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Hydrogeochemical assessment of groundwater quality in the Soutpansberg Basin around Tshikondeni, Limpopo Province, South Africa

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Abstract: The objective of this study was to investigate the impact of anthropogenic and natural sources of contamination on the groundwater quality of the unconfined aquifer system of the Soutpansberg Basin around Tshikondeni. Fifteen groundwater samples were collected and analysed for physical and chemical parameters. Groundwater samples were analysed for pH, EC, TDS, major cations (Na^+ , Ca^{+2} , K^+ , and Mg^{+2}), major anions (Cl^- , SO_4^{-2} , NO_3^- , CO_3^{3-} and HCO_3^-). Groundwater in this area was found to be above the desirable Department of Water and Sanitation (DWS) and World Health Organisation (WHO) limits for domestic and irrigation purposes. After the physicochemical analysis of groundwater, samples shows that, the type of water that predominates in the study area is $\text{Na}^+ - \text{K}^+ - \text{Ca}^{+2} - \text{Mg}^{+2}$ type during the summer of the year 2008, based on hydro-chemical facies. Interpretation of hydro-geochemical data suggests that leaching of ions followed by weathering and anthropogenic impact (mainly mining and agricultural activities) control the chemistry of groundwater in the study area. Groundwater suitability for drinking purpose was also evaluated by the synthetic pollution index (SPI), it suggested that most of the samples fall in seriously polluted categories. The calculated values of SAR, Na%, RSC, PI, and MH have shown that except at few locations, most of groundwater samples are not suitable for agricultural and domestic purposes.

Keywords: Groundwater; Hydrogeochemistry; Water quality; major ions; South Africa

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Groundwater is the most reliable water supply source for domestic, agricultural and industrial use in South Africa and other countries across the world. In terms of South Africa's overall water consumption, groundwater contributes only some 15% of the total volume consumed (DWAF 2002). This percentage contradicts the fact that over 300 towns and 65% of the population are entirely dependent upon this resource for their water supply. Lack of reliable hydrogeological information has been identified as one of the reasons why groundwater has generally not been developed to its full potential. It is estimated that some 12 million people in South Africa are still without an adequate supply of water to meet their basic needs (DWAF 2002). However, despite its reliability, this precious and vital resource is under increasing threats attributed to above ground anthropogenic activities related to uncontrolled urbanisation, mining, nonstop waste disposal and poor land use management. Also, the usefulness of groundwater to humans essentially depends on its chemical status, thus assessment of groundwater quality is important for socio-economic development of most developing and developed countries of the world. Geochemical processes, regional geology and land use pattern are major factors for controlling groundwater chemistry (Matthess 1982; Kumar *et al.* 2006; Liu *et al.* 2008; Zhu & Schwartz 2011).

Groundwater quality is an important factor in the context of sustainable water management, the integrity of underlying aquifers are mainly affected by pollution from above ground sources (Kumar *et al.* 2013) particularly solid waste disposal and mining activities. Once groundwater is contaminated; its quality cannot be restored and it is very expensive, and difficult to clean it up.

The main objective of this study was to investigate the impact of anthropogenic and natural sources of contamination on the groundwater quality of the Soutpansberg Basin around the

Tshikondeni area, and to determine whether the water in this system is within the acceptable limit for human consumption, irrigation and livestock as set aside by the DWS previously DWAF and the WHO.

Study area

The study area is situated around the Tshikondeni coal mining town of the Soutpansberg Basin in the Limpopo Province of South Africa (Fig. 1). The dominant land use/land cover includes shrubs, subsistence agriculture, and coal mining activities.

Physiography and climate

The Soutpansberg basin is characterized by a region of varied physiography ranging from irregular plains with moderate relief; lowlands with hills and low Mountains (Kruger 1983). The project area is underlain by Karoo rocks consisting of weather resistant sandstones which form 'kopjes' or topographic highs, surrounded by plains and valleys consisting of shale and basalt. The climate of the basin is located in the hot-arid zone where the rainfall decreases to <400 mm. The area is situated in the summer rainfall region and rainfall occurs in the form of heavy thunderstorms or soft rain. The area is characterised as being hot and dry resulting in high evaporation rates and low rainfall. It is characterized by cool, dry winters (May–August) and warm, wet summers (October–March), with April and September being transition months. Temperature range from 0.9 to 39.9°C and the area is generally frost free (SAWS 2011).

Geology and Geohydrology of the Soutpansberg basin

The regional geology is shown in Figure 1 and consists of three main lithological groups: (1) the Limpopo Mobile Belt; (2) the Soutpansberg Group; and (3) the Karoo Supergroup rocks:

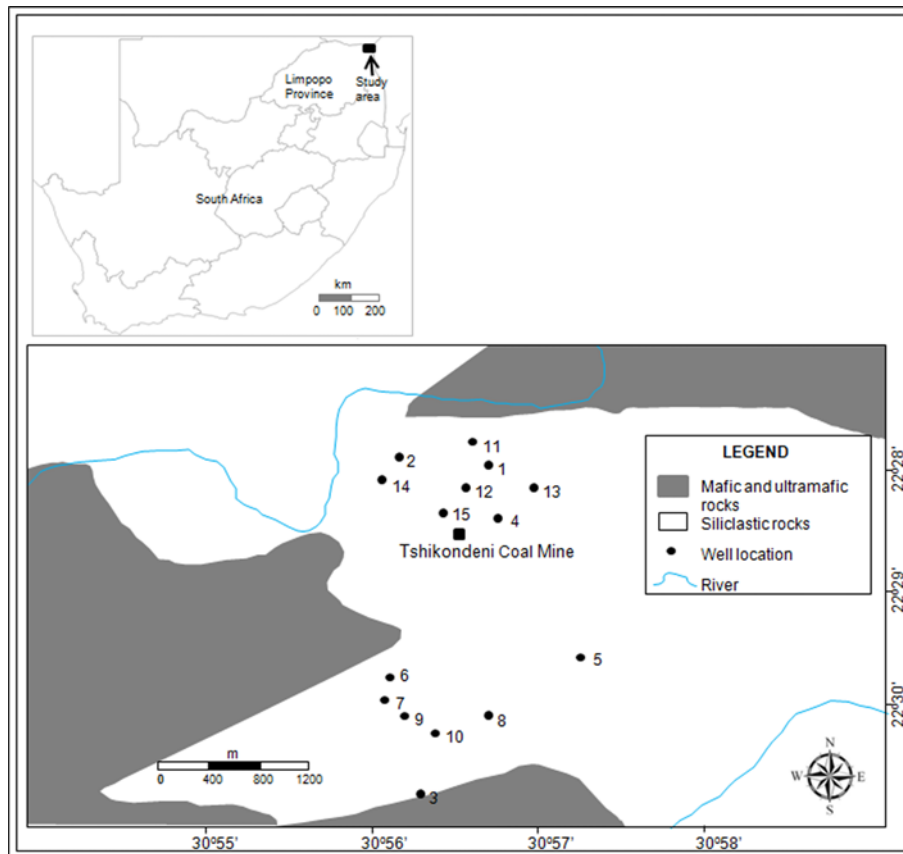


Fig. 1. Map of the study area in the Soutpansberg Basin.

The Karoo Sequence strata were deposited on the Limpopo Mobile Belt (LMB) basement and/or Soutpansberg Group strata between 300 and 180 Ma. The Karoo deposits are preserved in rift basins and are often terminated against major east-west trending faults on their northern margins. The dips are between 3° and 20° to the north with coal located at the base of the sequence. Brandl & McCourt (1980) considered three stratigraphic periods namely the Permian, Triassic and Jurassic Periods. The Permian Period consists of three formations (the diamictite Tshidzi, clastic Madzaringwe and Mikambeni Formations), while the Triassic Period consists of three formations (the clastic Fripp, Solitude and Klopferfontein). The Jurassic consists of the clastic Bosbokpoort and Clarens Formations (Malaza *et al.* 2013).

The Soutpansberg Group strata were deposited into rift basins controlled by major fault systems between 1900 and 1600 Ma. The strata consist of basaltic lavas, arenites, conglomerates and shales attaining a maximum preserved thickness of 5000 m. Dips can vary from 20° to 80° to the north. The Lebombo Group is comprised of olivine rich lavas and basaltic rocks. It is part of the Mesozoic Karoo Igneous Province (Malaza *et al.* 2013).

Groundwater flow in the study area is towards the Mutale and Luvuvhu Rivers. Elevated salt content is indicative of the arid climate and contact with upper Karoo strata. The Tshidzi Formation is generally considered to be an aquitard rather than an aquifer, as the diamictite and shales have very low hydraulic conductivities and virtually no primary voids (Vivier 1996). Even though the Dwyka Group is considered to be an aquitard, there are a few localities where there are exploitable aquifers and this is where the diamictite was fractured significantly (Woodford & Chevallier 2002). The quality of the groundwater improves in fractures or jointed zones, where significant groundwater movement and turnovers take place, with Electrical Conductivity (EC) values ranging between 25 and 200 mS/m (Meyer 2001).

The other sedimentary formations (Madraringwe, Mikambeni, Fripp, Solitude, Klopferfontein and Clarens) are composed of

sandstone, conglomerate, shale and coal and are characterized by significantly low (virtually absent) primary porosity and permeability. Secondary properties of these rocks – such as the degree, density, continuity and interconnection of fracturing – control the occurrence, storage and movement of groundwater. The fact that many of the coarser sediments are lens-shaped further complicates these aquifers, as the life-span of a borehole drilled into such structures may thus be limited, if not frequently recharged (Vivier 1996). The EC values vary between 70 and 1200 mS/m with the majority below 300 mS/m. The majority of yields are generally between 0.1 and 2 l/s. Higher yields can occasionally be obtained by targeting occasional folds, faults and joint structures, where favourable recharge conditions exist. These fractured systems are recharged by mostly rivers and infiltrated water from precipitation where high yielding boreholes associated with fault systems have been developed. These aquifer types are utilized by rural home-steads for portable water and farmers for irrigation and livestock.

Methodology

Groundwater samples from different land use/land cover sites (mining, industrial and rural sites) were sampled in 2011 and physicochemical analyses were performed according to APHA (2005) guidelines. All locations of sampling points were recorded with the help of global positioning system (GPS). Clean sampling bottles and caps were rinsed in the lab and again three times with the water to be sampled prior to sampling. Most of the samples were obtained directly from hand pumps after allowing the water to run for at least 5 min to stabilize the variation in electrical conductivity (EC) and temperature (Reimann *et al.* 2003). Field parameters such as pH, EC, TDS and Temperature were measured in the field due to their unstable nature. The pH and temperature of the water sample was measured with a digital HANNA pH-meter (Model HI 98129). EC and TDS were measured with a portable conductivity, TDS and salinity meter (Model EC400 Ex Stik II). The water samples were

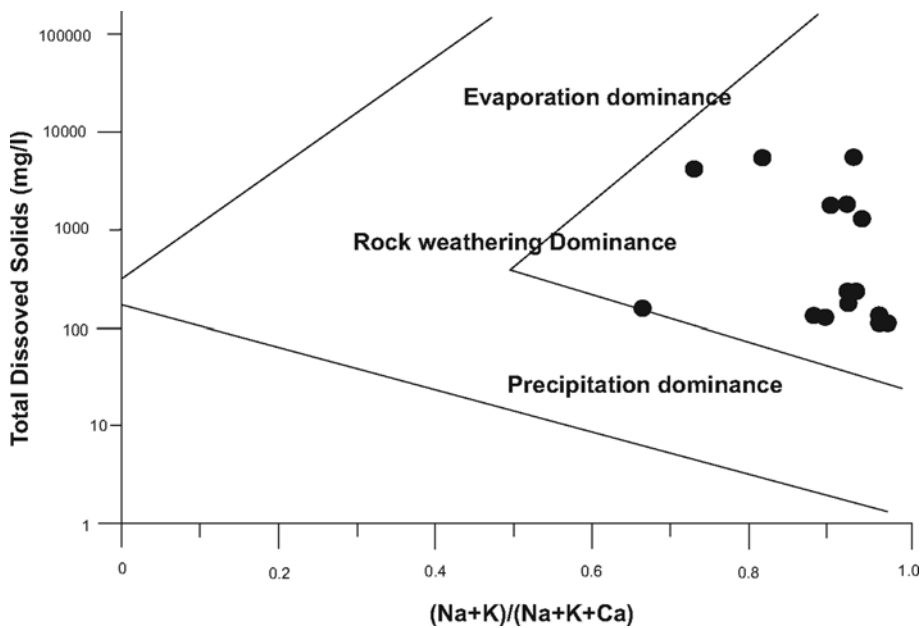


Fig. 2. Gibbs diagram of the study water samples.

chemically analysed using Atomic Absorption Spectrophotometer (AAS) (PYE UNICAM SP-9) and titrimetric method according to APHA (1999). The analytical results were evaluated in detail and compared with water quality guidelines of WHO (1984) and DWAF (2002).

After field and laboratory analysis of water samples, the geochemical data of samples were used for the graphical representation and data evaluation using the following standard diagrams:

Gibbs diagram: The Gibbs diagram (Gibbs 1970) is a widely used method to establish the relationship of water composition and

source conditions/characteristics. Three distinct fields such as precipitation dominance, evaporation dominance and rock-water interaction dominance areas are shown in the Gibbs diagram (Fig. 2).

Hydrogeochemical facies: The Piper's trilinear diagram (Piper 1944) includes two triangles, one for plotting cations and the other for plotting anions (Fig. 3). Cations and anion fields are combined to show a single point in a diamond shaped field and inference is drawn for the hydrogeochemical facies of water. Lithology, solution kinetics and flow patterns of the aquifer control hydrochemistry of the facies. Hydrochemical facies can be classified on the basis of

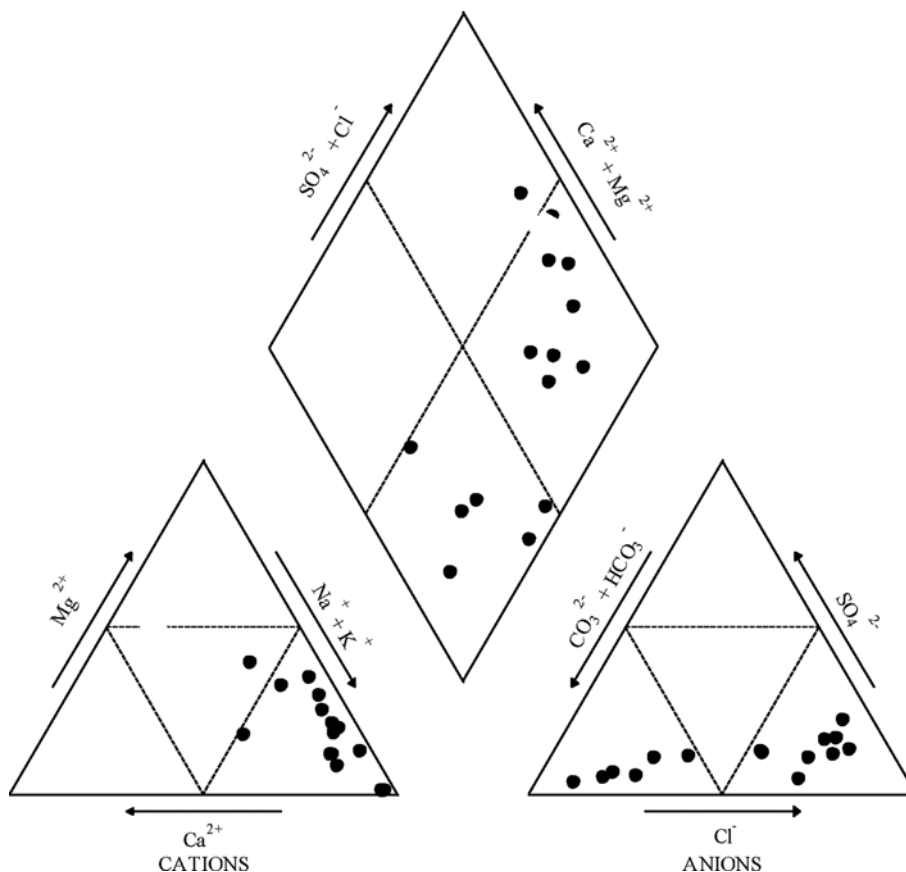


Fig. 3. Piper trilinear diagram for hydrogeochemical facies.

Table 1. Statistical summary of physicochemical parameters

Parameter	Unit	Minimum	Maximum	Mean
pH	–	7.25	9.32	8.11
EC	µS/cm	43	2481	860
Calcium	mg/l	1.5	485	142.2
Magnesium	mg/l	0.33	1007.34	294.92
Sodium	mg/l	69	4197	1297
Potassium	mg/l	1.2	26.8	12
Bicarbonate	mg/l	78.64	1106.36	588.12
Chloride	mg/l	29	7890	2166
Sulphate	mg/l	13.4	1870.3	595.6
Nitrate	mg/l	0.1	4.4	0.7

dominant ions with the support of Piper's trilinear diagram; it reveals a common composition and origin of ions in water samples.

Results and Discussion

Table 1 shows the maximum, minimum and mean concentrations of various parameters. The order of cation dominance was $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^-$ for anions. The general chemical nature of groundwater can be understood by plotting major cation and anion concentrations in a Piper trilinear diagram (Piper 1944). $\text{Na}^+\text{-Cl}^-$ was the major water type dominant in this area. The next dominant water type was mixed $\text{Mg}^{2+} - \text{Ca}^{2+} - \text{SO}_4^{2-}$ (Fig. 3).

Drinking water quality

Groundwater used for domestic purposes, such as drinking and cooking, should be free from toxic chemicals and pathogens. The concentration of various ions in the groundwater samples was compared with the Department of Water Affairs and Forestry (DWAf 2002) and World Health Organisation (WHO 2002) standards, which are given in Table 2. The groundwater in this area was thus seen to be unfit for domestic consumption and agricultural purposes, based on the major ion analysis carried out in this study. The groundwater samples were classified regarding Total Dissolved Solids (TDS) and Total Hardness (TH) (Tables 3–5). Only 33.3% of the groundwater was fresh and suitable for drinking purposes. Most of the groundwater was not suitable for drinking purposes and irrigation purposes based on TDS (Freeze & Cherry 1979; Davis & DeWiest 1966).

Irrigation water quality

Groundwater suitability for irrigation purpose in this study area was assessed using Sodium Percentage (Na%), Magnesium Hazard (MH), Residual Sodium Carbonate (RSC), Sodium Absorption Ratio (SAR), Permeability Index (PI) and United States Department of Agriculture (USDA) classification. Groundwater in most of the study area was found to be unsuitable for irrigation.

Table 2. Comparison of groundwater samples with DWAf and WHO standards

Parameter	DWAf (2002)		WHO (2004)	
	Highest desirable limit	Maximum desirable limit	Highest desirable limit	Maximum desirable limit
Ph	6–9	4–10	6.5–8.5	6.5–9.2
TH (mg/l)	<100	–	>100	–
Calcium (mg/l)	<150	150–300	75	200
Magnesium (mg/l)	<70	70–100	50	150
Chloride (mg/l)	<200	200–600	200	600
Sulphate (mg/l)	<400	400–600	200	400
Sodium (mg/l)	<200	200–400	–	200
Nitrate (mg/l)	<100	–	<100	–

Table 3. Freeze & Cherry (1979) classification of groundwater based on TDS (mg/l)

TDS (mg/l)	Water type	Number of samples	Percentage
<1000	Fresh	5	33.3
1000–10 000	Brackish	8	53.3
10 000–100 000	Saline	2	13.3
>100 000	Brine	0	0

Table 4. Davis & DeWiest (1966) classification of groundwater based on TDS (mg/l)

TDS (mg/l)	Classification	Number of samples	Percentage
<500	Desirable for drinking	2	13.3
500–1000	Permissible for drinking	3	20
1000–3000	Useful for irrigation	1	6.7
>3000	Unfit for drinking and irrigation	9	60

Table 5. Suitability for irrigation based on USDA classification

EC (µS/cm)	Salinity Class	Percentage of samples	Remark on quality
<250	C1	40	Excellent or low
250–750	C2	0	Good to medium
750–2250	C3	60	Permissible or high
2250–5000	C4	0	Unsuitable or very high

Alkali and salinity hazard (SAR)

The exchangeable sodium percentage/capacity of water is expressed (equation 1) by sodium absorption ratio (SAR) (Richards 1954), as:

$$\text{SAR} = \text{Na}^+ \div \sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+}) \div 2} \quad (1)$$

Where cationic concentrations are in milliequivalents per litre (meq/l). High sodium content in water may produce harmful effects in most soils and requires special management of water and soil, which includes application of gypsum. High bicarbonates and relatively low calcium in water is also known to be hazardous for irrigation (Richards 1954) (Fig. 4). Salt content in irrigation water causes an increase in soil solution osmotic pressure (Thorne & Peterson 1954).

All the groundwater samples collected from this area were hazardous based on the basis of SAR. Water used for irrigation can be classified into four types, C1, C2, C3 and C4 based on salinity hazard and S1, S2, S3 and S4 based on Sodium hazard. Figure 4 shows the plot of groundwater samples grouped on the above basis. Most groundwater samples fall under C3S4, which is totally not

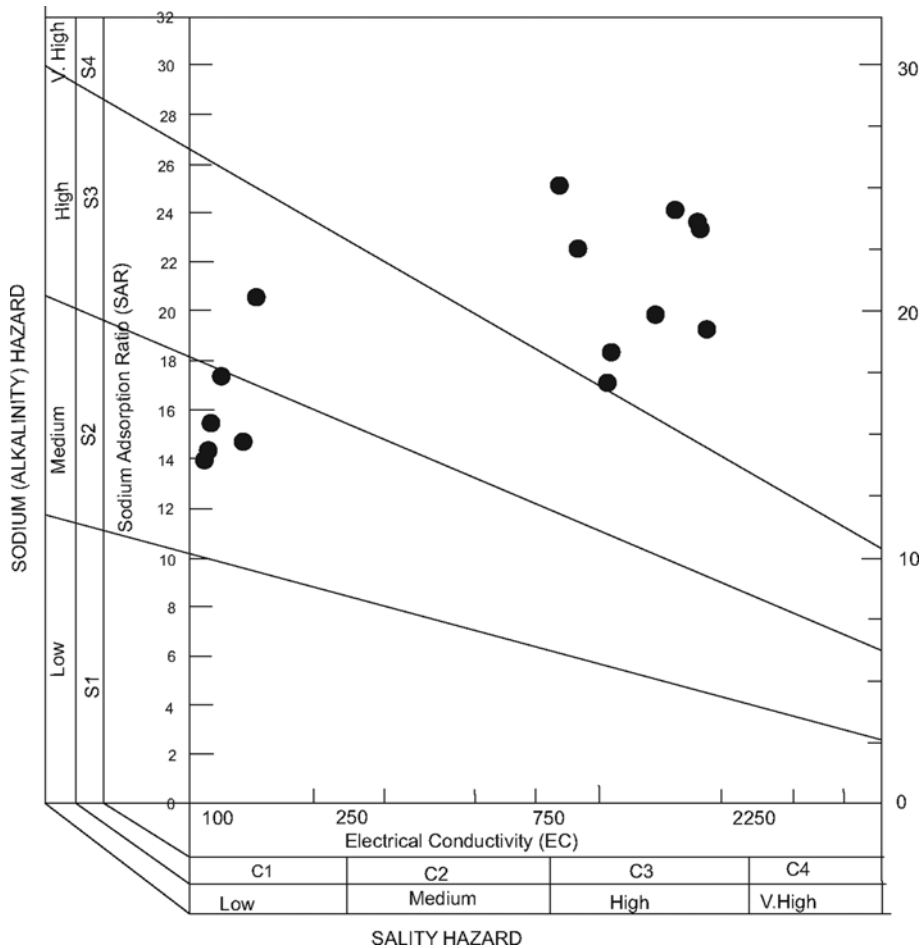


Fig. 4. United States Salinity Laboratory (USSL) salinity diagram of groundwater for classification of irrigation water (after Richards 1954)

permissible for irrigation. Comparatively few samples were grouped under C2S1 (which is permissible for irrigation). Only one sample fell under C1S3 which is not permissible for irrigation. Thus the groundwater in this area was seen not to be suitable for irrigation based on salinity hazard and sodium hazard. Irrigation water having high EC content will affect root area and water flow. Groundwater in this area was grouped according to the guidelines established by the United States Salinity Laboratory (Freeze & Cherry 1979) based on EC (Table 5).

Sodium percentage (Na%)

EC and Sodium concentration are very important in classifying irrigation water. The total concentration of soluble salts in irrigation water can be expressed for the purpose of classification of irrigation water as low ($EC < 250 \mu S/cm$), medium ($250 - 750 \mu S/cm$), high ($750 - 2250 \mu S/cm$) and very high ($2250 - 5000 \mu S/cm$) salinity zones (Richards 1954) (Fig. 5). The Na% is calculated using the formula (equation 2) given below, where the concentrations are in meq/l.

$$Na\% = \frac{(Na^+ + K^+)}{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)} \times 100 \quad (2)$$

The Na% in this area is given in Table 6. Groundwater was unsuitable for irrigation in 33% of the samples while 47% were doubtful and only 20% were permissible. EC and Na% are plotted in Figure 5 which showed that most of the groundwater samples were not permissible for agriculture.

Residual sodium carbonate (RSC)

The higher concentration of bicarbonate and carbonate ions compared to alkaline earths (Ca and Mg) has the possibility of complete precipitation of Ca and Mg (Raghunath 2000). To compute the effects of carbonate and bicarbonate, residual sodium carbonate (RSC) has been measured as expressed (equation 3): Higher value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton 1950). According to the US Department of Agriculture (USDA), water having more than 2.5 of RSC is not suitable for irrigation purposes. If RSC values have greater than 5 meq/l then it will be considered harmful to the growth of plants.

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \quad (3)$$

In the present study, groundwater samples show RSC values ranging from 10.2 to -60 meq/l. According to RSC classification 46.7% of groundwater lies in safe category ($RSC < 2.5$ meq/l) and remaining 53.3% samples in the unsafe region ($RSC > 2.5$ meq/l) (Table 7). Therefore, almost 50% of the groundwater in the study area can be suitable for irrigation purposes.

Permeability index (PI)

Doneen (1964) classified irrigation water based on the permeability index (PI). PI is defined as (equation 4):

$$PI = \frac{Na^+ + \sqrt{HCO_3^-} \times 100}{(Ca^{2+} + Mg^{2+} + Na^+)} \quad (4)$$

Where concentrations were in meq/l. Class I and class II waters are considered to be good and suitable for irrigation while class III water is unsuitable for irrigation (Doneen 1964). Figure 6 shows that three groundwater samples were not suitable for irrigation based on PI

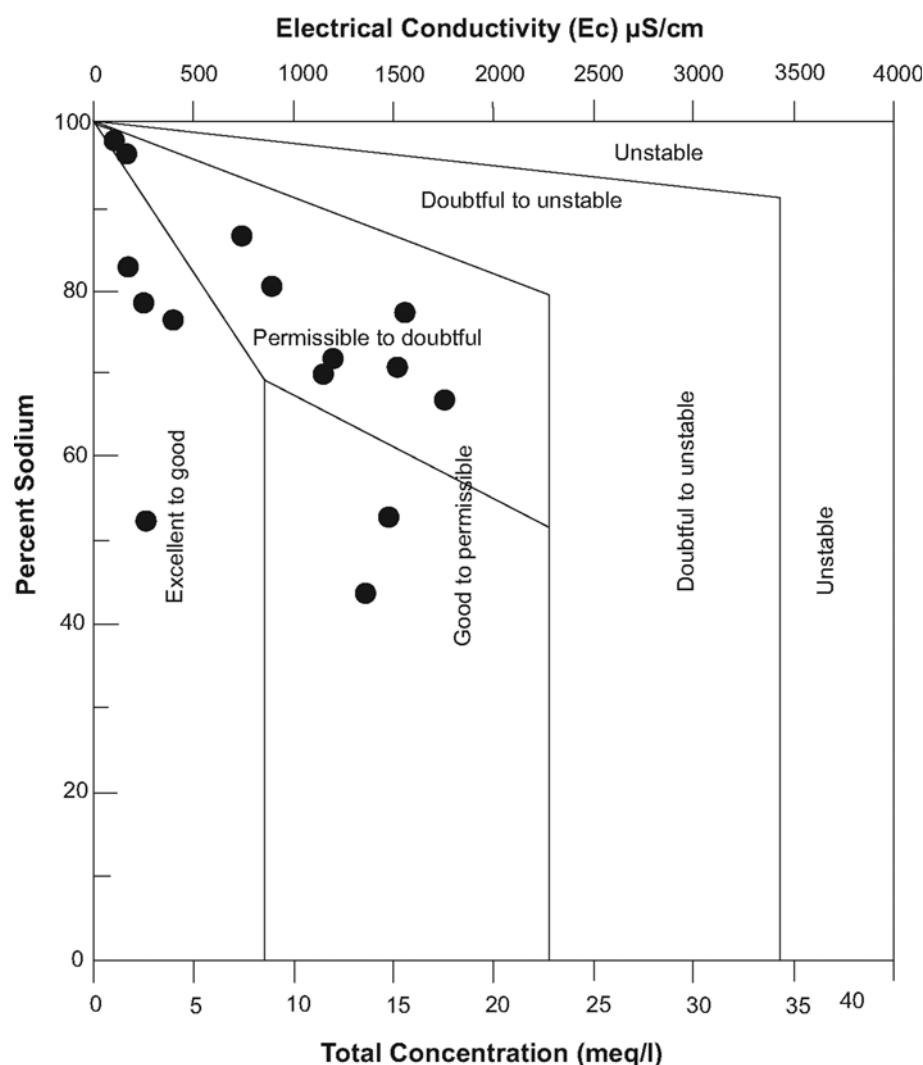


Fig. 5. Plot of Na% v. EC in groundwater (after Wilcox 1955).

whereas the rest of the samples were good. In general, the groundwater falls within the permissible category for irrigational use, except for some locations where it was unsuitable based on MH.

Magnesium hazard (MH)

Magnesium in groundwater affects the soil quality by converting it into alkaline, and decreases the crop yield (Gowd 2005). Szabolcs & Darab (1964) proposed magnesium hazard (MH) or magnesium

ratio (MR) value for irrigation water as expressed by equation (5):

$$MH = \frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}} \times 100 \quad (5)$$

Where concentrations were given in meq/l (Szabolcs & Darab 1964). MH above 50 is considered to be unsuitable for irrigation. Groundwater had an MH above 50 in 67% of the samples, thus not being fit for irrigation. In the analysed water samples, 33.3% of the sample lies in the safe region (MH values, <50) and remaining 67.7% in the unsafe region. Therefore, most of the groundwater samples are not suitable for irrigation uses.

Table 6. Suitability for irrigation based on sodium percent

%Na	Suitability for irrigation	Number of samples	Percentage
<20	Excellent	0	0
20–40	Good	0	0
40–60	Permissible	3	20
60–80	Doubtful	7	47
>80	Unsuitable	5	33

Table 7. USDA classification of groundwater based on RSC

Number of samples	RSC Standard (>/<2.5)	Percentage
7	<2.5	46.7
8	>2.5	53.3

Conclusions

Groundwater composition in the study area is largely controlled by natural sources of contamination and processes such as ion-exchange, silicate weathering and calcium carbonate dissolution across the basin. These processes are responsible for the concentration of sodium, calcium, potassium, and magnesium as well as carbonate and bicarbonate concentrations in the groundwater samples analysed. Groundwater samples categorization suggests that $Na^+ - Cl^-$ was the major hydrofacies dominant in this area. The next dominant hydrofacies was mixed $Mg^{2+} - Ca^{2+} - SO_4^{2-}$. The suitability of groundwater for irrigation was assessed from Na%, EC, RSC, SAR, MH, PI and USDA classification. The groundwater in this area was seen to be not suitable for drinking and domestic purposes. The calculated values of SAR, Na%, RSC, PI, and MH reveal that, barring a few locations, most groundwater samples are not suitable for

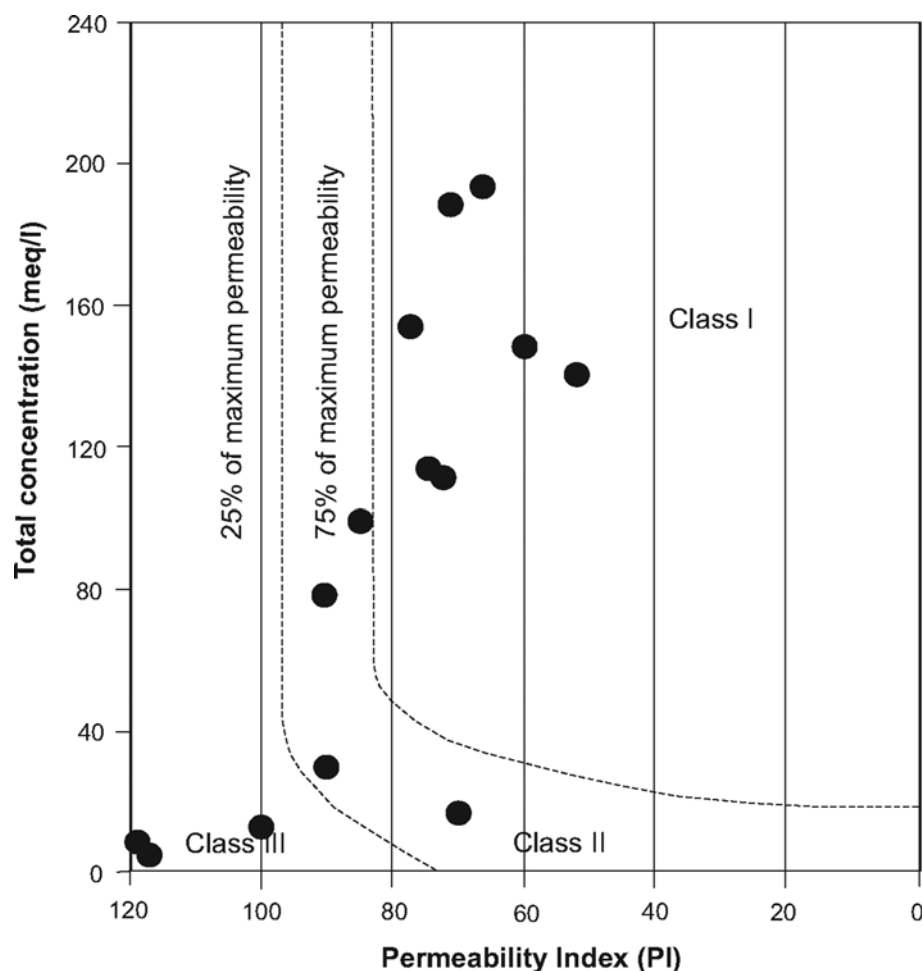


Fig. 6. Doneen (1964) classification of irrigation water based on the permeability index (PI).

irrigation and drinking purposes. Therefore, proper management and remediation strategies should be taken before the utilization of groundwater in the area. In a majority of the samples, the analysed major parameters are not desirable for both drinking and irrigation.

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