70.7 mg/l with an average of 40.21 mg/l; points out that Na^+ content is within the permissible limit as prescribed by WHO (2017) and BIS (2022). The concentration of K^+ in the study area grades from 0.10 to 5.30 mg/l with an average of 1.61 mg/l. Chief sources of Na^+ are the sodic plagioclases, household wastes and irrigation return flows; while the potash feldspars (orthoclase and microcline) are the geogenic and potassium fertilizers are anthropogenic sources of K^+ (Karunanidhi *et al.*, 2019).

In the groundwater samples HCO_3^- and SO_4^{2-} are the prevailing dominant anions while NO_3^- and Cl^- are the other minor contributing anions, with the dominance sequence as $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$.

The HCO_3^- content ranges from 157.07 to 670.17 mg/l, with average of 410.08 mg/l. HCO_3^- is formed by release of CO_2 into the soil zone by decay of organic matters, weathering of minerals and from carbonic acid formed by reaction of water with atmospheric CO_2 during rain. In the present study the concentration of SO_4^{2-} has been found in the grade between 127.4 to 656.9 mg/l. The occurrence of SO_4^{2-} in groundwater divulges anthropogenic contamination, such as fertilizers and moreover from oxidation of sulphide minerals added in fertilizers as well as soil conditioners. The NO_3^- concentration shows its variation from 49.5 to 182.5 mg/l with an average value of 135.71 mg/l. The influence of sewage wastes, septic tank leakages, agricultural compost and decay of animal bodies could be the source of NO_3^- (He *et al.*, 2019). It is extremely soluble and exceptionally mobile plant nutrient and its higher level of concentration in groundwater is a potential threat to human health. About 65% of the groundwater samples from the study area have NO_3^- concentration more than the prescribed limit set by WHO (2017) and BIS (2022).

The desire limit for Cl^- in potable groundwater is 200 mg/l (WHO, 1997), which can further be relaxed up to 1000 mg/l (permissible limit) for Indian conditions (BIS, 1991). Thus, excess of Cl^- is an indicator of pollution and also considered as tracer for groundwater contamination. Furthermore, anthropogenic sources like household wastes, septic tank leakages and return flows from irrigation could be the possible source of Cl^- in groundwater (Laxman *et al.*, 2019). The Cl^- content from the groundwater samples range from 49.15 to 289.6 mg/l. 32% of the groundwater samples from the study area exceeds the limit of desirable value of Cl^- as prescribed by WHO (2017).

Statistical Evaluation

Bivariate Correlation

The Pearson's correlation coefficients involving the pairs of groundwater parameters are presented in Table 3. The very positive correlations of TDS with Ca^{2+} (r = 0.76), Na^+ (r = 0.73), K^+ (r = 0.74), SO_4^{2-} (r = 0.75) and Cl^- (r = 0.76) specify prolific input of these ions to the groundwater chemical composition. Positive correlation of pH with alkalinity (r = 0.72), Na^+ (r = 0.31) and F^- (r = 0.69) as well as significant negative correlation between Ca^{2+} and F^- (r = - 0.44) suggests prevalence of alkaline environment for dissolution of

Table 3: Correlation matrix of hydrochemical parameters from study area

	pH	EC	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	NO_3^{-}	HCO_3^{-}	SO_4^{2-}	Cl^{-}	F^{-}
pH	1.00	-	-	-	-	-	-	-	-	-	-	-	-	-
EC	-0.31	1.00	-	-	-	-	-	-	-	-	-	-	-	-
TDS	-0.29	1.00	1.00	-	-	-	-	-	-	-	-	-	-	-
TA	0.72	0.45	0.51	1.00	-	-	-	-	-	-	-	-	-	
TH	-0.25	0.76	0.71	-0.63	1.00	-	-	-	-	-	-	-	-	-
Ca^{2+}	-0.43	0.71	0.76	-0.68	0.92	1.00	-	-	-	-	-	-	-	-
Mg^{2+}	-0.23	0.34	0.41	-0.59	0.92	0.66	1.00	-	-	-	-	-		-
Na^{+}	0.31	0.73	0.73	-0.64	-0.31	0.39	0.21	1.00	-	-	-	-	-	
K^{+}	-0.34	0.51	0.74	0.21	-0.42	0.41	0.35	0.51	1.00	-	-	-		-
NO_3^{-}	0.41	0.68	0.81	0.13	-0.19	0.65	0.52	0.39	0.61	1.00	-	-	-	-
HCO_3^{-}	0.67	0.31	0.31	-0.57	-0.34	0.21	-0.21	0.44	0.45	-0.24	1.00	-	-	-
SO_4^{2-}	-0.31	0.65	0.75	0.21	0.82	0.77	0.51	0.72	0.63	0.33	0.73	1.00	-	-
Cl^{-}	-0.28	0.78	0.76	-0.48	0.31	0.73	0.28	0.79	0.68	0.71	0.31	0.48	1.00	
F^{-}	0.69	-0.23	-0.19	0.73	-0.27	-0.44	-0.35	0.33	0.14	-0.33	0.11	-0.32	0.15	1.00

fluorite (CaF_2) in groundwater and elimination of Ca^{2+} through precipitation of calcite. It is a common finding that the Na^+ rich groundwater contains relatively higher amount of F^-; which is supported by the positive correlation coefficient (r = 0.33) between Na^+ and F^-. Significant positive correlations of TH with Ca^{2+} (r = 0.92), Mg^{2+} (r = 0.92) and SO_4^{2-} (r = 0.73) divulge the contribution of these ions to the hardness of groundwater. Positive correlation of Ca^{2+} with Mg2+ (r = 0.66), SO_4^{2-} (r = 0.77) and Cl^- (r = 0.73); Na^+ with SO_4^{2-} (r = 0.72) as well as Cl^- (r = 0.79) suggest their origin from rock-water interaction. The close positive interrelationship between K^+, SO_4^{2-} and NO_3^{-} with correlation coefficient values of 0.61, 0.63 and 0.68 suggest their derivation from non-geogenic sources like composts, fertilizers, soil conditioners and return flows from irrigation etc. Out of total 90 correlation coefficient values in the matrix (except their own correlation values), 36 times the r-values are greater than 0.50 in the present study. The percentage of these values comes as 'moderate' interaction of chemical paramaters among themselves (r-values < 25% - low; between 25 to 50% - 'moderate'; 50-75% - strong and 75 to 100% - very strong).

Factor Analysis

The factor analysis extracts carried out on the basis of Kaiser Criterion (Kaiser 1958), brings out only three factors are found to be greater than one, and thus, are statistically significant (Table 4). These three factors with eigenvalues of 6.280, 2.800 and 2.821 account for 45.491%, 20.283% and 20.435% of variances respectively, cumulating to 86.208% of the total variance of the hydrogeochemical dataset. These three factors can be used to assess the dominant hydrochemical processes in operation in the study area without losing any significant information.

The first factor has strong positive loadings on TDS (0.941), TH (0.936), Ca^{2+} (0.891), Mg^{2+} (0.911), Na^+ (0.856), HCO_3^- (0.899) and Cl^- (0.846). Since it includes TDS and five ions present in basement rocks, it may be regarded as the geogenic factor. The second factor is significantly loaded on K^+ (0.956), SO_4^{2-} (0.943) and NO_3^- (0.901). Because these three are present in fertilizers and soil conditioners used by people to enhance crop production, this factor may be regarded as anthropogenic. The third factor strongly loaded on pH (0.967), TA (0.912) and F^- (0.942) is obviously alkalinity factor. Though TDS primarily belongs to Factor-1, it shows low affinity (0.334) for Factor-2, which may be due to the contributions of SO_4^{2-} and NO_3^- to TDS.

The factor loadings in three-dimensional rotated space (Fig.2) illustrate the grouping of parameters, wherein the inter-parameter correlation coefficients faithfully match with the inter-parameter distances (Fig.2). *For example*, high correlation (0.932) between Na^+ and Cl^- is represented by their closeness while moderate correlation (0.711) between Mg^{2+} and HCO_3^- is represented by their relatively wide separation.

Health Risk Assessment

In the present investigation, the concentration of NO_3^- found

Table 4: Factor analysis data of groundwater parameters from study area

Groundwater parameters	Factor -1	Factor - 2	Factor - 3
pH	0.023	-0.014	0.967
TDS	0.941	0.334	0.075
TA	0.087	-0.153	0.912
TH	0.936	0.122	0.018
Ca^{2+}	0.891	0.069	0.168
Mg^{2+}	0.911	0.178	-0.105
Na^{+}	0.856	0.156	0.192
K^{+}	0.072	0.956	0.011
HCO_3^{-}	0.899	-0.134	0.088
Cl-	0.846	0.157	0.152
SO_4^{2-}	0.355	0.943	-0.091
NO_3^{-}	0.199	0.901	-0.186
F^{-}	0.183	-0.052	0.942
Eigenvalues	6.280	2.800	2.821
Percentage of total variance	45.491	20.283	20.435
Cumulative percentage of total variance	45.491	65.773	86.208

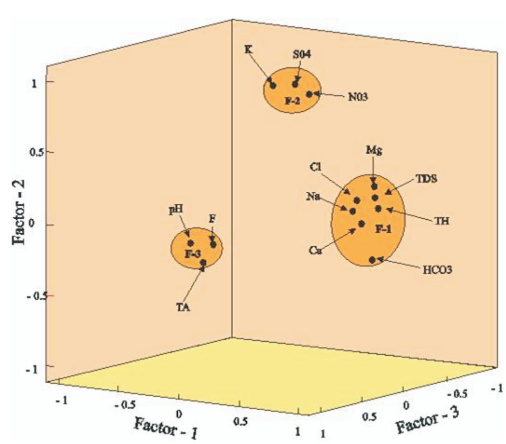

Fig.2. Factor loadings in three-dimensional rotated space for groundwater samples from study area

to vary from 49.50 to 182.50 mg/l. with average value of 135.71mg/l against the permissible limit of 45 mg/l recommended by BIS (2022) and WHO (2017). It is now a medical fact beyond the doubt that the higher concentration of NO_3^- causes methemoglobinemia popularly known as blue baby syndrome. This happens when there is not enough oxygen in the blood that gives bluish appearance to the skin. Table 5 shows the health hazard quotient (H*Q*) by ingestion (oral) of NO_3^- for children, and adults (men and women) in the study area. The health hazard quotient values (mg/kg/day) due to NO_3^- ranges from 0.21 to 3.93 (average: 1.14) for children and from 0.21 to 2.62 (average: 1.11) for adults.

Similarly, in the present investigation, the concentration of F^- found to vary from 0.5 to 1.9 mg/l. with average value of 0.99 mg/l against the permissible limit of 1.0 mg/l recommended by BIS (2022) and WHO (2017). Table 5 shows the health hazard quotient (H*Q*) by ingestion (oral) of F^- for childrens and adults in the study area. The health hazard quotient values (mg/kg/day) due to F^- ranges from 0.45 to 4.2 (average: 1.51) for children and from 0.33 to 2.99 (average: 1.08) for adults.

As per the allowable limit of *HHQ* for non-carcinogenic risk, it should not exceed 1.0 in the drinking water (USEPA, 2014). The present study suggests that NO_3^- may cause adverse health effects in the order of children > adults, which are the potential non-carcinogenic concern. Also, the study suggests that F^- may cause adverse health effects in the order of children > adults, which are the potential non-carcinogenic concern. It is observed that the children are more affected with respect to non-carcinogenic risk compared to adults because of their smaller body weights than adults. Similar observations have also been reported in different regions of the world (Wu and Sun, 2016; Zhang *et al.*, 2018; Karunanidhi *et al.*, 2019).

Rock-Water Interaction

Geogenic Processes

The interrelationship between Na^+ *vs* Cl^- interprets the rock-water interaction (Fig.3a), and points out towards the silicate weathering as well as sources of calcium and bicarbonate (Lakshmanan *et al.*, 2003). The scatter points falling below the equiline reveal high Na/Cl ratio, which is due to water-rock interaction, most likely by feldspar weathering (Zhu *et al.*, 2008). Similarly, the points which lie above the equiline indicate excess of Cl^-, which is caused by human interventions (domestic waste, animal waste, septic tanks, *etc*. The feldspars, pyroxenes and amphiboles are the primary sources of Ca^{2+} in groundwater samples from Deccan Trap while the feldspars, calcite and clay minerals are the probable sources of Ca^{2+} from the sedimentary rock (Murkute and Badhan, 2011). The principal sources of Mg^{2+} in natural water are the magnesium-bearing minerals like pyroxenes, olivine and amphiboles (Singh *et al.*, 2010). The Ca^{2+}+ Mg^{2+} *and* SO_4^{2-}+ HCO_3^- interrelationship (Fig.3b), brings out the two parts, above and below the equiline. The points above the equiline represent the silicate weathering (Lakshmanan *et al.*, 2003), and also suggest excess of SO_4^{2-} + HCO_3^- values, moreover is indicative of excess of alkalinity (HCO_3^-) in the groundwater. Thus, the silicate weathering suggested by the dominance of SO_4^{2-} + HCO_3^- reveals dissolution of silicate minerals, thereby, falling trend calcium content in groundwater (Ramesh and Elango, 2011).

The interrelationship of Ca^{2+} and SO_4^{2-} also divulges the carbonate dissolution, as depicted by the points in fig. 3c below the equiline (Ramesh and Elango, 2011). The change in the concentration of these cations and anions is responsible for dissolution of calcite and gypsum. Moreover, the dispersion of SO_4^{2-} on the pertinent sites is the source of gypsum formation. Many times, the presence of clayey rock material in the aquifer facilitates the reverse cation exchange by liberating Ca^{2+} and Mg^{2+} ions. The interrelationship diagram of Ca^{2+} + Mg^{2+} *and* SO_4^{2-} + HCO_3^- (Fig.3b), also focuses on the reverse ion exchange in the groundwater (Adimallaa and Wu, 2019). The points lying below the equiline are indicative of carbonate dissolution. The scatter plot of Ca^{2+} and SO_4^{2-} (Fig. 3d) reveals the scattering of sampling points which expresses that gypsum dissolution is highly masked by the other factors also for instance recharge water chemistry, precipitation, evaporation

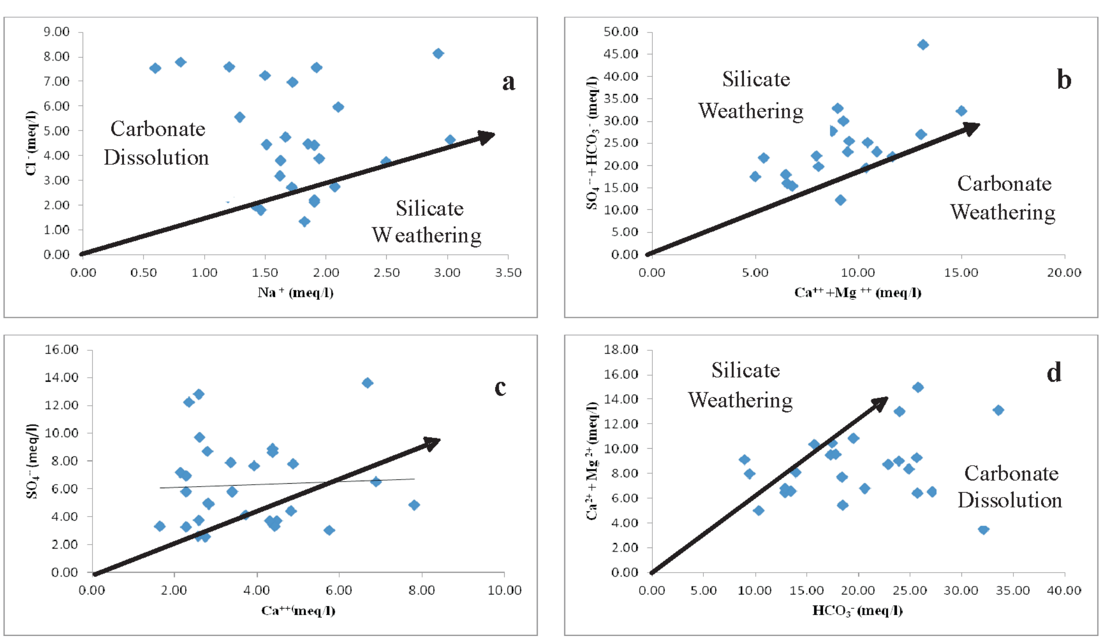

Fig.3. Scatter plots of : **a)** scatter diagram of Na^+ *vs* Cl^-), **b)** Ca^{2+}+ Mg^{2+} *and* SO_4^{2-}+ HCO_3^-, **c)** SO_4^{2-} *vs* Ca^{2+}, and **d)** Ca^{2+}+ Mg^{2+} and HCO_3^-

Table 5: Health risk assessment of nitrate and fluoride for children and adults from study area

Sample Location	Health Risk Assessment for Nitrate							Health Risk Assessment for Fluoride						
	NO_3^- (mg/l)	Children HQ Oral	Children HQ Dermal	THI	Adult HQ Oral	Adult HQ Dermal	THI	F^- (mg/l)	Children HQ Oral	Children HQ Dermal	THI	Adult HQ Oral	Adult HQ Dermal	THI
Parsoda	172.8	1.02E+03	2.69E+00	1.01	7.08E+01	2.38E+00	0.71	1.3	1.58E+00	5.20E-01	2.10	1.10E+00	4.04E-01	1.51
Khatoda Bk	161.1	8.83E+02	2.51E+00	0.88	6.15E+01	2.22E+00	0.61	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Durgadi	151.7	7.83E+02	2.36E+00	0.78	5.46E+01	2.09E+00	0.54	1.2	1.35E+00	5.19E-01	1.87	9.39E-01	4.02E-01	1.34
Shivpur	128.4	5.61E+02	2.00E+00	0.56	3.91E+01	1.77E+00	0.39	1.6	2.40E+00	6.92E-01	3.09	1.67E+00	5.35E-01	2.20
Pardi	51.7	9.10E+01	8.04E-01	0.92	6.34E+01	7.11E-01	0.6	0.5	2.34E-01	2.16E-01	0.45	1.63E-01	1.67E-01	0.33
Khadki	172.9	1.02E+03	2.69E+00	1.02	7.09E+01	2.38E+00	0.71	0.7	4.59E-01	3.03E-01	0.76	3.20E-01	2.34E-01	0.55
Umarvihira	160.6	8.78E+02	2.50E+00	0.88	6.12E+01	2.21E+00	0.61	1.6	2.40E+00	6.92E-01	3.09	1.67E+00	5.35E-01	2.20
Akola	72.7	1.80E+02	1.13E+00	1.81	1.25E+01	1.00E+00	1.26	0.7	4.59E-01	3.03E-01	0.76	3.20E-01	2.34E-01	0.55
Chopan	182.5	1.13E+03	2.84E+00	1.13	7.90E+01	2.51E+00	1.79	0.5	2.34E-01	2.16E-01	0.45	1.63E-01	1.67E-01	0.33
Chana Bk	163.8	9.13E+02	2.55E+00	0.91	6.36E+01	2.25E+00	1.63	0.9	7.58E-01	3.89E-01	1.15	5.28E-01	3.01E-01	0.83
Mandawa	98.4	3.29E+02	1.53E+00	0.33	2.30E+01	1.35E+00	0.23	1.6	2.40E+00	6.92E-01	3.09	1.67E+00	5.35E-01	2.20
Tanagala	121.9	5.06E+02	1.90E+00	0.50	3.52E+01	1.68E+00	0.35	0.5	2.34E-01	2.16E-01	0.45	1.63E-01	1.67E-01	0.33
Sigarpathar	150.1	7.67E+02	2.34E+00	0.76	5.34E+01	2.06E+00	0.53	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Hatloni	93.9	3.00E+02	1.46E+00	0.30	2.09E+01	1.29E+00	0.21	0.9	7.58E-01	3.89E-01	1.15	5.28E-01	3.01E-01	0.83
Korpana	168.6	9.67E+02	2.62E+00	0.97	6.74E+01	2.32E+00	0.67	1.7	2.70E+00	7.35E-01	3.44	1.88E+00	5.69E-01	2.45
Tulsi	78.3	2.09E+02	1.22E+00	0.21	1.45E+01	1.08E+00	1.46	0.9	7.58E-01	3.89E-01	1.15	5.28E-01	3.01E-01	0.83
Heti	151.1	7.77E+02	2.35E+00	0.77	5.41E+01	2.08E+00	0.54	1.1	1.13E+00	4.76E-01	1.61	7.89E-01	3.68E-01	1.16
Sheraj Bk	162.7	1.28E+04	4.12E+02	1.32	8.53E+01	3.64E+02	1.88	0.6	3.37E-01	2.59E-01	0.60	2.35E-01	2.01E-01	0.44
Matha	49.5	3.89E+03	3.81E+01	3.93	2.59E+01	3.37E+01	2.62	1.5	2.11E+00	6.49E-01	2.75	1.47E+00	5.02E-01	1.97
Borgaon Kh	178.1	1.40E+04	4.93E+02	1.44	9.34E+01	4.36E+02	1.77	0.7	4.59E-01	3.03E-01	0.76	3.20E-01	2.34E-01	0.55
Dhanoli T	91.8	7.22E+03	1.31E+02	1.35	4.81E+01	1.16E+02	1.92	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Dhanoli	153.8	1.21E+04	3.68E+02	1.24	8.06E+01	3.25E+02	1.38	1.9	3.38E+00	8.22E-01	4.20	2.35E+00	6.36E-01	2.99
Amuldhara	176.1	1.38E+04	4.82E+02	1.43	9.23E+01	4.27E+02	1.65	0.7	4.59E-01	3.03E-01	0.76	3.20E-01	2.34E-01	0.55
Raipur	168.7	1.33E+04	4.43E+02	1.37	8.84E+01	3.91E+02	1.23	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Marakgondi	160.6	1.26E+04	4.01E+02	1.30	8.42E+01	3.55E+02	1.77	1.2	1.35E+00	5.19E-01	1.87	9.39E-01	4.02E-01	1.34
Loni	99.6	7.83E+03	1.54E+02	1.79	5.22E+01	1.36E+02	1.35	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Kargaon Bk	172.6	1.36E+04	4.63E+02	1.40	9.05E+01	4.10E+02	1.45	0.7	4.59E-01	3.03E-01	0.76	3.20E-01	2.34E-01	0.55
Sonpur	93.8	7.38E+03	1.37E+02	1.75	4.92E+01	1.21E+02	1.03	1.5	2.11E+00	6.49E-01	2.75	1.47E+00	5.02E-01	1.97
Naranda	151.8	1.19E+04	3.58E+02	1.22	7.96E+01	3.17E+02	1.27	0.8	5.99E-01	3.46E-01	0.94	4.17E-01	2.68E-01	0.69
Zoting	131.7	1.04E+04	2.70E+02	1.06	6.90E+01	2.39E+02	1.14	0.5	2.34E-01	2.16E-01	0.45	1.63E-01	1.67E-01	0.33
Min	49.50	9.10E+01	8.04E-01	0.21	6.34E+01	7.11E-01	0.21	0.50	2.34E-01	2.16E-01	0.45	1.63E-01	1.67E-01	0.33
Max	182.50	1.40E+04	4.93E+02	3.93	9.34E+01	4.36E+02	2.62	1.90	3.38E+00	8.22E-01	4.20	2.35E+00	6.36E-01	2.99
Average	135.71	5.07E+03	1.40E+02	1.14	3.39E+01	1.23E+02	1.11	0.99	1.08E+00	4.28E-01	1.51	7.51E-01	3.31E-01	1.08

and anthropogenic sources, as noted by Li *et al.* (2013) and Wu and Sun (2016).

Despite of all the scatter plots the log-log diagram of interrelationship of HCO_3^-/Na^+ *vs* Ca^{2+}/Na^+ (Fig.4a) as well as interrelationship of Mg^{2+}/Na^+ *vs* Ca^{2+}/Na^+ (Fig.4b) clearly points out the dominance of silicate weathering process of solute generation in groundwater regime of study area.

Anthropogenic Interventions

In the groundwater system of the agricultural rural expanse, the irrigation return flow is the prime source of Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, Cl^- and SO_4^{2-}. The negative correlation between NO_3^- and HCO_3^- (Fig.3) indicates the different sources for both the ions, where in NO_3^- is mainly consequential of anthropogenic interventions while HCO_3^- is derivative of lithological inputs (Subba Rao *et al.*, 2019). The strong negative relationship NO_3^- and HCO_3^- for the groundwater samples (Table 3) of the study area clearly demonstrates the anthropogenic interventions in the study area.

Ion Exchange Aspects

The interrelationship diagram of Ca^{2+}+ Mg^{2+} *and* SO_4^{2-}+ HCO_3^- (Fig.3b) suggests the control of anions over the cations and also substantiates the coexistence of ion exchange processes with other processes. To confirm the existence of ion exchange processes chloro-alkaline indices CAI-1 and CAI-2 as proposed by Schoeller (1977) were computed and are presented in Table 2. The values of CAI-1vary from 0.14 to 0.96 with an average of 0.69, while values of CAI-2 vary from 0.1 to 0.43 with average value of 0.11. This combination itself depicts the reverse ion exchange processes, in groundwater regime of study area, governed by the equation 3 proposed by Gugulothu *et al.* (2022) and also confirms the anthropogenic interventions.

Reverse ion exchange $Ca^{2+} + 2NaX \;\; 2Na^{+} + CaX_2$

Equation - 3

Conclusions

The conclusions drawn from present investigations in PG2 watershed of Chandrapur district, Maharashtra are as bellow:

The water samples have pH values ranging from 7.6 to 8.7, indicating dominantly alkaline nature. The range of EC and TDS values suggest involvement of several processes in groundwater system signifying contributions from both geogenic and non-geogenic sources. Almost 49% of groundwater samples show TH values exceeding TA, which clearly indicates that the groundwater from the study area is distinguished by noncarbonated hardness, which cannot be removed easily from the water. The Pearson's

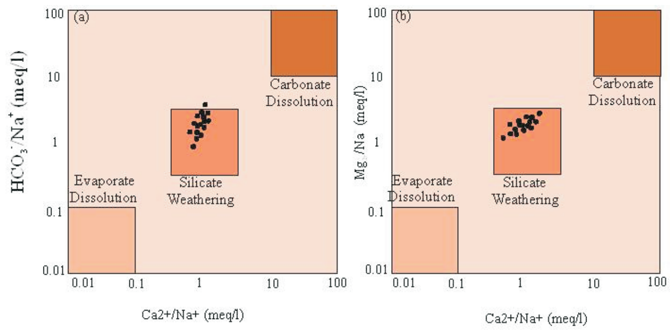

Fig.4. Log-log diagram of interrelationship: a) HCO_3^-/Na^+ *vs* Ca^{2+}/Na^+, b) Mg^{2+}/Na^+ *vs* Ca^{2+}/Na^+

correlation coefficients involving the pairs of groundwater parameters represent very positive correlations of TDS with Ca^{2+}, Na^+, K^+, SO_4^{2-} and Cl^- specify prolific input of these ions to the groundwater chemical composition. The significant negative correlation between Ca^{2+} and F^- (r = - 0.44) suggests prevalence of alkaline environment for dissolution of fluorite (CaF_2) in groundwater and elimination of Ca^{2+} through precipitation of calcite. The factor analysis brings out strong positive loadings on TDS, TH, Ca^{2+}, Mg^{2+}, Na^+, HCO_3^- and Cl^-. Since it includes TDS and five ions present in basement rocks, it may be regarded as the geogenic factor. The another factor, which is loaded on K^+, SO_4^{2-} and NO_3^-, reveals anthropogenic interventions. The present study suggests that NO_3^- and F^- may perhaps cause adverse health effects in the order of children > adults. The children are more susceptible with respect to non-carcinogenic risk compared to adults because of their smaller body weights than adults. The silicate weathering, carbonate dissolution, reverse ion exchange as well as an anthropogeneic interventions are the causes of change in chemical-behavior of groundwater regime of the study area at the rock-water interface.

Authors' Contributions

MPJ: Writing - Reviewing and Editing. **YAM:** Investigation, Conceptualization, Methodology, Writing - Original Draft.

Conflict of Interest

Authors express “No conflicts of Interest”.

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