IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

Multivariate Statistical Investigation And Hydrogeochemical Analysis Of Hard Rock Aquifer Groundwater Quality From Deccan Trap Basalt In Washim District, Maharashtra, India

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Abstract: In the current study, hard rock aquifers of the Deccan trap basalt in Maharashtra's Washim district were evaluated for hydrogeochemical and multivariate statistical investigation of groundwater quality. To prevent sampling bias, 139 groundwater samples were collected from the research region using a methodical grid design. All of these groundwater samples water quality characteristics were examined using titrimetric and sensor-based methods in accordance with conventional BIS and APHA protocols. An LED fluorimeter was used to measure the amount of uranium in each sample. The bulk of the samples fall into the Ca-Mg-HCO_3 hydrochemical facies, according to Piper's schematic categorisation. The bulk of samples fall under the rock dominance category, according to the Gibbs plot. Multivariate statistical techniques, including Pearson's correlation, hierarchical cluster analysis (HCA), and principal component analysis (PCA), were applied to explore the underlying structure of groundwater quality data and to identify the key factors governing its variability. The results indicated that both natural processes and anthropogenic activities play a significant role in shaping the groundwater chemistry. Most of the samples are within the desired to allowable range for drinking and agricultural use based on TDS.

Index Terms **– LED Fluorimeter, Multivariate Statistics, Groundwater quality.**

1.INTRODUCTION

Water is a vital component of all ecosystems and exists on Earth in three physical states: liquid, gas, and solid. About 71% of the planet's surface is covered by water, predominantly in the form of seas and oceans. Each year, waterborne diseases are responsible for approximately 3.4 million deaths, with children being the most affected (Osiemo et al., 2019). Due to significant population growth, industrialization, urbanization, and intensive agricultural activities, there has been an unprecedented increase in the demand for fresh water supply in recent decades (Dhanasekarapandian et al., 2016). The majority of people in India rely on groundwater resources for drinking as well as domestic, commercial, and agricultural purposes because of the scarcity of surface water, which is made worse by pollution, urbanization, and industrialization, as well as because groundwater is thought to be pollution-free (Raju et al., 2011). The vast majority of people living in rural areas of India rely mostly on groundwater. Irrigated agriculture is the biggest abstractor and primary consumer of around 65 percent of all agricultural area is irrigated by groundwater. (Foster et al., 2013; Raju et al., 1998). Although groundwater was once thought to be safer than surface water, pollutant loads in groundwater have increased recently as a result of poor waste management (Iqbal et al., 2009). Both natural and human activity influence groundwater crises. Natural elements like geology, topography, hydrology, meteorology, biology, and geochemical processes occurring in an aquifer all have an impact on the quality of the groundwater (Khatri et al., 2015). The groundwater bodies in an aquifer with distinct chemical components must be described using

the term hydrogeochemical facies (Ali et al., 2018). Understanding the hydrogeochemistry of groundwater in a specific location is crucial for determining its appropriateness for usage. Numerous writers have observed a substantial association between water quality measures (Kale et al., 2020; Kim et al., 2020; Malik et al., 2017; Tiwary et al., 2018). Hydrogeochemistry was previously evaluated solely through laboratory-based research, but today geospatial techniques are employed for water quality assessment (Hosseinifard et al., 2015), resource management (Graham et al., 2011), and accurate and cost-effective interpretation of groundwater data (Thakur et al. 2017). When it comes to predicting spatial variation and distribution, groundwater quality, and the locations of pollution sources, Geographic Information Systems (GIS) are an essential tool for groundwater resource management. To comprehend the effects of environmental changes and management methods in the past, present, and future, a Geographic Information System (GIS) is a crucial information tool (Kura et al., 2014; Singh et al., 2011; Swarna et al., 2012). Pictographic representations of groundwater quality for a variety of uses are the result of GIS application (Anbazhagan et al., 2004). For groundwater security and excellence maintenance, groundwater quality is essential. Therefore, it is crucial to assess the quality of the groundwater for both current and future generations. The Indo-Gangetic basin's alluvial plains' groundwater supplies exhibit a decline in both quality and quantity with time (Haritash, et al., 2008). Because it influences the suitability of water for domestic, commercial, and agricultural use, groundwater quality monitoring is crucial in any basin or populated region. In a variety of basins and urban areas, numerous researchers have examined the hydrochemical characteristics, groundwater pollution, and the quality status of the water for use in agriculture and drinking (Patel et al., 2016). In light of these factors, the primary goal of the current study was limited to assessing the chemical processes in groundwater in hard rock aquifers of Deccan trap basalt in Washim District of Maharashtra, India using geochemical evaluation, multimodal statistical analysis, conventional geochemical classification, and spatial distribution modelling.

2. MATERIAL AND METHODS

2.1 Study Area

The district of Washim is located in Maharashtra's eastern part of Vidharbha. The study area depicted in figure 1 lies in portions of Survey of India degree sheets 55 D, 55 H, 56 A, and 56 E. It is situated between north latitudes 19°61' and 21°16' and east longitudes 76°07' and 77°14'. The area of the district is approximately 5,150 square kilometres. The talukas of Washim district, located in the eastern part of Vidharbha, are Malegaon, Mangrulpir, Karanja, Manora, Washim, and Risod. Its boundaries are as follows: Buldhana to the west, Amravati to the northeast, Yavatmal to the east, Hingoli to the south, and Akola to the north. The Penganga is the main river in the area. The Risod tehsil is traversed by it. The main tributary of the Penganga, Kasa, eventually crosses the border between the districts of Washim and Hingoli. Shelgaon Rajgure hamlet is around a km away from the Kas river region. The Arunavati River originates in Washim Taluka and passes through Mangrulpir and Manora Talukas in the Yavatmal district. The Katepuna river originates in the mountains of the district and empties into the Akola district to the north via the Tehsil.

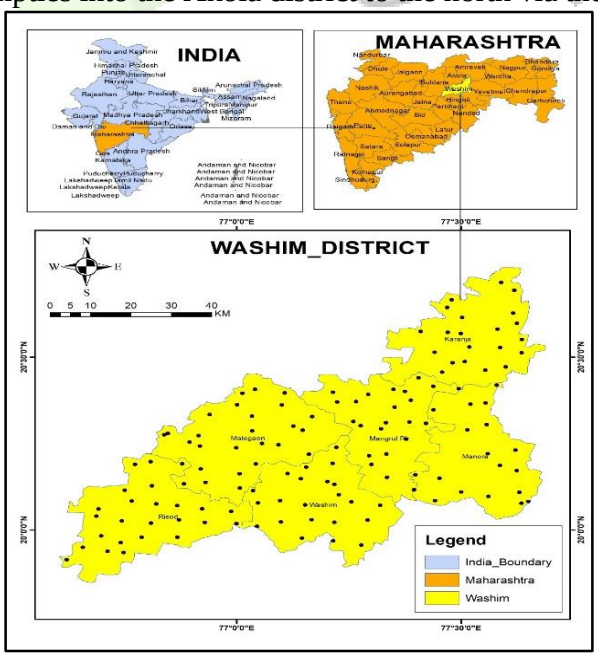

Figure 1: Research region map with location sampling point.

2.2 Geology and hydrogeology

Geologically speaking, the area is composed of strata of intertrappean beds scattered across the Deccan Traps, which are recent river alluvium and basaltic lava flows that originated between the Cretaceous and the Eocene (68–62 million years ago). The geological array is both localised and generalised. The Recent to Quaternary alluvium layer, composed of sand, silt, clay, and gravel, was exclusively deposited along the banks of the Penganga River. Deccan trap basalts from the Upper Cretaceous to Eocene make up almost the whole district. There are two types of basaltic lava flows: "aa" and "pahoehoe" flows. "Pahoehoe" floods are composite flows composed of several units with thicknesses ranging from one to many meters (CGWB 2019).

2.3 Sample collections

To assess the geochemistry of the groundwater, 139 samples were taken. Prior to data collection in the current investigation, a selection measure was devised to assist in identifying appropriate sampling locations for the assessment of groundwater quality. The samples that were collected using those hand pumps, open well, and borewell were active, functioning, and continuously used for human consumption and other everyday tasks. APHA 2017 standard procedures were adhered to for sample collection, preservation, and analysis. Samples were gathered in polyethylene containers that had been properly labelled and cleaned with groundwater samples prior to filling. Physicochemical parameters, including pH, electrical conductivity (EC), and total dissolved solids (TDS), temperature, oxidation reduction potential (ORP) and dissolved oxygen (DO) were measured onsite using a portable multiparameter probe (Model HI98194, Hanna Instruments). Major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, HCO_3^{-}, SO_4^{2-}, NO_3^{-}, PO_4^{3-}) were determined in the laboratory following APHA (2017) standard methods. Uranium concentration was analyzed using laser fluorimetry.

2.4 Statistical and hydrochemical analysis

Statistical and hydrogeochemical analyses were performed to interpret the groundwater quality data and identify the underlying processes influencing water chemistry. Statistical calculations, including descriptive statistics, correlation analysis, principal component analysis (PCA), and hierarchical cluster analysis (HCA), were carried out using SPSS (IBM STATISTICS VERSION 20) and Microsoft Excel. Hydrogeochemical diagrams, such as Piper, Chadha, Durov, and Gibbs plots, were prepared to classify groundwater types and to infer geochemical processes (Durov, 1948; Gibbs, 1970; Piper, 1944). Irrigation suitability was evaluated using Wilcox and United States Salinity Laboratory (USSL) diagrams, which assess salinity and sodium hazards were generated using Diagrammes and GW Chart Software (Wilcox, 1995; USSL, 1954). Water quality was classified according to established standards, such as the Bureau of Indian Standards (BIS, 2012) and World Health Organization (WHO, 2017) guidelines for drinking water, Food and Agriculture Organization (FAO) and United States Department of Agriculture (USDA) criteria for irrigation water quality. The main factors affecting the groundwater quality in the Washim district were examined using multivariate statistical approaches. To comprehend the origins of groundwater pollution, statistical approaches such principal component analysis, cluster analysis, and correlation are helpful (Wu et al., 2020). To determine each parameter's contribution to the overall quality, the correlation between the physiochemical parameters is first used to examine the strength of the relationships between them. Understanding the relationships between several water quality factors and keeping a focus on the chemical parameters are made easier by the correlation analysis (Rishi et al., 2020). In this investigation, the Pearson correlation coefficient (r) is used. Second, the groundwater samples and their ions are categorised based on their chemical properties using hierarchical cluster analysis (HCA). Using a preset selection criterion, it groups the items into clusters, with each variable in each cluster being similar to the others. Clusters produced in this way show significant interclass heterogeneity in addition to strong internal homogeneity (Kaur et al., 2020; Daughney et al., 2012). Hierarchical clustering, the most often used method, offers built-in similarity correlations between any variable and the entire set of data (Shrestha et al., 2007). Dendrograms are used to visualise the cluster analysis's outcome. The dendrogram provides a graphical depiction of clusters and their closeness while simplifying the underlying data. Principal component analysis (PCA) was utilized to identify the primary factors influencing groundwater quality in the study area. This method simplifies complex datasets by examining the relationships among multiple variables and revealing the common underlying processes (Kumar et al., 2011). PCA evaluates how strongly variables are associated with each other and their contribution to the variation observed in the groundwater samples (Bhimanagouda et al., 2020). The main output of PCA is a set of principal components (PCs), which are linear combinations of the original variables (Wu et al., 2014). Each PC explains a portion of the total variance in the data, quantified by its eigenvalue, while the remaining variance represents unexplained or residual variability (Beheraet al., 2018).

2.5 Analysis of physicochemical parameters

With the aid of a portable multiparameter meter kit (HANNA), the parameters that were examined in-situ were pH, electrical conductivity (EC), total dissolved solids (TDS), oxygen reduction potential (ORP), and dissolved oxygen (DO). In contrast, a departmental laboratory examined ex-situ parameters such as anions such as fluoride (F^-), chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), bicarbonates (HCO_3^-), total hardness (TH), and significant cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), and potassium (K^+). Using a UV spectrophotometer (Bio Era Single Beam UV–visible spectrophotometer), the concentrations of nitrate (NO_3^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}) were measured using turbidimetry, screening, and stannous chloride techniques. An Ion-Selective Electrode (ISE) was used to measure the concentration of fluoride, Chloride and Nitrate. The usual EDTA titration method was used to assess total hardness, while HCl titration was used to estimate bicarbonate (HCO_3^-). Flame photometry was used to quantify the cations of potassium (K^+) and sodium (Na^+). As previously stated, all parameters were analysed using the standard procedures recommended by the American Public Health Association (APHA, 1998). Using an LED fluorimeter (Quantalase Enterprises Pvt. Ltd., Indore, India), the uranium content of the water samples that were collected was determined. The measurement and identification of uranium traces in aqueous samples is accomplished by this instrumental method. The device operates on the basis of measuring the uranium complexes' fluorescence in an aqueous sample.

3. Results and discussion

3.1 Physico-chemical groundwater quality parameters

The groundwater quality during the post-monsoon season was assessed against (WHO, 2011) drinking water standards and compared with the (CGWB, 2019) findings for Washim District (Table 3.1).

The pH ranged from 6.55 to 8.14 with mean: 7.4, which is within the WHO permissible range 6.5–8.5. CGWB (2019) also reported pH in Washim groundwater between 6.7–9.6, indicating similar neutral to slightly alkaline conditions due to carbonate buffering in Deccan basalt aquifers. Total dissolve solid (TDS) varied between 201–2420 mg/L and mean 618.7 mg/L, with 12 samples exceeding the WHO limit of 1000 mg/L. CGWB (2019) reported TDS in the range of 187–1800 mg/L, with localized high values linked to evaporation and rock–water interactions. findings are consistent, confirming salinity hotspots in some areas. Fluoride was found between 0.22–1.01 mg/L and mean: 0.55 mg/L, below the WHO maximum limit of 1.5 mg/L and well within CGWB's observed mean of 0.4 mg/L. This indicates no significant fluoride risk. Chloride concentrations ranged from 18.1–171 mg/L and mean: 69.8 mg/L, within the WHO limit of 250 mg/L. Nitrate showed values of 2.6–45.7 mg/L with mean: 11.9 mg/L, with one sample exceeding the WHO limit of 50 mg/L. Elevated levels due to agricultural fertilizers and sewage. Sulphate ranged from 23.9–530 mg/L and mean 73.5 mg/L, below the WHO limit of 500 mg/L. While WHO does not specify limits for phosphate, your study recorded values up from 0.98- 30.5 mg/L and mean 8.0 mg/L, indicating localized anthropogenic inputs such as detergents or fertilizers. Uranium concentrations were between 0.51–15.8 µg/L with mean 3.7 µg/L, well below the WHO limit of 30 µg/L. CGWB (2019) did not report uranium for Washim explicitly but noted uranium hotspots in nearby Vidarbha districts at levels up to ~16 µg/L, confirming that findings indicate low uranium risk. Total hardness varied widely 86–1240 mg/L; mean: 310.4 mg/L, with 54 samples slightly exceeding the WHO limit of 300 mg/L. CGWB (2019) reported similar mean of 343.3 mg/L, with hardness attributed to basalt-derived calcium and magnesium. Specifically, calcium ranged 18.4–285.1 mg/L and mean 78.5 mg/L, exceeding the WHO limit of 100 mg/L in 37 samples, compared to CGWB's range of 6.4–233 mg/L. Magnesium was between 5.8–128.2 mg/L and mean 27.7 mg/L, with 14 samples above the WHO limit of 50 mg/L, aligning with CGWB's findings of 2.4–142.9 mg/L. Sodium 4.9–74.2 mg/L; mean: 16.0 mg/L and potassium range from 0.2–6.3 mg/L; mean: 2.3 mg/L were well below permissible limits. Alkalinity ranged from 91–354 mg/L mean: 167.7 mg/L, with eight samples above the desirable limit of 300 mg/L.

Overall, the groundwater quality during the post-monsoon season in Washim was generally within WHO (2011) permissible limits and closely matched the CGWB (2019) data for the district. Localized exceedances of TDS, nitrate, hardness, calcium, magnesium, and alkalinity were observed, largely attributed to geogenic factors (e.g., basaltic lithology and weathering) and anthropogenic activities (e.g., agriculture, wastewater), as also noted by CGWB. This consistency reinforces the need for regular monitoring and site-specific management strategies to maintain groundwater safety.

Table 3.1 : Physico-Chemical Characteristics of Groundwater in Washim District

Water Quality Parameters	WHO Permissible Limit (2011)	Statistics				
		Min	Max	Mean	Median	No. of sample above the permissible limit
pH	6.5-8.5	6.6	8.1	7.4	7.4	Nil
TDS (mg/L)	1000.0	201	2420	618.7	560	12
Fluoride (mg/L)	1.5	0.2	1	0.5	0.5	Nil
Chloride (mg/L)	250	18.1	171	69.8	66.1	Nil
Nitrate (mg/l)	50	2.6	45.7	11.9	9.1	Nil
Sulphate (mg/L)	500	23.9	330	72.1	57.9	Nil
Phosphate (mg/L)	-	1.0	30.5	8.0	7.3	-
Uranium (µg/L)	30	0.5	15.8	3.7	2.5	Nil
Total hardness (mg/L)	300	86.0	1240.0	310.4	241.0	54
Mg^{2+} (mg/L)	50	5.8	128.2	27.7	22.8	14
Ca^{2+} (mg/L)	100	18.4	285.1	78.5	59.3	37
K^{+} (mg/L)	12	0.2	6.3	2.3	2.1	Nil
Na^{+} (mg/L)	200	4.9	74.2	16.0	13.2	Nil
Total Alkalinity (mg/L)	300	91.0	354.0	167.7	151.0	08

The boxplots illustrate the variability of groundwater quality parameters in Washim District. pH, temperature, salinity, DO, fluoride, nitrate, phosphate, uranium, and potassium show in figure 3.1a moderate variability, with nitrate and uranium exhibiting higher dispersion and outliers, indicating localized geogenic or anthropogenic influences. ORP, chloride, sulphate, magnesium, calcium, sodium, total alkalinity, and bicarbonate shows in figure 3.1b reveal greater variability in ORP and sodium, reflecting heterogeneous redox conditions and salinity, while magnesium and calcium remain relatively stable. TDS, EC, and hardness parameters figure 3.1c display the widest ranges, with TDS and EC showing significant outliers, suggesting zones of high mineralization. Overall, the boxplots reflect the spatial heterogeneity of groundwater quality, influenced by natural and anthropogenic factors.

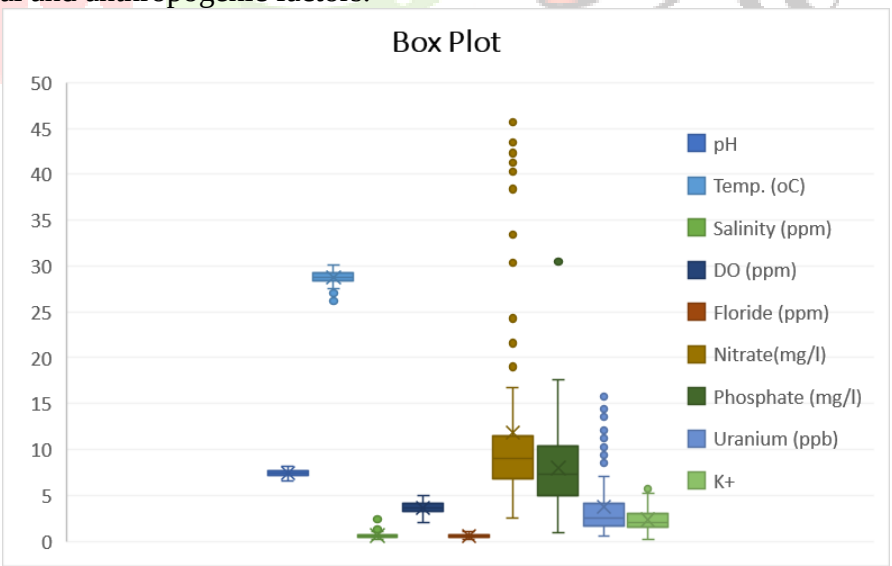

Figure3.1a : Boxplot Showing Variability of Selected Groundwater Quality Parameters in Washim District

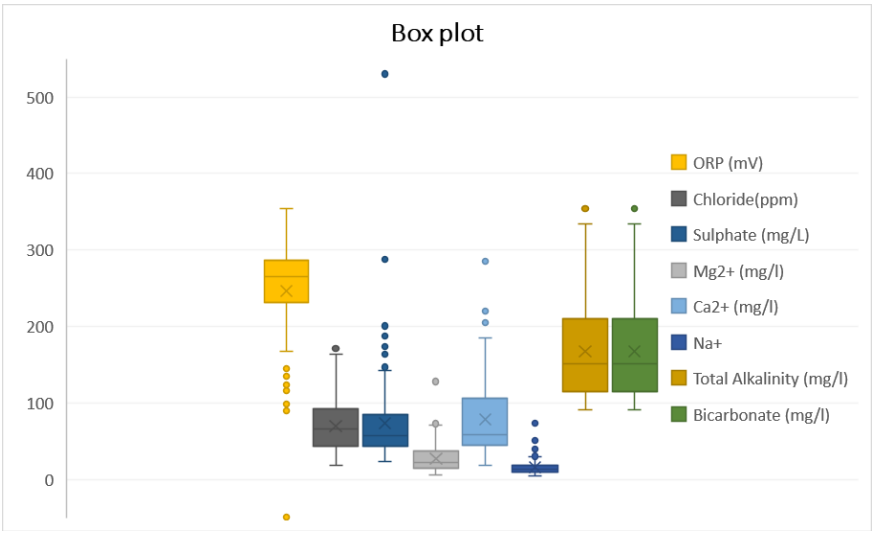

Figure 3.1b : Boxplot Showing Variability of Selected Groundwater Quality Parameters in Washim District

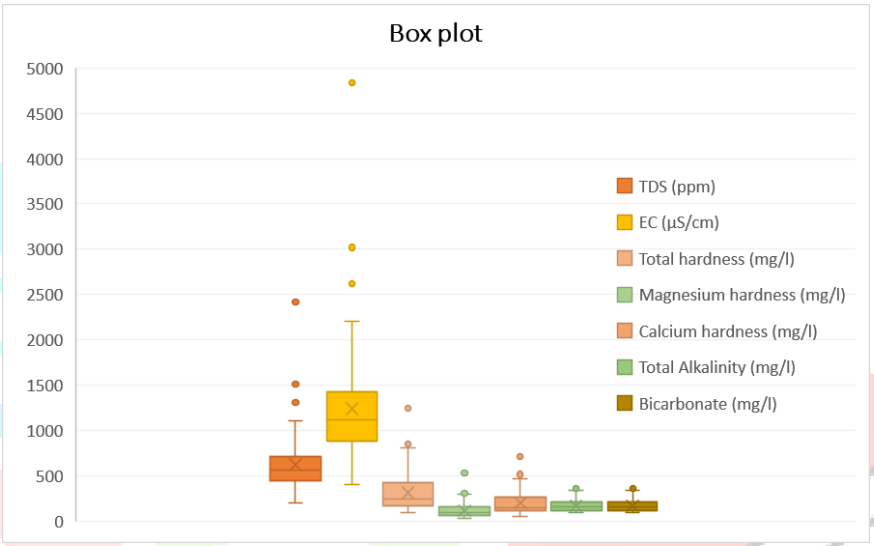

Figure3.1c : Boxplot Showing Variability of Selected Groundwater Quality Parameters in Washim District

3.2 Multivariate Analysis

3.2.1 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was conducted on 20 groundwater quality parameters to identify the key factors influencing water chemistry in the study area. The Kaiser–Meyer–Olkin (KMO) measure of sampling adequacy was 0.854, indicating the data were suitable for PCA, while Bartlett's Test of Sphericity was significant ($\chi^2 = 5490.443$, df = 190, $p < 0.001$), confirming sufficient correlations among the variables. PCA extracted four principal components (PCs) with eigenvalues greater than 1, collectively explaining 67.36% of the total variance in groundwater quality shown in table 3.2. Principal Component (PC1), accounting for 45.75% of variance, showed high positive loadings on EC, TDS, Salinity, TH, Mg^{2+}, Ca^{2+}, Na^{+}, NO_3^{-}, Cl^{-}, SO_4^{2-}, F^{-}, K^{+}, TA, and PO_4^{2-}, suggesting this factor represents mineralization processes and rock–water interaction contributing to groundwater salinity. Principal component PC2, explaining 9.35% of variance, had strong loadings on DO (positive), U (negative), ORP (positive), and PO_3 (negative), which likely reflects the redox conditions and possible anthropogenic contamination. Principal component PC3, contributing 6.16% of variance, loaded heavily on temperature and ORP, indicating the influence of temperature-driven processes and oxidation–reduction potential. Principal component PC4, explaining 6.10% of variance, showed prominent loadings on PA (alkalinity), pH, and ORP, suggesting this component is associated with carbonate buffering and pH regulation in the aquifer. The rotated component matrix confirmed that the first factor was dominated by parameters controlling salinity and hardness, while subsequent factors corresponded to redox-sensitive elements, thermal and pH-related processes, and localized anthropogenic inputs show in table 3.3. These findings highlight that groundwater quality is influenced primarily by natural geogenic processes, including mineral dissolution and ion exchange, with additional contributions from redox reactions, temperature variations, and human activities. The scree plot shows in figure 3.2 illustrates the eigenvalues associated with each principal component, arranged in descending order of importance. The plot

shows a steep decline in eigenvalues from the first to the second component, followed by a gradual levelling off, which indicates the point beyond which additional components contribute minimal variance to the data. This pattern suggests that the first two components capture most of the variability in the dataset, as they lie above the "elbow" of the curve a commonly used criterion to select the optimal number of components for interpretation (Cattell, 1966). In this study, the sharp drop after the second component and the subsequent flattening of the curve indicate that only the first two components were retained for further analysis.

Table 3.2 : Component Score Coefficient Matrix of the Groundwater Quality Parameters for the Extracted Principal Components

Component Score Coefficient Matrix				
	Component			
	1	2	3	4
pH	.006	-.241	.022	.462
TDS	.110	-.011	-.006	.044
EC	.110	-.010	-.006	.044
ORP	.020	.259	.358	.026
TEMP	.019	-.014	.685	.068
Salinity	.110	-.010	-.007	.046
DO	.008	.408	-.230	.148
F^-	.070	.065	-.068	-.078
Cl^-	.080	.198	.011	.147
NO_3^-	.087	-.028	.048	.067
SO_4^{2-}	.090	-.160	.144	.055
PO_4^{3-}	.062	-.234	-.020	.055
U	.033	-.306	-.091	.074
TH	.099	.037	.000	-.060
Mg^{2+}	.101	-.012	.034	-.047
Ca^{2+}	.092	.067	-.023	-.065
Na^+	.082	-.096	-.032	-.106
K^+	.061	-.090	.197	-.103
PA	.030	.071	.034	.702
TA	.058	.014	-.294	.145
Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.				

Table 3.3 : Eigenvalues and Variance Explained by Extracted Principal Components

Total Variance Explained									
	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings		
Component	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	9.193	45.965	45.965	9.193	45.965	45.965	9.150	45.749	45.749
2	1.864	9.319	55.284	1.864	9.319	55.284	1.870	9.350	55.099
3	1.224	6.120	61.404	1.224	6.120	61.404	1.232	6.160	61.259
4	1.190	5.951	67.355	1.190	5.951	67.355	1.219	6.096	67.355

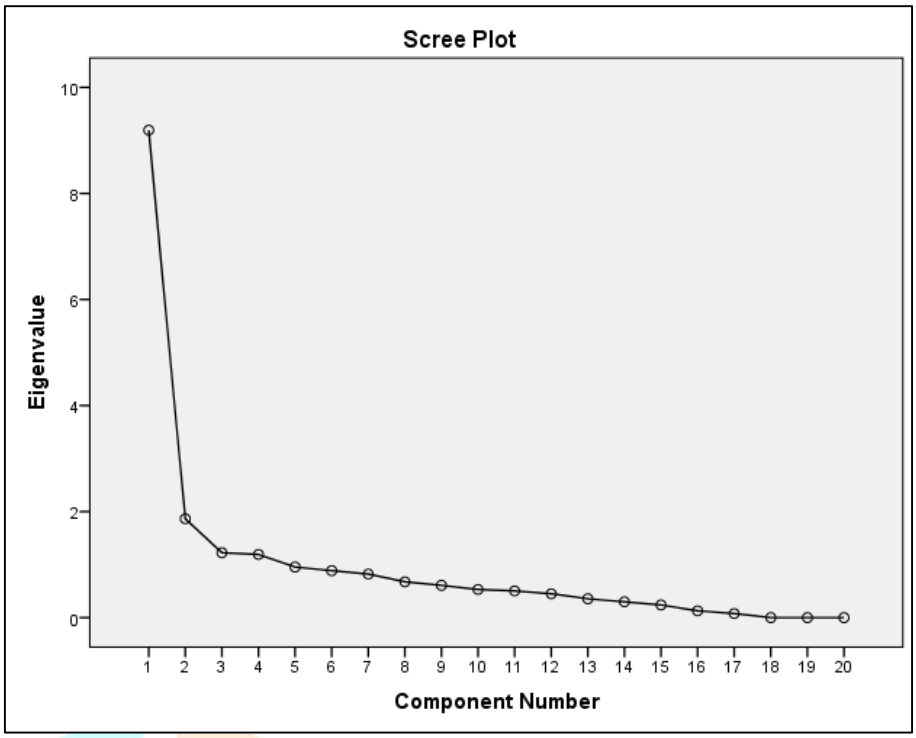

Figure 3.2 :. Scree Plot of Principal Component Analysis

3.2.2 : Hierarchical Cluster Analysis (HCA)

Hierarchical Cluster Analysis (HCA) was performed on 19 groundwater quality parameters using the squared Euclidean distance as the similarity measure and Ward's method for linkage. The proximity matrix indicated significant variability among the parameters, with the smallest distances observed between DO and ORP, Salinity and EC, TDS and EC, and the largest distances between highly dissimilar parameters such as pH and EC, and K and EC. The agglomeration schedule showed how variables progressively combined into clusters across 19 stages, with a notable increase in the agglomeration coefficient at the final stages, suggesting that the most meaningful clusters are formed before the large jump in distance. Based on the dendrogram and the agglomeration schedule, the parameters grouped into three main clusters:

- Cluster 1: EC, TDS, Salinity, TH, Mg^{2+}, Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-}, F^{-}, TA representing parameters associated with mineralization and hardness, primarily controlled by rock–water interaction.
- Cluster 2: DO, ORP, U, PO_4^{3-}, and pH reflecting redox-sensitive parameters and possible anthropogenic influences.
- Cluster 3: Temperature, PA, and K^{+} suggesting a separate influence of thermal processes and alkalinity control.

These clusters indicate that groundwater quality in the study area is predominantly shaped by geogenic factors, including mineral weathering and dissolution (Cluster 1), with secondary contributions from redox processes and human activities (Cluster 2), and minor influence from temperature-related processes and alkalinity buffering (Cluster 3). The dendrogram figure 3.3 shows clearly illustrates the distinct grouping of parameters and supports the interpretation that different hydrogeochemical processes contribute differently to water chemistry.

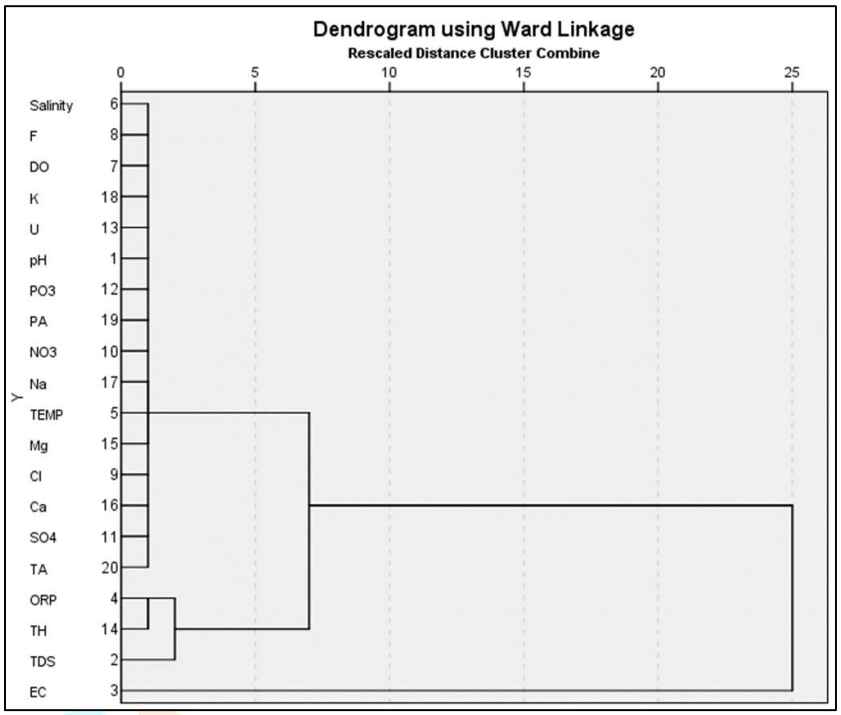

Figure 3.3 : Dendrogram of Groundwater Quality Parameters Using Ward's Linkage Method

3.2.3 Pearson's correlation

The correlation analysis shows in table 3.4 highlights strong positive relationships among the major groundwater quality parameters. TDS, EC, and salinity are perfectly correlated (r = 1.000) and show strong associations with hardness (r = 0.927), calcium (r = 0.907), magnesium (r = 0.903), and nitrate (r = 0.817), reflecting the influence of mineral dissolution and anthropogenic inputs. Uranium exhibits significant positive correlations with TDS (r = 0.489), EC (r = 0.489), total hardness (r = 0.406), calcium (r = 0.371), magnesium (r = 0.439), nitrate (r = 0.662), and bicarbonate (r = 0.200), indicating that uranium mobility is favored in saline, hard, and bicarbonate-rich groundwater. These findings suggest that groundwater chemistry in the study area is governed by both geogenic and anthropogenic processes, which also control the distribution of uranium. Below table Colour scale bar explaining the meaning of colours (blue → negative, yellow → none, red → positive).

Table 3.4 : Pearson correlation coefficients among uranium and major groundwater quality parameters (n = 139). All values are significant at $p < 0.01$ unless otherwise noted.

Parameter	TDS									
TDS	1	**EC**								
EC	1	1	**TH**							
TH	0.927	0.927	1	**Ca**						
Ca	0.907	0.907	0.986	1	**Mg**					
Mg	0.903	0.903	0.962	0.903	1	**Na**				
Na	0.742	0.742	0.718	0.691	0.718	1	**Cl**			
Cl	0.783	0.783	0.757	0.761	0.705	0.457	1	**NO_3**		
NO_3	0.817	0.817	0.764	0.756	0.731	0.594	0.68	1	**HCO_3**	
HCO_3	*0.23*	*0.23*	*0.167*	0.15	*0.184*	0.284	0.082	*0.167*	1	**U**
U	0.489	0.489	0.406	0.371	0.439	0.348	0.318	0.662	*0.2*	1

3.3 Hydrogeochemical Processes

To understand the hydrogeochemical evolution of groundwater in the study area, Piper, Gibbs, Chadha, and Durov diagrams were constructed. These diagrams illustrate the major water types and the dominant geochemical processes influencing groundwater composition.

3.3.1 Hydrogeochemical facies (Water Types)

The water facies are categorised using the Piper trilinear diagram according to the dominating ions (Piper, 1944). Major ions are shown in two base triangles as major cations and major anions in a piper diagram. The Piper diagram shows in figure 3.4 most groundwater samples in Washim District fall in the Ca–Mg–HCO_3 field, indicating fresh water influenced by carbonate mineral dissolution. A few samples trend toward Cl^- and SO_4^{2-} facies, suggesting minor effects of evaporation or contamination. Similar findings have been reported in other regions of India, where Ca–Mg–HCO_3 type water dominates, reflecting rock–water interaction and recharge processes (Saikia et al., 2021; Koliyar et al., 2021).

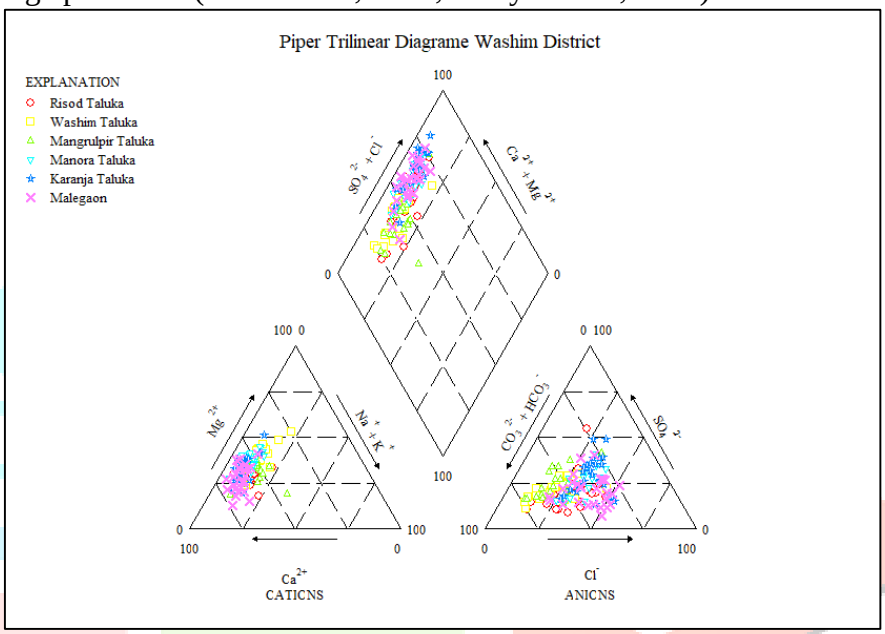

Figure 3.4 : Piper diagram illustrating the hydrogeochemical facies of groundwater in Washim District.

3.3.2 Geochemical Processes

The Gibbs diagrams shows in figure 3.5 illustrate the dominant processes controlling groundwater chemistry in Washim District. In both plots TDS vs. $Na^+/(Na^+ + Ca^{2+})$ (Gibbs I) and TDS vs. $Cl^-/(Cl^- + HCO_3^-)$ (Gibbs II) shows in figure 3.6 most samples cluster within the rock dominance field, indicating that water–rock interaction, mainly carbonate and silicate weathering, governs groundwater composition. A few samples trend toward the evaporation dominance field, particularly at higher TDS levels, suggesting localized evaporative concentration. No samples fall in the precipitation dominance field, confirming minimal direct rainfall influence on groundwater chemistry in this semi-arid region. (Alam, 2013; Raju et al., 2011).

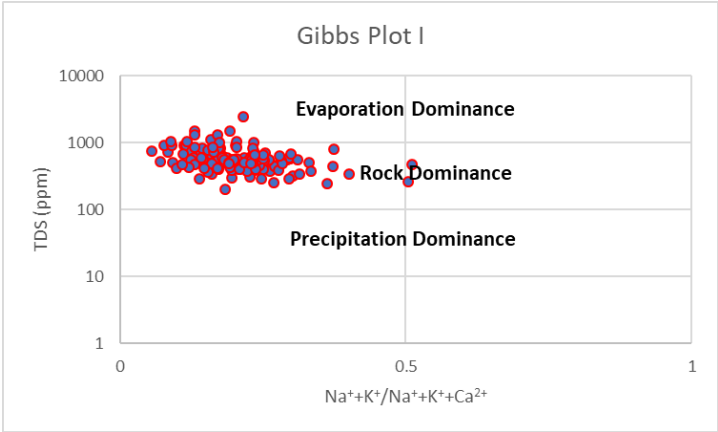

Figure 3.5 : Mechanism controlling groundwater chemistry (Gibbs I).

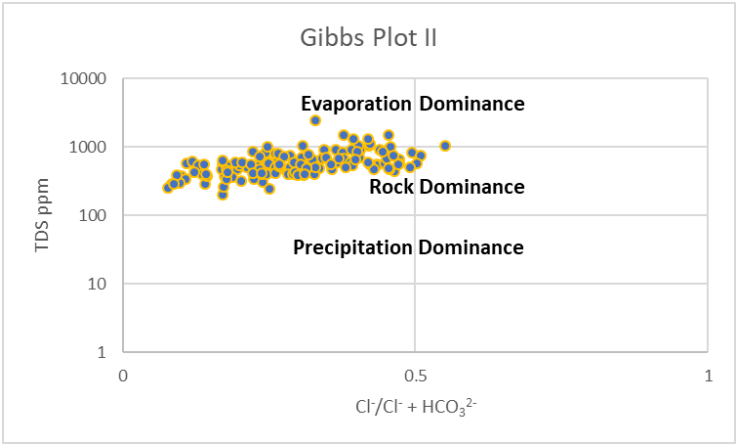

Figure 3.6 : Mechanism controlling groundwater chemistry (Gibbs II).

The Durov plot shows figure 3.7 in that most groundwater samples fall in the Ca-Mg-HCO_3 and Ca–Mg–SO_4/Cl fields, indicating that groundwater chemistry is mainly controlled by rock weathering with some influence from evaporation and anthropogenic sources.

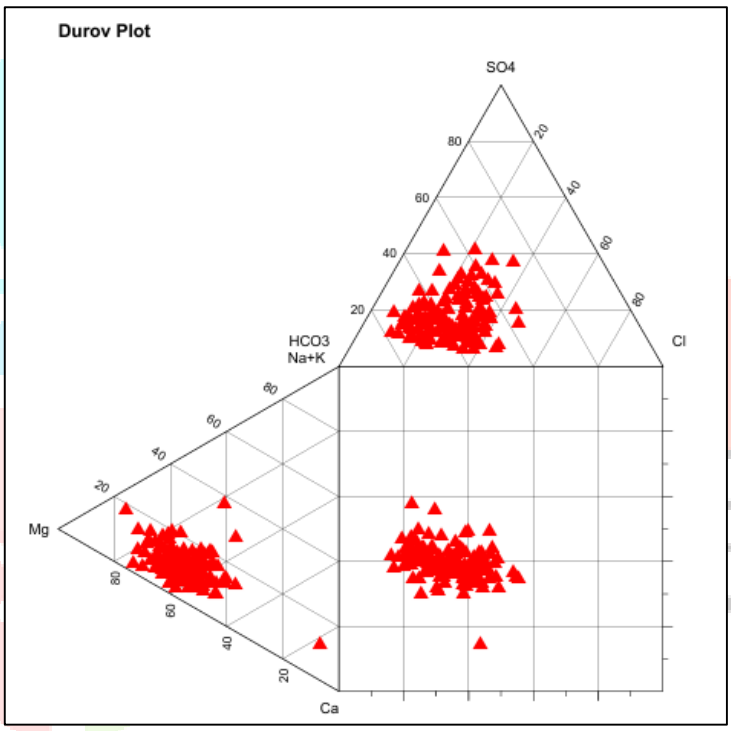

Figure 3.7 : Durov plot of groundwater samples.

4. Conclusion

The groundwater quality in Washim District during the post-monsoon season was largely within WHO (2011) limits and consistent with CGWB (2019) data, though localized exceedances of TDS, nitrate, hardness, calcium, and magnesium were observed due to natural and anthropogenic factors. Multivariate and hydrogeochemical analyses revealed that water chemistry is primarily controlled by rock-water interactions, mineral dissolution, and redox processes, with minor human influences. The dominance of Ca–Mg–HCO_3 facies confirms carbonate weathering as the main mechanism. Regular monitoring and targeted management are recommended to sustain groundwater quality and mitigate localized contamination risks.

Authors Contribution:

NAD: Investigation, Writing-Original Draft, Formal Analysis. **GVK:** Supervision, Reviewing and Editing. **RGK:** Statistical analysis. **ALT:** Help in Sampling.

Conflict of Interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements:

The authors thank Principal, Shri Shivaji College of Arts, Commerce and Science, Akola for the facilities provided for the research work. Sincere appreciation is given to the Department of Chemistry Science's laboratory staff and research colleagues.

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