

Geostatistical Analyses for Validation of Hydrogeochemical Behaviour of Groundwater from Neoproterozoic Aquifers of Chandrapur District, Central India

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Abstract

The study area, signifying the rural part from Central India, has the groundwater as the only source for all water-utilities. Here, the Neoproterozoic Penganga limestone forms the main groundwater-bearing aquifer systems. The three factors are resulted from geostatistical analysis; wherein the 47.334% has been regarded as the geogenic factor, 24.298% represents anthropogenic input and 14.374% is alkalinity factor. The phenon line at $r = 0.55$ value illustrates three distinct clusters as an outcome of factor analysis responsible for above mentioned factors. The high values of EC and TDS (1016 to 2519 $\mu\text{S}/\text{cm}$ and 650.2 – 1612.2 mg/l, respectively) signify the involvement of multiple combinations of cations and anions, undoubtedly from the both geogenic and non-geogenic sources. Silicate weathering is found to be a major geogenic reason responsible for the release of solute; while the non-geogenic inputs are introduced through the household waste, irrigation-return-flow, animal wastes and the use of agricultural and soil nourishments.

Keywords: Geostatistical Analyses, Hydrogeochemical Behaviour, Groundwater, Neoproterozoic Aquifers, Chandrapur District, Central India

Introduction

The hydrogeochemical behaviour of the groundwater is the consequential of the interaction between the chemical-ions of minerals phases, released from the aquifer-rocks at the rock-water interface (Das *et al.*, 2012; Xu *et al.*, 2018; Mahanta and Goswami, 2024). This complex process, which governs the groundwater-chemistry has also the geogenic-control in deciding groundwater quality (Si *et al.*, 2009; Li *et al.*, 2011; Mahanta and Goswami, 2024). The anthropogenic interventions also pose further deterioration of the groundwater quality (Ravikumar *et al.*, 2011; Agoubi *et al.*, 2013; Bauder *et al.*, 2014; Amiri *et al.*, 2015; Adimalla and Qian 2019; Eyankware *et al.*, 2020; Murkute *et al.*, 2025).

In recent investigations, it has been pointed out that groundwater-contaminants are the carriers of hazards to human health and hence the studies are concentrated on apprehension of geostatistical, geochemical as well as health related complications (Hirojeet *et al.*, 2015; Zhang *et al.*, 2019; Eyankware *et al.*, 2020; Gogulothu *et al.*, 2022, Hota *et al.*, 2025; Divya *et al.*, 2026). In fact, such interconnected investigations will contribute in framing the policies and strategies for remedial measures, planning, regulations

to alleviate groundwater contamination, done by geogenic as well as anthropogenic-inputs.

The present investigation focuses on PG2 watershed representing the Penganga River catchment from Chandrapur district, Maharashtra, Central India; wherein the source for all water-utilities is the only groundwater. The groundwater quality tests have been carried out from the adjoining catchments; however, there is unsatisfactory information on groundwater-quality-characters. Thus, it is attempted here to examine the groundwater hydrogeochemistry of involving geostatistical approach. Accordingly, the factor as well as cluster evaluations have comprehensively been initiated to recognize the numerous governing factors of hydrogeochemical characteristics (Hota *et al.*, 2023, Chatterjee *et al.*, 2023). In addition, the multiple regression analysis and human health risk assessment have also been considered (Wu and Sun, 2016; Subba Rao, 2020; Gogulothu *et al.*, 2022; Das *et al.*, 2023). Present study paves the initial step in understanding the hydro-geochemistry of the study area and its implications in quality issues pertaining to health risk analysis.

Study Area

The PG2 watershed, named after the River Penganga, lies 90 km on southwest tip of Chandrapur city (latitude - 19°38'32":19°48'23" N and longitude - 78°50'12":79°05'51" E) and

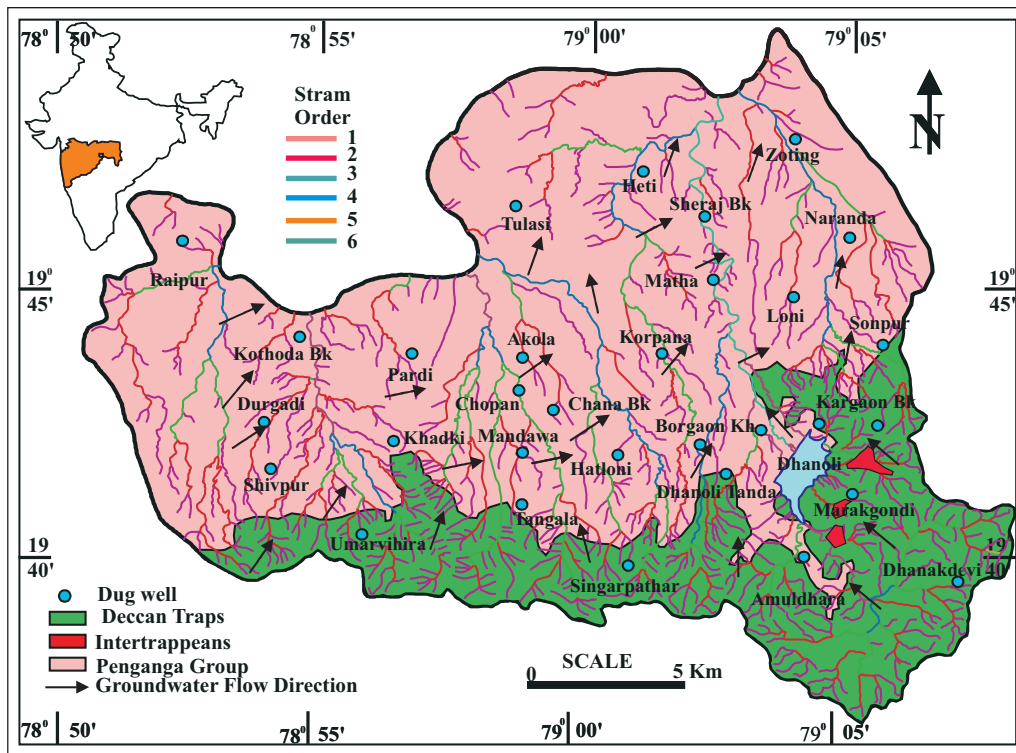


Fig. 1. Location, geological and sample-collection map of study area

sprawls over 339.98 km². It comes under semi-arid climatical surroundings. The minimum temperature remains 8°C in and it goes up to 46°C. Humidity varies from 7 to 91% with 1200 mm monsoon-rainfall. The watershed drains down through the dendritic drainage system and eventually meets the Penganga River, which flows from northern-tip of watershed.

Geology and Hydrogeology

The aquifer of Neoproterozoic Penganga limestones (Fig.1) covers the whole northern and central part of watershed, wherein the driven dug wells have usual diameter from 3 to 6 m, depth up to 20 meters below ground level (mbgl) and yield of 50 to 250 m³/day (GSDA, 2015). The overlying Deccan Trap-basalts are well disposed on the southern boundary of the watershed. Seldom, the inter-trappean sedimentary beds, partially covered by Basaltic flows, are also exposed. The dug wells penetrated in basalts have a depth and diameters up to 20 mbgl and from 2 to 6 m respectively,

with the groundwater yield of 50 to 200 m³/ day from these wells (GSDA, 2015).

Material and Methods

The hydrogeochemical survey for groundwater-sample collections was completed during pre-monsoon 2024. Though, all wells have installed electric pumps for water abstraction, the samples were collected by pre-rinsed polyethylene samples-collector. The sample bottles were kept ready before the field visits and forty-five groundwater samples abstracted from dug-wells, filtered and then collected in one-liter pre-rinsed polyethylene bottles and subjected to analytical measures of major cations and anions.

All the physico-chemical parameters have been investigated as per the APHA (2012) and analytical data have been summarized in Table 1.

The Pearson's bivariate r-values have been employed to find

Table 1: Analytical data for 45 groundwater samples from study area

Particulars	pH	EC	TDS	TA	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	mg/l					
										CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	NO ₃ ⁻
Min	7.6	1016.0	650.2	150.0	312.8	70.5	33.3	43.1	0.6	7.8	150.3	70.7	101.4	0.5	49.5
Max	8.7	2519.0	1612.2	420.0	879.8	195.3	97.6	149.5	5.3	24.6	548.3	271.3	318.5	1.9	182.5
Avg	8.1	1713.4	1096.5	280.2	577.5	136.6	57.5	84.1	2.0	12.8	338.6	138.5	186.7	1.1	139.5
STDEV	0.3	335.2	214.5	57.1	130.5	30.1	19.4	27.7	1.0	3.1	105.9	47.0	51.7	0.4	39.5
COV	4.0	19.6	19.6	20.4	22.6	22.0	33.7	33.0	51.6	23.9	31.3	33.9	27.7	35.8	28.3
BIS (2020) Acceptable Limits	6.5 - 8.5	-	-	-	200	75	30	-	-	200	200	250	200	1.0	45
WHO (2017) Acceptable Limits	6.5 - 9.2	-	-	-	100	75	30	-	10	200	150	250	200	1.0	50

STDEV – Standard Deviation, COV – Covariance

out the interrelationship of all parameters with their progression towards positiveness or negativeness. The distinct geostatistical scrutinizes encompassing the factor and the cluster analyses have been employed to understand hydrogeochemical processes governing the groundwater chemistry. Besides, the multiple-regression analysis was considered to deal with TDS parameter as a linear regression on some of the constituent cations-anions.

Hydrogeochemical Behavior of Groundwater

The minimum and maximum values of pH, recorded from Penganga limestones are 7.6 and 8.7, respectively. The average value of EC value (1713.4 μS/cm), advocates multifold progression in groundwater characterization (Subba Rao, 2017). The high TDS (max: 1612.2 mg/L) contribute the salinity to the groundwater and as per Subba Rao *et al.*, (2021) such conditions suggest contributions from geogenic sources, in addition to non-geogenic sources fitting to agricultural practices as well as the introduction of domestic-leftover. The 18% of groundwater samples have TH value less than 500 mg/L as per WHO (2017). The concentration of Ca²⁺ varies from 70.5 to 195.3 mg/L; the Mg²⁺ content ranges from 33.3 – 97.6 mg/L. The Na⁺ content ranges from 43.1 to 149.5 mg/L and the K⁺ concentration varies from 0.6 – 5.3 mg/L.

Generally, in the soil zone, CO₂ is released and HCO₃⁻ is produced by the disintegration in mineral-suites, CO₂ influence at the atmospheric-stage, in addition to partial or complete decomposition of the organic matter; nevertheless, higher concentration of HCO₃⁻ (ranging from 150.3 to 548.3 mg/L, in study area) in the groundwater system is due to the prevalent mineral-dissolution (Mohapatra and Goswami, 2012; Subba Rao, 2018). The NO₃⁻ contents (49.5 - 182.5 mg/l) in groundwater commonly corroborates the interaction with dairy waste, sewage waste, septic-pond outflows, decay of agricultural rotten-products as well as partially decomposed animal-body parts (Raju *et al.*, 2009; Murkute, 2014; Subba Rao *et al.*, 2021; He *et al.*, 2019; Murkute *et al.*, 2025). The SO₄²⁻ (101.4 – 318.5 mg/l) in groundwater of present study area possibly have been released through the gypsum mineral, added as the soil conditioner and from redox reaction of sulphide-based mineral-suites added in composts as well as manures (Hota *et al.*, 2025). The anthropogenetic responsible factors like domestic wastes and sewage-outflows are the usual source of Cl⁻ (70.7 - 271.3 mg/l; Laxman *et al.*, 2019). Fluoride content grades between 0.5 - 1.9 mg/l, wherein the chief sources of F⁻ anion are the phosphatic

fertilizers leaching in substrate with the mineral suites like fluorite, apatite, hornblende, biotite *etc.* (Murkute, 2014). The highest value of CO₃²⁻ content from the study area is 24.6 mg/l; wherein the possible source is the carbonate generating minerals at the rock water interface in the host rock (Das *et al.*, 2023).

Geostatistical Evaluation

The interrelationship of various geostatistical investigations with the hydrogeochemistry of groundwater from the study area is discussed herewith.

Correlation Coefficient (r)

Pearson's bivariate r-values (Table 2) reveals momentous positive relationship between pH and TA ($r = 0.594$). The TDS exhibits positive correlation with Ca²⁺, Mg²⁺, Na⁺, HCO₃⁻ and Cl⁻ ($r = 0.772, 0.754, 0.738, 0.829$ and 0.737 , respectively); similarly, it unravels moderate positive connection with SO₄²⁻ ($r = 0.447$), K⁺ ($r = 0.322$) and NO₃⁻ ($r = 0.299$). The constructive (+ ve) correlations among the Ca²⁺ and Mg²⁺ ($r = 0.422$), Na⁺ ($r = 0.483$) and HCO₃⁻ ($r = 0.697$) shows the ion-origin clearly from like-geogenic-source (Cl⁻, NO₃⁻, SO₄²⁻ are not geogenic) (Subba Rao *et al.*, 2021); while, positive r-values, (TH) with Ca²⁺ ($r = 0.834$), Mg²⁺ ($r = 0.853$), Na⁺ ($r = 0.568$), HCO₃⁻ ($r = 0.804$) and Cl⁻ ($r = 0.602$) found to pertain with groundwater hardness. The positive association among Na⁺ with Cl⁻ ($r = 0.936$) and Na⁺ with HCO₃⁻ ($r = 0.590$) suggests their derivation from domestic wastes and from geogenic origin; whereas the correlations exhibited through the high positive values between SO₄²⁻ and K⁺ ($r = 0.875$) as well as NO₃⁻ and K⁺ ($r = 0.686$) put-on view the agrochemical background (Das *et al.*, 2023).

Factor Analysis

The 3 significant factors derived in present study have correspondingly eigenvalues of 5.662, 3.410 and 1.749, which account for 40.443%, 24.356% and 12.489% of variances, along with the overall variance 77.288 %. The factor 1 reveals very robust positive loadings arranged over the TDS (0.936), TH (0.905), Ca²⁺ (0.746), Mg²⁺ (0.780), Na⁺ (0.810), CO₃²⁻ (0.757), HCO₃⁻ (0.865) and Cl⁻ (0.834), representing the involvement of TDS, TH with the present three cations and three anions may evidently be correspond to the geogenic influence. The cations-anions in second factor

Table 2: Pearson's bivariate correlation coefficients (r) between pairs of groundwater parameters (above diagonal) and apparent correlation coefficients deduced from dendrogram (below diagonal)

	pH	TDS	TA	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	CO ₃ ²⁻	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	F ⁻
pH	1.00	-0.231	0.594*	-0.228	-0.231	-0.156	-0.233	0.148	-0.131	-0.296*	-0.225	0.081	0.061	0.086
TDS	-0.005	1.00	-0.147	0.904*	0.772*	0.754*	0.738*	0.322*	0.790*	0.829*	0.737*	0.447*	0.299*	0.232
TA	0.594	-0.005	1.00	-0.137	-0.150	-0.083	-0.276	0.134	-0.167	-0.258	-0.223	0.180	0.249	0.251
TH	-0.005	0.904	-0.005	1.00	0.834*	0.853*	0.568*	0.190	0.667*	0.804*	0.602*	0.341*	0.175	0.073
Ca ²⁺	-0.005	0.750	-0.005	0.750	1.00	0.422*	0.483*	0.065	0.525*	0.697*	0.495*	0.247	0.149	0.080
Mg ²⁺	-0.005	0.568	-0.005	0.568	0.568	1.00	0.475*	0.250	0.597*	0.660*	0.520*	0.326*	0.145	0.043
1.00	-0.005	0.611	-0.005	0.189	0.611	0.568	1.00	-0.028	0.622*	0.590*	0.936*	0.032	0.000	-0.020
K ⁺	-0.005	0.189	-0.005	0.189	0.189	0.189	0.189	1.00	0.303*	-0.056	-0.085	0.875*	0.686*	0.641*
CO ₃ ²⁻	-0.005	0.599	-0.005	0.599	0.599	0.568	0.599	0.189	1.00	0.635*	0.565*	0.365*	0.312*	0.371*
HCO ₃ ⁻	-0.005	0.817	-0.005	0.817	0.750	0.568	0.611	0.189	0.599	1.00	0.622*	0.027	-0.191	-0.080
Cl ⁻	-0.005	0.611	-0.005	0.611	0.611	0.568	0.936	0.189	0.599	0.611	1.00	-0.064	-0.029	-0.054
SO ₄ ²⁻	-0.005	0.189	-0.005	0.189	0.189	0.189	0.189	0.875	0.189	0.189	0.189	1.00	0.751*	0.623*
NO ₃ ⁻	-0.005	0.189	-0.005	0.189	0.189	0.189	0.189	0.719	0.189	0.189	0.189	0.719	1.00	0.624*
F ⁻	-0.005	0.189	-0.005	0.189	0.189	0.189	0.189	0.628	0.189	0.189	0.189	0.628	0.628.	1.00

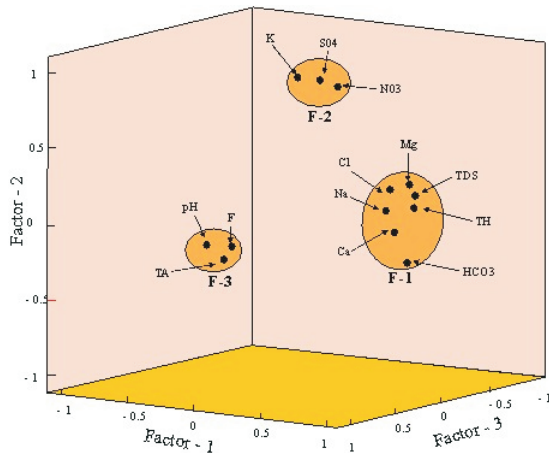


Fig. 2. Factor loadings of hydrogeochemical parameters of study area in block-diagram

loaded on K^+ (0.901), SO_4^{2-} (0.917), NO_3^- (0.863) and F^- (0.807) corresponds to fertilizers and soil condition enhancer and hence clearly conveys anthropogenic influence; while the last factor (3), loaded over the pH (0.914) and TA (0.872) is noticeably an alkalinity factor. All the factor loadings in block-diagram (Fig.2) exhibit matching-up with the deductions of the factor loadings (Table 3), once again confirming their interrelationships.

Cluster Analysis and Phenon Line

The cluster analysis brings out (i) the dendrogram (Fig.3) with the phenon line demarcation on $r = 0.55$ and (ii) three cluster-collections, in which cluster 1 comprises Total dissolved solids, total hardness, some cations (Ca^{2+} , Mg^{2+} and Na^+) and some anions (Cl^- and HCO_3^-); cluster 2 encompasses cation (K^+), some anions (SO_4^{2-} , NO_3^- and F^-); while cluster 3 embraces pH and TA. The cophenetic correlation coefficient in tune of 0.902 value rationally substantiates the greater accuracy of this analysis. The dendrogram also exhibits the conformism on factors and also the perceptible coefficients amongst the groundwater characters, as presented in

Table 3: Varimax rotated factor loadings of fourteen groundwater parameters

Parameter	Factor 1	Factor 2	Factor 3
pH	-0.136	0.058	0.914
TDS	0.936	0.297	-0.121
TA	-0.267	0.139	0.872
TH	0.905	0.176	-0.114
Ca^{2+}	0.746	0.118	-0.191
Mg^{2+}	0.780	0.177	-0.006
Na^+	0.810	-0.105	-0.124
K^+	0.064	0.901	0.062
CO_3^{2-}	0.757	0.343	-0.105
HCO_3^-	0.865	-0.134	-0.206
Cl^-	0.834	-0.174	-0.069
SO_4^{2-}	0.176	0.917	0.058
NO_3^-	0.049	0.863	0.087
F^-	0.01	0.806	0.029
Eigenvalue	5.662	3.410	1.749
Percentage of total variance	40.443	24.356	12.489
Cumulative percentage of total variance	40.443	64.799	77.288

Extraction Method: Principal Component Analysis.
 Rotation Method: Varimax with Kaiser normalization
 Highest positive values are shown in bold numbers

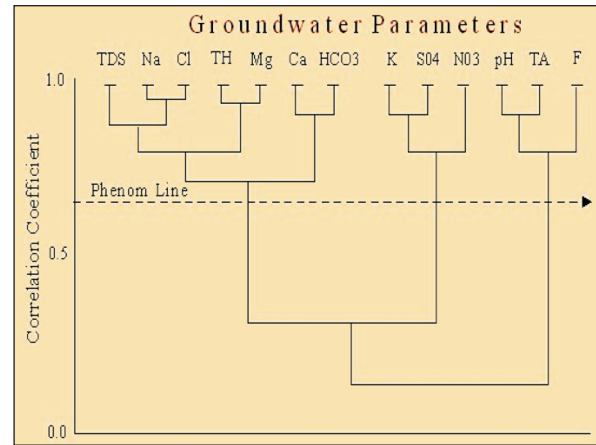


Fig. 3. Dendrogram and phenon line for hydrogeochemical parameters of study area

Table 4. The parameters of cluster 1 show geogenic relevance and hence significantly contribute towards the TDS content in groundwater (Murkute and Pradhan, 2025).

Multiple-Regression Statistics

Although, factor and cluster statistical-analyses classify the groundwater parameters into closely related groups, the multiple regression-statistics depict the TDS parameter as a linear regression on some of the constituent cations-anions. Here, the scientific reckoning is “ $TDS = 22.46 + 0.958 Ca^{2+} + 1.023 Mg^{2+} + 0.949 Na^+ + 1.450 K^+ + 0.6 CO_3^{2-} + 0.99 HCO_3^- + 1.005 Cl^- + 0.963 SO_4^{2-} + 0.975 NO_3^- + 3.222 F^-$ ”. The calculated 'F' value 5456.581 (Table 4) for the regression comparison exceeding the critical value (2.90) confirms the numerical significance of the equational values. The values derived through the computation of 'F' for cations (Ca^{2+} , Mg^{2+} and Na^+); anions (CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-} and NO_3^-) surpass the limiting (7.45) value at the significance-level of 0.01, which suggest significant involvement of these cations-anions to the TDS.

Discussion

The pH value of Penganga limestones (7.6 to 8.7), the average EC value (1713.4 $\mu S/cm$) and the high TDS (max: 1612.2

Table 4: Complete ANOVA for testing the significance of regression equation and individual ions

Source of variation	Sum of squares	Degrees of freedom	Mean squares	F
Regression	2023955.031	10	202395.503	5456.581§
Ca^{2+}	39862.626	1	39862.626	1074.679*
Mg^{2+}	16538.228	1	16538.228	445.870*
Na^+	33877.092	1	33877.092	913.326*
K^+	48.480	1	48.480	1.307
CO_3^{2-}	414.700	1	414.700	11.180*
HCO_3^-	493481.299	1	493481.299	13304.252*
Cl^-	97124.788	1	97124.788	2618.483*
SO_4^{2-}	117797.803	1	117797.803	3175.828*
NO_3^-	68760.139	1	68760.139	1853.773*
F	6.964	1	6.964	0.188
Deviation	1261.141	34	37.092	---
Total variation	2025216.172	44	---	---

§ $F_{v1=10,v2=34,\alpha=0.01} = 2.90$ * $F_{v1=1,v2=34,\alpha=0.01} = 7.45$

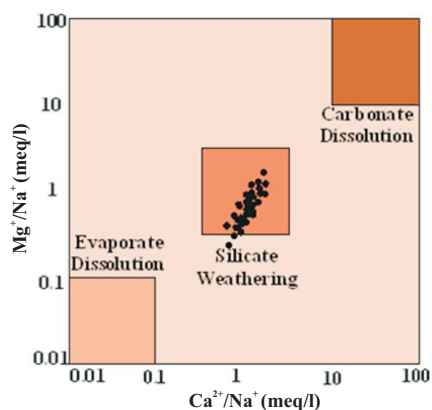


Fig. 4. Interrelationship of Mg^{2+}/Na^+ and Ca^{2+}/Na^+

mg/l) clearly advocate the multifold progression in groundwater characterization (Subba Rao, 2017) and suggest the contributions from geogenic sources. The 82% of groundwater samples have TH value exceeding the 500 mg/L maximum permissible limit (MPL) of WHO (2017).

Typically, the plagioclase-feldspar (calcic) existing in the mineral composition of rocks is the typical geogenic-cause of calcium-cation liberation; which ultimately gets dissolved in groundwater (Hota *et al.*, 2023). The amphiboles, pyroxenes, mica as well as gypsum and dolomite traces escalate ion exchange of Mg^{2+} concentration in water, beneath the surface (Subba Rao., 2021; Gogulothu *et al.*, 2022), yet again pointing out the geogenic response. The common dominance of both calcium-magnesium cations in some of the samples, may unravel strong and long-period-weathering of Mg^{2+} rich carbonate rock (dolomite) exhibiting the natural-geogenic liberation; the strong-involvement of pesticides, fertilizers, household wastes, sewage tank and their spill-ways anthropogenically place the Mg^{2+} in groundwater beneath the aquifers (Thivya *et al.*, 2018; Roy *et al.*, 2018; Mgbenu and Egbueri., 2019). Both the sodic and potassic feldspars (microcline and orthoclase) represent the geogenic discharge; conversely the potassium-enriched manures, household domestic wastes, return-flows of irrigation correspond to the anthropogenic over-concentration of Na^+ and K^+ (Gupta *et al.*, 2008; Subba Rao *et al.*, 2020).

About 98% of the collected samples, NO_3^- concentration is above the MPL after WHO (2017) and BIS (2020). The SO_4^{2-} (101.4 – 318.5 mg/L) in groundwater of present study area possibly have been released from gypsum, which is added as the soil conditioner and from redox reaction of sulphide-based mineral-suites added in composts and manures (Hota and Goswami, 2018; Hota *et al.*, 2025). The anthropogenic factors like domestic wastes and sewage-outflows are the usual source of Cl⁻ (70.7 - 271.3 mg/L; Laxman *et al.*, 2019). Fluoride content grades between 0.5 - 1.9 mg/L, wherein the chief sources of F⁻ anion are the phosphatic fertilizers leaching in substrate with the mineral suites like fluorite, apatite, hornblende, biotite etc. (Murkute, 2023). The highest value of CO_3^{2-} content from the study area is 24.6 mg/L; wherein the possible source is the carbonate generating minerals at the rock water interface in the host rock (Das *et al.*, 2023). The scatter graph of $[Mg^{2+}/Na^+]$ and $[Ca^{2+}/Na^+]$ clearly signifies the foremost influence of silicate-weathering pointing out the geogenic source of solute generation (Fig. 4); (Murkute, 2014; Li *et al.*, 2019). The $SO_4^{2-} + HCO_3^-$ and $Ca^{++} + Mg^{++}$ interrelationship (Fig. 5) corroborates the silicate

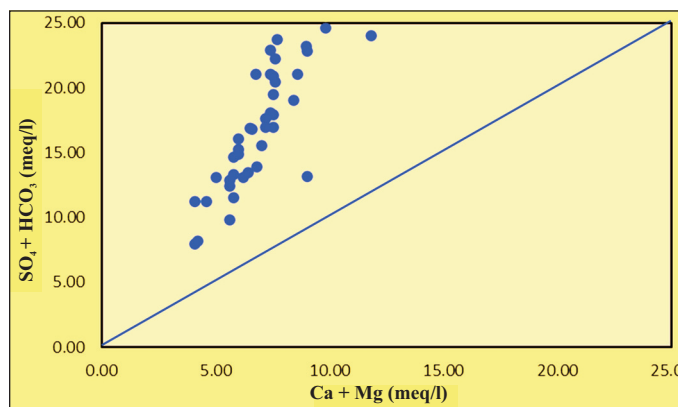


Fig. 5. Scatter diagram of $SO_4^{2-} + HCO_3^-$ and $Ca^{++} + Mg^{++}$ Interrelationship

weathering process of geogenic origin for source of solute generation (Ramesh and Elango 2011). The covariation-count of $NO_3^- + Cl^- / HCO_3^-$ vs TDS (Table 2) demonstrates the positive correlation (0.419), unveiling the nongeogenic influence (Murkute, 2014; Abu-alnaeem *et al.*, 2018; Subba Rao *et al.*, 2021).

Conclusions

The alkaline phase of groundwater from study area with high values of EC and TDS (1016 to 2519 $\mu S/cm$ and 650.2 – 1612.2 mg/L, respectively) confirms multiple contributions of cations and anions, certainly from both geogenic and non-geogenic sources. Silicate weathering is found to be evident geogenic reasons in groundwater regime accountable for the release of solute; while the non-geogenic inputs are introduced through the household waste, irrigation-return-flow, animal wastes and the use of agricultural and soil nourishments. The three factors conceivable for variances, resulted through factor analysis, 47.334% has been regarded as the geogenic factor, 24.298% represents anthropogenic input and 14.374% is alkalinity factor. The phenon line at $r = 0.55$ value also depicts three distinct clusters as shown in the outcome of factor analysis

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Author Contributions

YM: Investigation, Writing of Original Draft, Editing and Finalization of Manuscript. **MJ:** Field work and Figure Drafting and Writing of Original Draft of the Manuscript. **SRH:** Statistical Analysis and Interpretation, **RNH:** Statistical Analysis, Interpretation and Figure Drafting, **SG:** Writing of Draft, Interpretation and Editing of Revised Draft of the Manuscript.

Conflict of Interests

There are no financial and non-financial competing interests.

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