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Assessment of Groundwater Chemistry and Quality Characteristics in an Alluvial Aquifer and a Single Plane Fractured-Rock Aquifer in Bloemfontein, South Africa

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Abstract**—**The evolution of groundwater chemistry and its quality is largely controlled by hydrogeochemical processes and their understanding is therefore important for groundwater quality assessments and protection of the water resources. A study was conducted in Bloemfontein town of South Africa to assess and compare the groundwater chemistry and quality characteristics in an alluvial aquifer and single-plane fractured-rock aquifers. 9 groundwater samples were collected from monitoring boreholes drilled into the two aquifer systems during a once-off sampling exercise. Samples were collected through low-flow purging technique and analysed for major ions and trace elements. In order to describe the hydrochemical facies and identify dominant hydrogeochemical processes, the groundwater chemistry data are interpreted using stiff diagrams and principal component analysis (PCA), as complimentary tools. The fitness of the groundwater quality for domestic and irrigation uses is also assessed. Results show that the alluvial aquifer is characterised by a $Na\text{-}HCO_3$ hydrochemical facie while fractured-rock aquifer has a $Ca\text{-}HCO_3$ facie. The groundwater in both aquifers originally evolved from the dissolution of calcite rocks that are common on land surface environments. However the groundwater in the alluvial aquifer further goes through another evolution as driven by cation exchange process in which Na in the sediments exchanges with Ca^{2+} in the $Ca\text{-}HCO_3$ hydrochemical type to result in the $Na\text{-}HCO_3$ hydrochemical type. Despite the difference in the hydrogeochemical processes between the alluvial aquifer and single-plane fractured-rock aquifer, this did not influence the groundwater quality. The groundwater in the two aquifers is very hard as influenced by the elevated magnesium and calcium ions that evolve from dissolution of carbonate minerals which typically occurs in surface environments. Based on total dissolved levels (600-900 mg/L), groundwater quality of the two aquifer systems is classified to be of fair quality. The negative potential impacts of the groundwater quality for domestic uses are highlighted.

Keywords**—**Alluvial aquifer, fractured-rock aquifer, groundwater quality, hydrogeochemical processes.

I. INTRODUCTION

ASSESSMENT of groundwater chemistry and its influence on the groundwater quality is an important facet of hydrogeological investigations. The evolution of groundwater chemistry is controlled by hydrogeochemical processes that occur as the groundwater interacts with of rocks [1], [2]. It is therefore important to be able to identify and describe these dominant hydrogeochemical processes in order to assess the evolution of the groundwater chemistry and quality [3]-[5]. Groundwater-rock interaction can occur during the groundwater recharge process by precipitation but also during the movement of the groundwater within the aquifer. The initial chemical signatures of the groundwater chemistry are acquired during the rainfall process, followed by the reactions during recharge and movement within the aquifer. Hydrogeochemical investigations therefore attempt to understand the various hydrogeochemical processes shaping the quality of the ground during its transit time from precipitation, recharge and discharge zones.

In nature, the types of hydrogeochemical process can vary depending on aquifers types. The duration and nature of interaction between groundwater and rocks is influenced by groundwater flow rates and flow patterns which vary from one aquifer to the other. A good example is the difference in properties between alluvial and fractured-rock aquifers, and the potential influence on hydrogeochemical processes. Fractured-rock aquifers are typically characterised by high groundwater rates which could reduce time for rock-water interaction as compared alluvial aquifers. While case studies investigating hydrogeochemical processes in a single aquifer system are common, the studies to compare the hydrogeochemical processes between different aquifer systems are rare. The current study was therefore designed to assess and compare the groundwater chemistry and quality characteristics in an alluvial aquifer and single plane fractured-rock aquifers. The study sites are located in Bloemfontein town of South Africa (Fig. 1).

II. METHODS AND MATERIALS

A. Study Sites Description

Fractured-Rock Aqiufer

The site is located at the University of the Free State in South Africa (Fig. 1). The aquifer consists of a single-horizontal bedding plane-fracture zone as the main groundwater preferential flow path. The fractured zone is located about 21 meters below ground level (mbgl) and is situated between the upper and lower matrix aquifer layers of high storativity but low permeability. 9 samples were collected from boreholes drilled to intersect the fracture. During low-

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flow purging, the groundwater mostly comes from the fracture itself thus groundwater samples collected are representative of fracture water. A comprehensive hydrogeological conceptual model of this aquifer system is in [6].

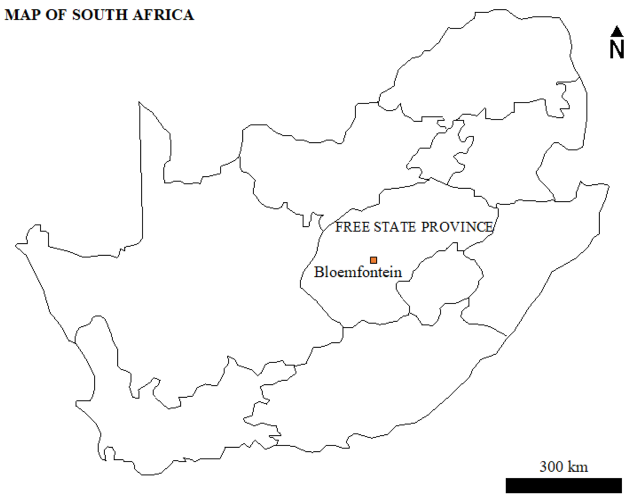

Fig. 1 Map of South Africa showing the location of the study sites in the Free State Province of South Africa

Alluvial Aquifer

The aquifer is characterised by shallow (10 mbgl) unconsolidated sediment deposits that were deposited on top of shale bedrock. The gravel-sand hydrofacies mainly consist of coarse sand and gravel deposits of different types that represent channel deposits of different depositional environment. Gravel-sand deposits are a common phenomenon along most of the major alluvial rivers. The gravel-sand hydrofacies are typically characterised by high hydraulic conductivities and thus are targeted for groundwater supply purposes in most of the river basins. Reference [7] gives a detailed description of the hydrogeological properties of this aquifer system.

B. Sample Collection

A total of 9 samples were collected from boreholes drilled into the two aquifer system during a once-off sampling event June 2016. Low-flow purging (pumping rate of < 0.03 L/s) method is used to collect samples. Low-flow purging minimizes drawdown of the water column in the well in order to avoid disturbance of the stagnant water in the well screen, and draw fresh water through the screen [8], [9]. Temperature, pH and electrical conductivity (EC) were continuously monitored in purged water. Samples were only collected once these parameters had achieved some form of stabilisation. Stabilization of field chemistry parameters indicates when the formation water is accessed during purging [10]. Samples were collected into clean and labelled 500 ml polyethylene bottles which were first rinsed with water to be sampled before samples were collected. After sampling, the bottles were tightly closed to prevent interaction with atmospheric gases and then stored under cool conditions (~6 °C). Samples were delivered to the analytical laboratory within 24 hours.

C. Laboratory Analysis

Groundwater samples were analysed for the dissolved constituents of major ions and trace elements. The analysis was conducted by the Institute of Groundwater Studies (IGS) Water Quality Laboratory at the University of Free State in South Africa. The ion balance error (IBE) for the analysis was -3.8% to 1.9% and -3.6% to - 2.5% for samples from the alluvial aquifer and single plane fractured-rock aquifer respectively.

D. Data Analysis and Interpretation

The Stiff diagrams were used classify the groundwater according to hydrochemical facies. PCA of the major ions is to identify dominant hydrogeochemical processes controlling the evolution of groundwater chemistry and quality. The IBM SPSS Software program was used for the PCA. Saturation indices (SI) for mineral phases were calculated using the PHREEQC hydrogeochemical model [11]. Groundwater quality was assessed for domestic use suitability based on indices of Total Dissolved Solids (TDS) [12] and hardness [13].

III. RESULTS AND DISCUSSION

A. Statistical Description of Data

Table I shows a statistical descriptive of the chemistry data for the groundwater samples collected from the alluvial aquifer. The pH of alluvial aquifer groundwater ranges 7.67-7.96 and is indication of alkaline conditions. The dominance of the major ions is in the order of HCO_3; Na; Cl Mg; Ca and K. The concentrations of Na and HCO_3 spread widely from the average as indicated by the standard deviation of 12.09 and 21.35 respectively.

TABLE I
STATISTICAL SUMMARY OF THE GROUNDWATER CHEMISTRY DATA FROM ALLUVIAL AQUIFER

Parameter	**Minimum**	**Average**	**Standard deviation**	**Maximum**
pH	7.67	7.83	0.082	7.96
Ca	31.05	34.95	2.626	40.26
Mg	41.38	44.26	3.967	54.24
Na	86.11	108.38	12.09	129.96
K	6.61	7.24	0.290	7.72
HCO_3	380	413.56	21.35	435
F	0.53	0.60	0.079	0.70
Cl	55.30	59.21	2.784	65.39
Br	0.32	0.41	0.075	0.57
NO_3(N)	0.000	0.09	0.059	0.092
SO_4	21.2	25.30	2.500	30.3
Fe	0.021	0.02	0.007	0.041
Ni	0.027	0.02	0.002	0.027
Si	22.128	24.79	2.038	29.441
Sr	0.043	0.65	0.042	0.741
V	0.041	0.05	0.004	0.057
Zn	0.015	0.02	0.003	0.025

All the ions are measured as total ions and are expressed in mg/L; NO_3 (N) - Nitrate as nitrogen.

Statistical summary of the groundwater chemistry data from single-plane fractured-rock aquifer system is presented in

Table II. The average pH of 6.93 shows the presence of slightly acidic conditions in fractured-rock aquifer. The dominance of the major ions concentration is in the order of: HCO_3; Ca; Cl; Na; Mg; SO_4 and K.

TABLE II
STATISTICAL SUMMARY OF THE GROUNDWATER CHEMISTRY DATA FROM SINGLE-PLANE FRACTURED-ROCK AQUIFER SYSTEM

Parameter	Minimum	Average	Standard deviation	Maximum
pH	6.81	6.93	0.08	7.09
EC	73.7	84.50	10.52	111
Ca	72.7	82.39	6.19	94.4
Mg	32.4	35.87	2.97	42.2
Na	42.5	56.62	13.66	92.1
K	4.19	5.08	0.77	6.68
HCO_3	323	336.89	9.48	356.0
F	0.31	0.39	0.07	0.56
Cl	43	67.99	21.93	121
Br	0.29	0.54	0.19	0.89
NO_3(N)	2.26	3.17	0.58	4.37
SO4	56.3	75.86	25.47	141.8
AL	0.028	0.06	0.02	0.070
Fe	0.05	0.05	0.02	0.082
Se	0.017	0.02	0.00	0.028
Si	16.41	19.12	1.10	20.25
Sr	0.653	0.76	0.10	0.947
Zn	0.03	0.04	0.01	0.054

B. Single-Plane Fractured-Rock

1. Hydrochemical Facies and Hydrogeochemical Processes

The groundwater samples from the single-plane fractured-rock aquifer indicate an overly dominant Ca-HCO_3 hydrochemical facie as indicated on the stiff diagrams (Fig. 2). Ca-HCO_3 hydrochemical is typical of recently recharged groundwater. Carbonate rocks dominated by calcite minerals often occurs in abundance on the near surface environment and these can react with weak carbonic acid from rainfall to give rise to a Ca-HCO_3 hydrochemical facie [14]. The dissolution of calcite ($CaCO_3$) by weak carbonic acid (H_2CO_3) is described by the hydrogeochemical process presented in (1). This reaction releases Ca^{2+} and bicarbonate HCO_3^- ions which become dominant in the groundwater system to give rise to the Ca-HCO_3 hydrochemical facie.

$$H_2CO_{3(aq)} + CaCO_{3(s)} \leftrightarrow Ca^{2+}{}_{(aq)} + 2HCO^-_{3(aq)} \quad (1)$$

Due to high groundwater flow rates in typical fracture-rock aquifers, the water in the fracture has limited opportunity to interact with the matrix of the main formation, thus it is most likely retain the hydrogeochemical signatures acquired during the recharge process.

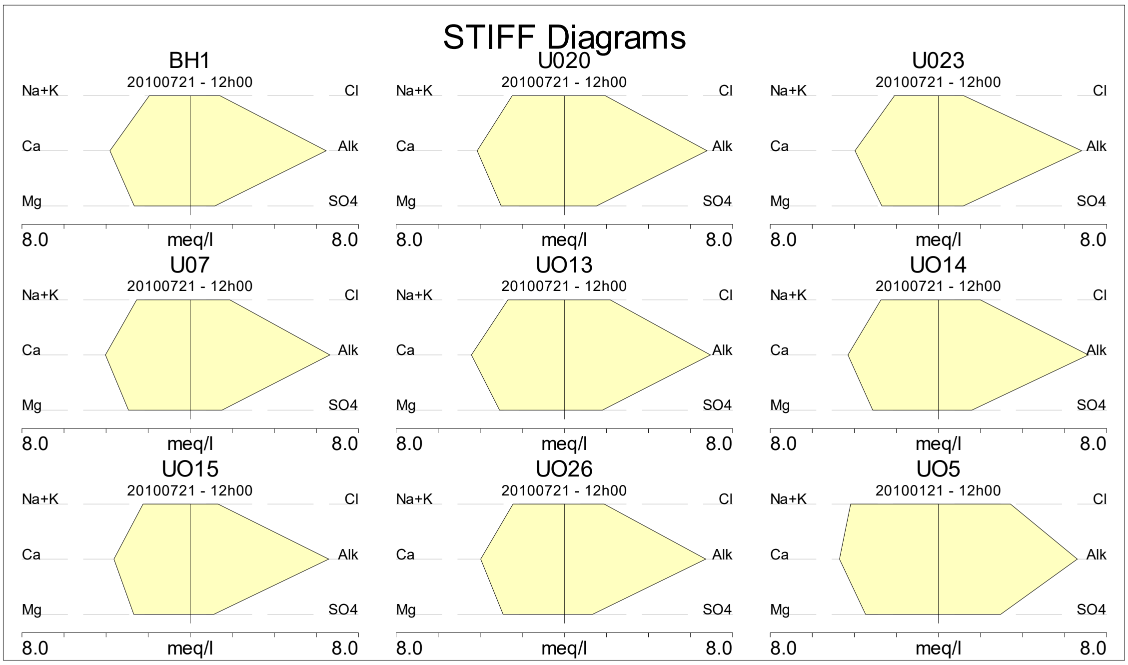

Fig. 2 Stiff diagrams showing the Ca-HCO_3 hydrochemical facies of the single-plane fractured-rock aquifer

An attempt was also made to use PCA to identify the main hydrogeochemical processes controlling the evolution of the groundwater chemistry and hence its quality in the single-plane fractured-rock aquifer system. Table III shows the results of the PCA for the major ions detected in the fractured-rock aquifer.

Principal component 1 (PC1) is strongly correlated with all the groundwater chemistry parameters with the exception of HCO_3 and pH. Principal component increases with increasing EC, Ca, Mg, Na, K, Cl, SO_4 and NO_3 parameters. This implies that PC1 represents a process that leads to simultaneous increase of these 8 parameters. The EC is generally a measure of the TDS, hence should naturally increase with the increase in these 7 ion concentrations. On the other hand, PC1 is negatively but weakly correlated to pH as indicated by a low factor lading of 0.249 and this strongly suggests that the process is not pH dependent. It is difficult to think of any hydrogeochemical processes which could simultaneously result in the increase of Ca, Mg, Na, K, Cl, SO_4 and NO_3 ion concentrations in a groundwater system while at the same time being independent of pH. By nature, groundwater tends to accumulate readily dissolved ions as it moves through flow paths and this process is not always chemical. In this aquifer system, the groundwater moves through high transmissive fractures thus there is very limited time and space for reacting with the fracture formation. Accumulation of those ions is bound to occur along flow path through physical transportation process. The HCO_3 has negative relationship to the ions because in nature the HCO_3 ion is part of the total carbonate alkalinity which would generally decrease from the recharge area as the conditions tends to be reduced. The second PC2 is strongly negatively correlated to pH. However its contribution is very much limited as indicated by low factor loadings of the rest of Table IV shows the SI of calcite, dolomite, fluorite and gypsum calculated for the samples collected from the single-plane fractured-rock aquifer. With the exception of UO5 borehole, the groundwater in the single-plane fractured-rock aquifer is oversaturated with respect to calcium, dolomite and fluorite minerals as indicated by positive SI. This implies that the groundwater cannot dissolve calcite, dolomite and fluorite minerals it comes in contact with rocks with having these rocks. Due to their oversaturation, these minerals have the potential to precipitate out of the solution. It has been inferred that the groundwater chemistry evolved from dissolution of carbonate rocks. Fluorite is also known to occur as a constituent of calcite and dolomite minerals in a wider range of environments [15]. It is therefore possible that by this time the groundwater had sufficiently dissolved these minerals to reach an oversaturation state. Gypsum is slightly saturated in the groundwater (exception of UO5 borehole); this could be due to the indirect influence of ions released during the dissolution carbonate minerals.

TABLE III
RESULTS OF THE PCA FOR THE MAJOR IONS DETECTED IN THE FRACTURED-ROCK AQUIFER

Parameters	Rotated components	
	PC1	PC2
pH	-0.25	-0.88
EC	0.99	0.03
Ca	0.86	0.10
Mg	0.99	0.33
Na	0.99	0.06
K	0.91	0.32
HCO_3	-0.01	0.45
F	0.82	-0.34
Cl	0.99	0.10
NO_3(N)	0.94	0.18
SO_4	0.99	0.04

TABLE IV
SI OF CALCITE, DOLOMITE, FLUORITE AND GYPSUM

Parameters	Calcite	Dolomite	Fluorite	Gypsum
UO5	-0.06	-0.13	-1.54	-1.48
U07	2.34	4.48	0.99	0.52
UO13	2.23	4.24	1.12	0.60
UO14	2.28	4.36	1.06	0.54
UO15	2.28	4.37	1.15	0.39
U020	2.28	4.35	0.91	0.53
U023	2.38	4.53	1.01	0.43
UO26	2.36	4.52	1.13	0.47
BH1	2.47	4.72	1.08	0.42

2. Groundwater Quality of the Fractured-Rock Aquifer

TDS

Table V shows the groundwater quality classification for single-plane fractured-rock aquifer based on TDS levels [12]. Based on the TDS, the groundwater is classified as fair. With the exception of the anthropogenic influence, recently recharged groundwater is typically fresh and lowly mineralised. All the analysed elements (Table II) are below the drinking water quality guidelines [16].

TABLE V
GROUNDWATER QUALITY CLASSIFICATION OF THE SITE BASED ON THE [12] TDS INDEX

Quality	TDS (mg/L)	Number of samples
Excellent	<300	0
Good	300-600	0
Fair	600-900	9
Poor	900-1200	0
Unacceptable	>1200	0

Hardness

Based on the index for the groundwater of hardness [13], the groundwater is classified as very hard (Table VI). While water hardness does not have known negative human health impacts, it can affect the taste of the water, effectiveness of detergents and reduce the efficiency of water heating equipment through the scaling effects.

TABLE VI
CLASSIFICATION OF GROUNDWATER HARDNESS IN THE SINGLE PLANE FRACTURED-ROCK AQUIFER BASED ON [13] INDEX

Hardness class	Total hardness as $CaCO_3$ (mg/L)	Number of samples
Soft	<60	0
Moderately hard	60-120	0
Hard	120-180	0
Very hard	>180	9

C. Alluvial Aquifer

Hydrochemical Facies and Hydrogeochemical Processes

The alluvial aquifer is characterised by a Na-HCO_3 hydrochemical facie as shown on the Stiff diagrams (Fig. 3). The Na-HCO_3 evolves from the recently recharged groundwater Ca-HCO_3 characteristics. Ca-HCO_3 is typical of recently recharged groundwater evolving from the dissolution of calcite rocks in the environment during the interaction with rainwater and groundwater recharge process. Due to the influence of cation exchange (CE) process, Na in the sediments exchanges with Ca^{2+} in the Ca-HCO_3 hydrochemical type to result in the current Na-HCO_3 hydrochemical type.

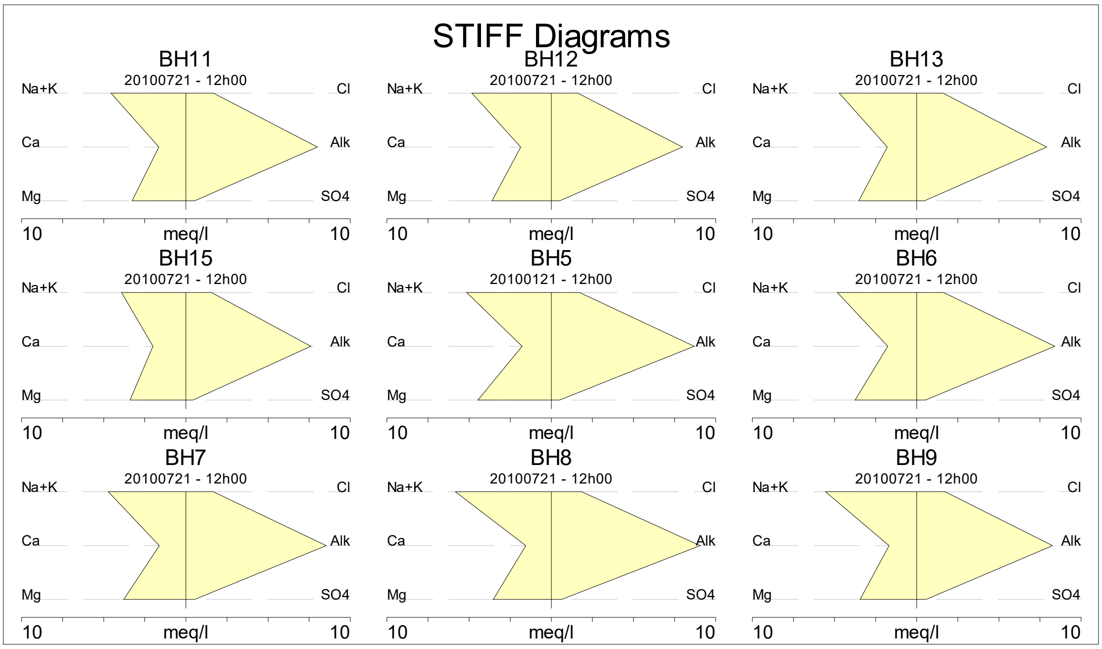

Fig. 3 Stiff diagrams showing the Na-HCO_3 hydrochemical facies of the alluvial aquifer

TABLE VII
RESULTS OF THE PCA FOR THE MAJOR IONS DETECTED IN THE ALLUVIAL AQUIFER

Parameters	**Rotated component**	
	1	2
pH	-0.40	-0.78
Ca	-0.90	-0.10
Mg	-0.05	0.95
Na	0.87	0.27
K	0.18	0.89
HCO_3	0.81	0.51
F	0.69	0.64
Cl	0.94	0.18
Fe	0.39	0.77
NO_3(N)	-0.13	-0.85
SO_4	0.98	0.04

TABLE VIII
SI OF CALCITE, DOLOMITE, FLUORITE AND GYPSUM

Borehole number	**SI**			
	Calcite	**Dolomite**	**Fluorite**	**Gypsum**
BH5	2.33	6.19	1.15	-0.59
BH6	2.85	6.00	1.16	-0.29
BH7	2.87	6.08	1.12	-0.33
BH8	2.88	6.04	1.08	-0.28
BH9	2.89	6.04	0.97	-0.30
BH11	2.98	6.22	1.05	-0.28
BH12	3.00	6.27	1.08	-0.32
BH13	3.08	6.36	0.89	-0.29
BH15	3.69	6.44	1.34	-0.31

In comparison to the fractured-rock aquifer, the transmissivities in the alluvial aquifer are relatively lower thereby potentially allowing time for interaction between the recharged groundwater sediments leading to the CE process. The presence of the quaternary sediment formation provides potential Na exchangeable sites for the CE process. This results in different hydrogeochemical processes and therefore different hydrochemical facies in the single-plane fractured-rock and alluvial aquifer.

Table VII shows results of the PCA for the major ions detected in the alluvial aquifer. Component 1 has a strong positive correlation to Na, HCO_3, SO_4, F and Cl. The component has also a strong negative correlation to Ca and a negative weak correlation to pH. The component 1 might possibly explain 2 hydrogeochemical processes. Firstly it is the cation ion exchange where Na in the sediments exchanges with Ca from the groundwater system. This results in generally negative relationship between the two cations where Ca concentration in the groundwater decreases while Na increases. The increase in Na, SO_4, F and Cl could be generally linked with to groundwater water interactions with weak sediment minerals while HCO_3 could be due to carbonate rocks dissolution.

Component 2 has strong positive correlation to Mg, K, F and Fe but is also negatively correlated to pH and NO_3 (N). The strong correlation of the component to Mg, K, F and Fe can be explained by interaction of the groundwater with biotite [$K(Fe, Mg)_3$ $AlSi_3$ O10 $(F, OH)_2$] minerals in the sediments as the pH decrease. Dissolution of biotite has the potential to release Mg, K, F and Fe into the groundwater system. The negative correlation to NO_3 (N) suggests some reduction process associated with pH decrease leading to the depletion of NO_3 (N).

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Just like the single-plane fractured-rock aquifer, the groundwater in the alluvial aquifer is oversaturated with respect to calcium, dolomite and fluorite minerals as indicated by positive SI (Table VIII). This implies that the groundwater cannot dissolve calcite, dolomite and fluorite minerals if it comes in contact with rocks having these minerals. Due to their oversaturation, these minerals have the potential to precipitate out of the solution. However unlike the single-plane fractured-rock aquifer, the alluvial aquifer is undersaturated to gypsum.

Groundwater Quality in the Alluvial Aquifer

TDS

Table IX shows the groundwater quality classification for the alluvial aquifer based on TDS levels [12]. Just like the fractured-rock aquifer, the groundwater is classified as fair. All the analysed elements (Table I) are below the [16] drinking water quality guidelines.

TABLE IX
GROUNDWATER QUALITY CLASSIFICATION OF THE SITE BASED ON THE TDS INDEX [12]

Quality	TDS (mg/L)	Number of samples
Excellent	<300	0
Good	300-600	0
Fair	600-900	9
Poor	900-1200	0
Unacceptable	>1200	0

Hardness

Based on the index for the groundwater of hardness [13] (Table V), the groundwater is classified as very hard. The potential negative effects are similar to the ones highlighted under the single-plane fractured-rock aquifer.

TABLE X
CLASSIFICATION GROUNDWATER HARDNESS IN THE ALLUVIAL AQUIFER BASED ON THE INDEX [13]

Hardness class	Total hardness as $CaCO_3$ (mg/L)	Number of samples
Soft	<60	0
Moderately hard	60-120	0
Hard	120-180	0
Very hard	>180	9

IV. CONCLUSIONS

The study highlights the importance of application of stiff diagrams and PCA as complimentary tools to investigate hydrogeochemical processes in aquifers. The value of understanding hydrogeochemical process controlling the evolution of groundwater chemistry is prior to the evaluation of groundwater quality is demonstrated.

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