

# Hydro-chemical characterization and geospatial analysis of groundwater for drinking and agricultural usage in Nashik district in Maharashtra, India

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#### Abstract

Groundwater qualities in Nashik District of Maharashtra were analyzed using hydro-geochemical characterization and geospatial techniques for sixty-one (n=61) representative samples. GIS-based WQI was computed for planning and monitoring the groundwater qualities in the study region. Piper trilinear and Gibbs diagram were plotted to determine the variation in hydro-geochemical facies and to understand the functional sources of chemical constituents. The analytical results cleared that the nature of the groundwater is highly alkaline. Majority of the samples were within the desirable and maximum permissible limits as decided by Bureau of Indian Standards for each parameter. Piper diagram shows about 39.34% samples belong to  $Ca^{2+}$ – $Mg^{2+}$ – $Cl^-$ – $SO_4^{2-}$  type, signifying permanent hardness and 57.37% samples belong to  $Ca^{2+}$ – $Mg^{2+}$ – $HCO_3^-$  type suggesting temporary hardness. Only 3.25% samples fall under Na<sup>+</sup>-K<sup>+</sup>-Cl<sup>-</sup>-SO<sub>4</sub><sup>2-</sup> type. Alkaline earth exceeds alkalis in 96.72% samples of the groundwater. The WQI suggests that 59% sites have excellent and good quality water; and about 41% sites characterized by poor quality water, which are unsuitable for drinking purposes. WQI values for TDS, TH, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, NO<sub>3</sub> and SO<sub>4</sub><sup>2-</sup> are more than the permissible limits. Hierarchical cluster analysis corroborates the spatial analysis results of WQI and proved statistically. The present investigation indicates significant dominance of agriculture and rock weathering that influence the groundwater chemistry in Nashik district.

 $\textbf{Keywords} \ \ Groundwater \cdot Hydro-geochemical \cdot Geospatial \ techniques \cdot Water \ quality \\ Index \cdot Correlation \ analysis \cdot Nashik$ 

## 1 Introduction

Water quality degradation due to contamination by biological, toxic (Zolekar 2018), organic and inorganic pollutant (Kanwar 1961) is a one of the major environmental issues in India (Murty and Kumar 2011; Adimalla 2019a). Many water sources are

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unsecure for domestic, agricultural and industrial use (Reza and Singh 2010; Sadat-Noori et al. 2013; Tiwari et al. 2017; Adimalla et al. 2020). Population growth, economic development, droughts and water environment-related issues, etc., have increased water stress in the developing country. Further, majority of population in India is facing extremely high water stress. About 38.55% of 1123 BCM [Billion Cubic Meter] usable water in India is groundwater (Bhat 2014). Central Water Commission (CWC 2016) of India has reported that the ground water level has been decreasing in India due to unchecked exploitation and scanty and unpredictable rainfall. Many states in India like Maharashtra, Utter Pradesh, Karnataka, Chhattisgarh, Madhya Pradesh, Odisha, Telangana, Andhra Pradesh, Jharkhand and Rajasthan show severe droughts and degradation of groundwater qualities. It is a one of the important natural sources for drinking, agriculture, industrial and domestic activities (Ramakrishnaiah et al. 2009; Zolekar and Bhagat 2014, 2015; Tiwari et al. 2017). The groundwater is clean and less polluted compared to the surface water. The quality of groundwater is depleting due to the increasing use of groundwater to meet the requirement of drinking for a growing population (Ramakrishnaiah et al. 2009), contaminated discharge from industry (Malik et al. 2009; Chaurasia and Tiwari, 2011), domestic sewage, solid waste (Thambayani and Mageswari 2013), excessive use of water and agro-chemicals, i.e., herbicides, pesticides, inorganic fertilizers and organic compounds (Dinka et al. 2015; Adimalla 2019b). Apart from this, chemistry of the groundwater reflects weather inputs from weathering (rock-water interaction) (Park et al. 2005; Adimalla and Qian 2019), contamination from surface sources (Wick et al. 2012), mineral dissolution (Ledesma-Ruiz et al. 2015), ion exchange, (Appelo and Postma 1993; Tiwari et al. 2017), evaporation (Wick et al. 2012), etc. The groundwater chemistry determines its use for different purposes like drinking (Wagh et al. 2018), irrigation, domestic (Gaikwad et al. 2018), recreation, industrial, etc. (Krishna Kumar et al. 2015). Consequently, about 70-80% of the infections (diseases) are caused by polluted water to humans (FAO and WHO 2008). Many scholars have studied groundwater qualities for different uses like drinking, domestic, agriculture, industrial, recreation, environmental activities, etc. (Stigter et al. 1998; Babiker et al. 2007; Milovanovic 2007; Anju et al. 2010; Farhat et al. 2010; Ketata-Rokbani et al. 2011; Ishaku et al. 2012; Wick et al. 2012; Benvenuti et al. 2013; Dohare et al. 2014; Srinivasamoorthy et al. 2014; Nguyen et al. 2014; Singh et al. 2015; Ledesma-Ruiz et al. 2015; Tarki et al. 2016; Selvakumar et al. 2017; Gaikwad et al. 2019).

The study area, Nashik district, has been recognized for intensive agriculture of grapes, onion, vegetable, etc., with extended agro-based industry. However, the groundwater resource in the study region is exploited for domestic, agriculture and drinking reason (Kanade 2010) and contaminated from different sources like extensively used fertilizers and chemicals, industrial wastage, domestic effluents and hospital discharge (Kadave et al. 2012; Selvakumar et al. 2017). The groundwater chemistry with spatial variation in the region is not analyzed to check the suitability for drinking water. Therefore, the study was focused on analysis qualities and hydro-geochemical characterization of groundwater for drinking and agricultural purposes. The hydrogeochemical parameters used in the context of groundwater quality and their detailed spatial explanation are distinct from other studies in the literature. For the first time, cluster analysis is compared with geospatial based WQI to identify suitable drinking water. The most important intention of this investigation is to evaluate the groundwater quality with hydro-geochemical characterization in groundwater for drinking suitability.



## 2 Study area

The Nashik district (15,500 km²) in north western part of Maharashtra lies between 19°35′ and 20°50′ N and 73°16′ and 74°56′ E (Fig. 1). It is the part of Western Ghat and Deccan Plateau. Flood basalt and several pockets of alluvium along the rivers are the major lithology types in the study area. Physiographically, western part of the Nashik district shows hilly dissected landforms, while the eastern region is considerably flat. The district shows a decreasing pattern of gradient from west (steep) to east (gentle). Godavari (southern part) and Girna (northern part) are the major east flowing rivers in this region. Black, red and pink are major soils in the region. The region shows dry climate except during the monsoon season. As the study area is a part of western Maharashtra, about 85% of annual rainfall received during the monsoon period (Todmal et al. 2018). The average annual rainfall decreases from west (3,400 mm) to the north-east (500 mm) section of Nashik district with a mean of 812 mm. Most of the tehsils located in the central and eastern part of Nashik District are drought prone (CWC 2016). The agriculture in some of the tehsils is entirely depends on groundwater. Groundwater is a major source of water for domestic, agricultural and industrial usage in Nashik.

# 3 Material and methodology

## 3.1 Laboratory analysis

The samples (n=61) were collected from Nashik district during pre-monsoon period for hydro-geochemical analysis for pH, total hardness (TH), total dissolved solids (TDS), magnesium  $(Mg^{2+})$ , sodium  $(Na^+)$ , calcium  $(Ca^{2+})$ , chloride  $(Cl^-)$ , bicarbonate  $(HCO_3^-)$ , nitrate  $(NO_3^-)$ , sulfate  $(SO_4^{2-})$ , fluoride  $(F^-)$ and potassium  $(K^+)$ . pH meter was used for measuring pH values during the field. The hydro-geochemical parameters were investigated in laboratory, using standard suggested by APHA [American Public Health Association] (1995). The concentration of bicarbonates was determined using acid titration technique. UV–VIS spectrophotometer was used for measuring of concentration of dissolved silica in water by the molybdosilicate method (APHA 1998). Ion chromatograph was used for analysis of  $F^-$ ,  $SO_4^{2-}$ ,  $CL^-$  and  $NO_3^-$ . Flame atomic absorption spectrophotometer was used for measuring major cations (i.e.,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$  and  $K^+$ ).

In addition to this, AQQA software package and MS Excel spreadsheet were used for preparation of piper trilinear and Gibb's diagrams, respectively. Dendrograph diagram was plotted in SPSS [Statistical Package for the Social Sciences] for HCA [Hierarchical Cluster Analysis].

#### 3.2 Water quality Index (WQI)

WQI is useful to determine physical, chemical and biological nature of water for drinking and domestic purposes (Wanda et al. 2012). Several researchers have carried out WQI quite successively to analyze the water quality for domestic, drinking, industrial, etc. purposes (Tiwari and Mishra 1985; Sadat-Noori et al. 2013; Batabyal and Chakraborty 2015; Singh and Hussian 2016; Tiwari et al. 2017; Adimalla et al. 2018). Therefore, WQI was



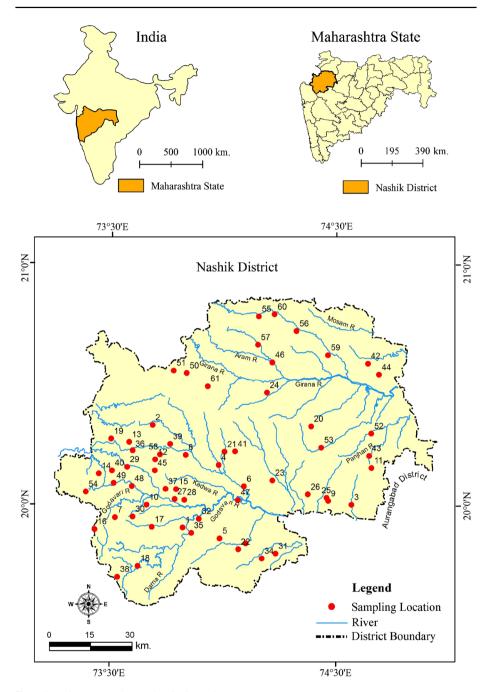


Fig. 1 Location o groundwater sites in the study area

used for hydro-geochemical characterization of groundwater and its suitability of drinking purpose on the basis of standard range suggested by World Health Organization (WHO 1997) and Bureau of Indian Standards (BIS) (Revised 2003).



The WQI has been calculated in four steps:

- (1) Weights were assigned for each of the 12 water quality parameters, i.e., pH, TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and F<sup>-</sup>based on relative importance in the overall water quality (Table 1). TDS, fluoride, chloride, nitrate, sulfate and sodium are most important parameters for determination of water quality; therefore, maximum weight (5) was assigned to them (Table 1) (Tiwari et al. 2017; Vasanthavigar et al. 2010). Bicarbonate shows less significance in formation water quality in the region and assigned a minimum weight (1). pH, calcium and magnesium (3) assigned weights 3, whereas potassium and total hardness 2 based on their importance (Table 1).
- (2) The relative weights for each criterion were calculated using equation (Eq. 1).

$$W_i = \frac{w_i}{\sum_{i=1}^n w_i} \tag{1}$$

where  $W_i$  shows relative weight,  $w_i$  is the weight of each criterion, and n is a number of criteria (Table 1).

(3) The quality rating range  $(q_i)$  was calculated (Eq. 2) by dividing the value of each sample of parameters  $(C_i)$  by its respective standards  $(S_i)$  suggested by WHO (1997) and BIS (2003) and multiplied by hundred (100).

$$q_i = \frac{C_i}{S_i} \times 100 \tag{2}$$

(4) Lastly, sub-index ( $SI_i$ ) was calculated (Eq. 3) using relative weights ( $W_i$ ) and quality rating scale ( $q_i$ ) for determination of WQI (Eq. 4).

$$SI_i = W_i \times q_i \tag{3}$$

Table 1 Weight of parameters

Chemical parameters	Standards (BIS 2003; WHO 1997)	Weight (w <sub>i</sub> )	Relative weight $(W_i)$	
Sulfate (SO <sub>4</sub> <sup>2-</sup> )	200	5	0.114	
Nitrate (NO <sub>3</sub> )	45	5	0.114	
Fluoride (F <sup>-</sup> )	1	5	0.114	
chloride (Cl <sup>-</sup> )	250	5	0.114	
Total dissolved solids (TDS)	500	5	0.114	
Sodium (Na <sup>+</sup> )	50	5	0.114	
pH	8.5	3	0.068	
Calcium (Ca <sup>2+</sup> )	75	3	0.068	
Magnesium (Mg <sup>2+</sup> )	30	3	0.068	
Potassium (K <sup>+</sup> )	100	2	0.045	
Total hardness (TH)	300	2	0.045	
Bicarbonate (HCO <sub>3</sub> <sup>-</sup> )	200	1	0.023	
-		$\Sigma \text{ wi} = 44$	$\Sigma Wi = 1$	

All concentration in mg/L excluding pH



$$WQI = \sum SI_i \tag{4}$$

where  $SI_i$  is the sub-index of each parameter.

## 3.3 Application of geospatial technique

GIS is a powerful tool for map making and spatial analysis, and it has been widely used all over the world for assessment of various groundwater applications (Sadat-Noori et al. 2013; Das et al. 2017; Das 2019; Adimalla et al. 2020). The inverse distance weighted (IDW) and kriging interpolation techniques are used in various disciplines for environmental spatial assessment (Zolekar and Bhagat 2015; Tiwari et al. 2017; Zolekar and Bhagat 2018). Deshmukh and Aher (2016) reported that the IDW interpolation technique is more precise and superior compare to kriging and Spline due to neighborhood attitude and radial basis characteristics of its. Therefore, IDW was used in the present work for the preparation of thematic interpolated maps (i.e., WQI) in Arc GIS software.

#### 4 Result and discussion

## 4.1 Variation in hydro-geochemical parameters

Minimum and maximum range, average and standard deviation (SD) values were calculated for physicochemical parameters analysis and given in Table 2. Concentration of hydro-geochemical parameters in groundwater in the region is within permissible limit for drinking purpose, excluding Ca<sup>++</sup>, Mg<sup>++</sup>, NO<sub>3</sub> and SO<sub>4</sub><sup>2-</sup> (Fig. 2). The pH indicates acidic or alkaline nature of the water and its strength. It controls the chemical composition with the quantity of organic and inorganic matters (Sadat-Noori et al. 2013) and Equilibrium among carbon dioxide, carbonate and bicarbonate (Hem 1985). The pH range observed from 7.3 to 8.3 with a mean value of 7.8 in the region, showing alkaline character of the groundwater samples (Fig. 2). These values show permissible limits (6.5–8.5) and indicate that water is suitable for drinking purpose.

The maximum TDS is observed in Rasalpur (1748 mg/L) and minimum in Harsul (141 mg/L). The average TDS value is about 499 mg/L. About 64% samples are observed in maximum desirable limit at Northern site of Nashik, and remaining samples are in highest permissible limit. None of the samples of TDS exceeded highest permissible limit (2000 mg/L) proposed by BIS (1998).

The hardness of the water owes to the observed alkaline earth, which is characterized by calcium and magnesium salt. Total hardness (TH) of the evaluated groundwater samples varies 141–1255 mg/L with a mean value 365 mg/L. Hardness value exceeds the maximum permissible limit at 7% of the analyzed sample. About 29% and 25% groundwater samples of hardness were concentrated within maximum desirable and maximum permissible limit, respectively, in the region.

#### 4.2 Cation chemistry

The concentration of major cations (i.e., Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>2+</sup> and K<sup>2+</sup>) was evaluated for understanding hydro-geochemistry analysis of groundwater. About 30% of groundwater



Table 2 Statistical summary of parameters (WHO 1997; BIS 2003)

7.8         0.2         7.0–8.5         6.5–9.2         6.5–8.5           18         499.7         335.2         500         500         300           53         364.9         218.1         100         500         300         300           55         364.9         218.1         100         500         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300         300	Parameters	Range	Average	SD	WHO (1997)		BIS (2003) (IS 10500)	
7.3-8.3         7.8         0.2         7.0-8.5         6.5-9.2         6.5-9.2         6.5-8.5           141-1748         499.7         335.2         500         1500         500         500           411-1255         364.9         218.1         100         200         75         75           6-248         75.6         43.4         75         200         75         75           1-168         42.8         31.0         30         150         30         -           9-222         64.4         49.0         50         200         -         -           02-75.2         7.4         16.0         100         200         -         -           92-549         266.1         97.3         200         600         200         200           25-613         131.6         106.8         250         600         250         45           7-56         26.6         18.1         -         50         600         200           4-528         111.8         103.6         200         600         200         200           6.1-0.8         0.3         0.1         0.6-1.5         1.5         1.0         1.0 <th></th> <th></th> <th></th> <th></th> <th>Maximum desirable</th> <th>Highest permissible</th> <th>Maximum desirable</th> <th>Highest permissible</th>					Maximum desirable	Highest permissible	Maximum desirable	Highest permissible
141–1748         499.7         335.2         500         500         500           141–1255         364.9         218.1         100         500         300           6–248         75.6         43.4         75         200         75           1–168         42.8         31.0         30         150         30           9–222         64.4         49.0         50         200         -           0.2–75.2         7.4         16.0         100         200         -           92–549         266.1         97.3         200         600         200           25–613         131.6         106.8         250         600         250           7–56         26.6         18.1         -         50         45           4–528         111.8         103.6         200         600         200           6.1–0.8         0.3         0.1         0.6-1.5         1.5         1.0	Hd	7.3–8.3	7.8	0.2	7.0–8.5	6.5–9.2	6.5–8.5	8.5–9.2
141–1255         364.9         218.1         100         500         300           6–248         75.6         43.4         75         200         75           1–168         42.8         31.0         30         150         75           9–222         64.4         49.0         50         200         -           0.2–75.2         7.4         16.0         100         200         -           92–549         266.1         97.3         200         600         200           25–613         131.6         106.8         250         600         250           7–56         26.6         18.1         -         50         45           4–528         111.8         103.6         200         600         200           6.1–0.8         0.3         0.1         0.6–1.5         1.5         1.0	TDS	141–1748	499.7	335.2	500	1500	500	2000
6-248         75.6         43.4         75         200         75           1-168         42.8         31.0         30         30           9-222         64.4         49.0         50         200         -           0.2-75.2         7.4         16.0         100         200         -           92-549         266.1         97.3         200         600         200           25-613         131.6         106.8         250         600         250           7-56         26.6         18.1         -         50         45           4-528         111.8         103.6         200         600         200           0.1-0.8         0.3         0.1         0.6-1.5         1.5         1.0	ТН	141–1255	364.9	218.1	100	500	300	009
1-168         42.8         31.0         30         150         30           9-222         64.4         49.0         50         200         -           0.2-75.2         7.4         16.0         100         200         -           92-549         266.1         97.3         200         600         200           25-613         131.6         106.8         250         600         250           7-56         26.6         18.1         -         50         45           4-528         111.8         103.6         200         200           0.1-0.8         0.3         0.1         0.6-1.5         1.5         1.0	Ca++	6-248	75.6	43.4	75	200	75	200
9-222         64.4         49.0         50         200         -           0.2-75.2         7.4         16.0         100         200         -           92-549         266.1         97.3         200         600         200           25-613         131.6         106.8         250         600         250           7-56         26.6         18.1         -         50         45           4-528         111.8         103.6         200         200           0.1-0.8         0.3         0.1         0.6-1.5         1.5         1.0	Mg++	1–168	42.8	31.0	30	150	30	100
0.2–75.2         7.4         16.0         100         200         –           92–549         266.1         97.3         200         600         200           25–613         131.6         106.8         250         600         250           7–56         26.6         18.1         –         50         45           4–528         111.8         103.6         200         200           0.1–0.8         0.3         0.1         0.6–1.5         1.5         1.0	Na	9-222	64.4	49.0	50	200	I	ı
92–549         266.1         97.3         200         600         200           25–613         131.6         106.8         250         600         250           7–56         26.6         18.1         -         50         45           4–528         111.8         103.6         200         600         200           0.1–0.8         0.3         0.1         0.6–1.5         1.5         1.0	×	0.2–75.2	7.4	16.0	100	200	I	1
25-613     131.6     106.8     250     600     250       7-56     26.6     18.1     -     50     45       4-528     111.8     103.6     200     600     200       0.1-0.8     0.3     0.1     0.6-1.5     1.5     1.0	$HCO_3$	92–549	266.1	97.3	200	009	200	009
7-56     26.6     18.1     -     50     45       4-528     111.8     103.6     200     600     200       0.1-0.8     0.3     0.1     0.6-1.5     1.5     1.0	CL	25–613	131.6	106.8	250	009	250	1000
4-528     111.8     103.6     200     600     200       0.1-0.8     0.3     0.1     0.6-1.5     1.5     1.0	$No_3$	7–56	26.6	18.1	I	50	45	100
0.3 0.1 0.6–1.5 1.5 1.0	SO4	4-528	111.8	103.6	200	009	200	400
	ц	0.1–0.8	0.3	0.1	0.6-1.5	1.5	1.0	1.5

All concentration in mg/L excluding pH

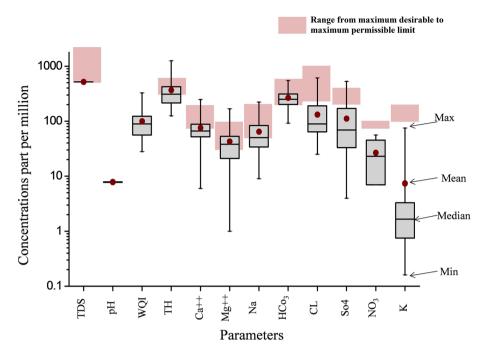


Fig. 2 Box plot for the minimum and average of the chemical constituents in groundwater (all values in mg/L except pH)

samples were dominant in calcium-rich water, and more than half (70%) of the groundwater samples go down under no dominant type. Figure 3 shows that Ca<sup>2+</sup> and Mg<sup>2</sup> are the major cations which represent alkaline nature of groundwater. The alkaline earths Ca<sup>2+</sup> and Mg<sup>2+</sup> ions ranged from 6 to 248 mg/L and 1 to 168 mg/L with a mean 75.6 mg/L and 42.8 mg/L, respectively (Fig. 2). Ca<sup>2+</sup> concentrations in 59% samples belong to the maximum desirable limit (75 mg/L), and 37.7% are within maximum permissible limit of 200 mg/L. Only 3.2% groundwater samples of Ca<sup>2+</sup> (2 samples) exceed acceptable (permissible) limit of 200 mg/L (BIS 1998). About 39% and 56% samples are within maximum desirable limit (30 mg/L) and maximum acceptable limit (100 mg/L) for Mg<sup>2+</sup> concentration. About 97% of the samples are within maximum permissible limit (200 mg/L). The concentration of alkaline earths (Ca<sup>2+</sup> and Mg<sup>2+</sup>) is 30%, and only 8% is of that alkali (Na<sup>+</sup> and K<sup>+</sup>) of the total cation concentration. In such circumstance, it can be stated that alkaline earths exceed alkali earth and water quality is normal (basic) on the basis of cation chemistry of groundwater.

### 4.3 Anion chemistry

The hydro-chemistry of groundwater was analyzed using the concentrations of major anions (i.e.,  $Cl^-$ ,  $SO_4^{2-}$  and  $HCO_3^-$ ). The concentration of bicarbonates in the water samples varies from 92 to 549 mg/L with a mean 266.1 mg/L. Piper diagram shows that 41% groundwater samples are weak acidic and fall into the bicarbonate zone (Fig. 3). About 56% samples are within no dominant zone and 3% are into strong acidic zone (chloride



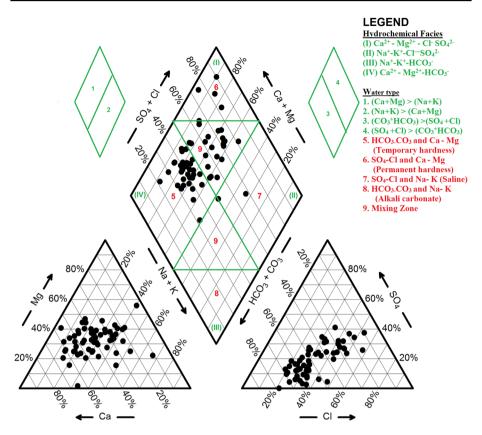


Fig. 3 Hydro-chemical facies shown on Piper's trilinear

type). None of the samples belong to the sulfate type (strong acidic zone). The minimum chloride is observed in Dahalewadi (25 mg/L) and maximum in Rasalpur (141 mg/L) in the study area. Chloride level in 87% sample was within desirable limit and 13% within maximum permissible limit prescribed by BIS (Fig. 2). Fluoride is a strong acid (Kale and Pawar 2017), but its concentration in all groundwater samples is well and within maximum permissible limit, therefore, not showing any spatial variation. Nawlakhe and Bulusu (1989) reported that the lower concentration of fluoride is safe for dental health but higher concentration is harmful for dental health, spinal cord, skeletal fluorosis and deformation of the ligaments. The concentrations of sulfate  $(SO_4^{2-})$  are between 4 and 528 mg/L with an average 111.8 mg/L (Fig. 2). Oxidative weathering of sulfide minerals, gypsum and anhydrite are source of the sulfate in water. Sulfate concentration is high in the groundwater sample in Vavi, where in 87% samples, its concentration does not exceed maximum desirable limit, and 12% samples from southern part are within maximum permissible limit. Diseases like methemoglobinemia, hypertensions, cancer, goiter, etc., can originate due to excessive level of nitrate in groundwater (Majumdar and Gupta 2000). Nitrate level in the measured groundwater samples varies from 7 to 56 mg/L with average value 26.6 mg/L. The concentration of NO<sub>3</sub> in 80% samples was within desirable limit, and 20% of groundwater samples belong to the maximum permissible limit in the Nashik district, prescribed by BIS.



## 4.4 Piper trilinear diagram

A piper plot is encompassing of three components, i.e., (i) lower left is representing cations (Mg, Cl and Na+K), (ii) lower right is indicating anions (Cl<sup>-</sup>,  $SO_4^{2-}$  and  $HCO_3^{-}$ ), and (iii) the middle diamond plot shows combination matrix conversion of two ternary figures (Piper 1994)(Fig. 3). It is a powerful tool for visualizing the large quantity of ions in groundwater samples. On piper plot, it clearly shows that out of 61 samples, 39.34% samples belong to  $Ca^{2+}$ – $Mg^{2+}$ – $Cl^{-}$ – $SO_4^{2-}$  types of water which indicates permanent hardness; 57.37% samples belong to  $Ca^{2+}$ – $Mg^{2+}$ – $HCO_3^{-}$  kind of water, which characterized temporary hardness and adequate recharge from fresh water (Srinivasamoorthy et al. 2014). From the plot, only 3.25% samples fall under  $Na^+$ – $K^+$ – $Cl^-$ – $SO_4^{2-}$  type (alkalis exceed alkaline earths). Hence, it may be stated that alkaline earth exceeds alkalis in 96.72% samples and week acid exceed strong acid in more than half (57%) of the groundwater samples. Magesh et al. (2012) has reported that such type of water does not create the salinity problems, and it is highly suitable for drinking and irrigation purposes. The diamond plot of piper diagram (Fig. 3) shows that permanent (8.19%) and temporary hardness (49.18%) in the study area (Fig. 3).

## 4.5 Gibbs analysis

Tiwari et al. (2017) and Khan and Jhariya (2018) have used Gibbs (1970) diagram for understanding major driving sources, controlling the chemistry of groundwater. Water element and lithological characteristics of aquifer such as rainfall, rock—water interaction and evaporation show close relationship (Krishna Kumar et al. 2015; Selvakumar et al. 2017). Majority of the samples show rock—water interactions (weathering dominance) (Fig. 4). Rock weathering is a major driving source for chemical constituents in groundwater in Nashik district.

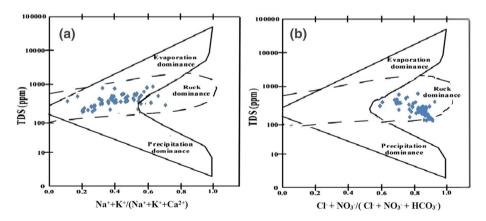


Fig. 4 Gibb's diagram: mechanism controlling groundwater chemistry



#### 4.6 Correlation matrix

TDS shows strong positive correlation with  $\mathrm{Mg^{2+}}$  (0.94),  $\mathrm{Cl^-}$  (0.95),  $\mathrm{SO_4^{2-}}$  (0.89)  $\mathrm{Ca^{2+}}$  (0.77),  $\mathrm{Na^+}$  (0.73) and moderate correlation with  $\mathrm{NO_3^-}$  (0.67) which shows that these ions are largely sourced from chemical fertilizers used in agriculture (Selvakumar et al. 2017). Further, groundwater elements, i.e.,  $\mathrm{Ca^{2+}}$  (0.91),  $\mathrm{Mg^{2+}}$  (0.93),  $\mathrm{Cl^-}$  (0.90),  $\mathrm{NO_3^-}$  (0.62) and  $\mathrm{SO_4^2}$  (0.98), have considerable positive correlation with TH (Table 3). Good and positive correlation appears between  $\mathrm{Ca^{2+}-Mg^{2+}}$  (0.70),  $\mathrm{Ca^{2+}-Cl^-}$  (0.74) and  $\mathrm{Ca^{2+}-SO_4^{2-}}$  (0.81) which are mostly obtained from natural procedure, i.e., dissolution and rock—water interaction (weathering) (Batabyal and Chakraborty 2015). It means that major cations are strongly correlated with alkaline earth and TDS. Cations are the most significant parameters for TDS. It shows strong and moderate correlation with major anions like  $\mathrm{Cl^-}$  (0.95),  $\mathrm{SO_4^{2-}}$  (0.89) and  $\mathrm{HCO_3^-}$  (0.48). Good associations were also observed between cation and anion, suggesting that they are derived from similar geochemical process. Calculated values of WQI demonstrate high and significant association with  $\mathrm{NO_3^-}$  (0.71),  $\mathrm{Ca^{2+}}$  (0.77),  $\mathrm{SO_4^{2-}}$  (0.89),  $\mathrm{Cl^-}$  (0.94), TH (0.96), TDS (0.98) and  $\mathrm{Mg^{2+}}$  (0.98), and moderately associated with  $\mathrm{Na^+}$  (0.66),  $\mathrm{K^+}$  (0.46) and  $\mathrm{HCO_3^-}$  (0.52) (Table 3).

## 4.7 Water quality Index

WQI classifies water quality on the basis hydro-chemical parameters into categories of excellent water (EW), good water (GW), poor water (PW), very poor water (VPW) and unsuitable for drinking purposes (UDP) (Table 4). WQI values vary from 28 to 328 with a mean value of 99 (Fig. 5). WQI shows positive correlation with TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup>.

About 25% of groundwater samples are classified into the class 'excellent water' from western site of the study area (Table 5; Fig. 5). The concentration of all hydro-geochemical parameters in these groundwater samples is less and within maximum desirable limit proposed by BIS. About 34% of analyzed groundwater samples are observed in western and northeastern part of study region and classified as 'good water' (Table 5; Fig. 5). The concentration of hydro-chemical is compared to excellent water, and all samples are within desirable and maximum permissible limit. Agriculture is developed in eastern section of the study region. Due to extensive use of chemical fertilizer, high TDS and TH of about 36% of groundwater samples are classified as 'poor water' for drinking (Table 5; Fig. 5). Only 3% and 2% land of groundwater samples is classified into the class 'very poor' and 'unfit water' for drinking (Table 5). There is need of protection of groundwater from intensive use of chemical fertilizer and contamination of agro-based industries.

## 4.8 Hierarchical cluster analysis (HCA)

HCA was used for identification of sites with close and similar characteristics. Dendrogram chart has been obtained using Ward's method (1963) for 61 groundwater samples in the study region (Fig. 6) and classified into five clusters. Cluster analysis demonstrated that about 84% groundwater samples concentrated in cluster I, II, III, IV and V are similar to WQI classes, i.e., UDP, VPW, PW, GW and EW, respectively. Some groundwater samples were mismatched to poor and very poor water cluster group. Clusters I, II and III comprise 27 sites and demonstrate the unfit and poor water quality for drinking purposes (Fig. 6). Highest concentrations of hydro-parameters are observed in scanty and less rainfall regions



**Table 3** Correlation matrix of parameters (n=61)

	ages constants manny or bara		(10 – 11) (100)										
	Hd	TDS	ТН	Ca <sup>2+</sup>	${ m Mg}^{2+}$	Na+	$K^+$	$HCO_3^-$	CI_	NO <sub>3</sub>	$SO_4^{2-}$	F	WQI
Hd	1	1											
TDS	0.04	1											
TH	0.08	$0.93^{**}$	1										
$Ca^{2+}$	0.05	$0.77^{**}$	$0.91^{**}$	_									
${ m Mg}^{2+}$	0.10	$0.94^{**}$	$0.93^{**}$	0.70	1								
Na+	-0.04	$0.73^{**}$	$0.49^{**}$	$0.25^{*}$	$0.62^{**}$	1							
$\mathbf{K}^{+}$	0.06	0.47**	$0.43^{**}$	0.37**	0.43**	$0.29^{*}$	_						
$HCO_{\overline{3}}^{-}$	0.14	$0.48^{**}$	$0.45^{**}$	$0.26^*$	$0.55^{**}$	$0.56^{**}$	$0.37^{**}$	1					
CI	0.05	$0.95^{**}$	$0.90^{**}$	0.74**	$0.91^{**}$	$0.63^{**}$	$0.48^{**}$	$0.35^{**}$	1				
$NO_3^-$	-0.09		$0.62^{**}$	$0.48^{**}$	99.0	$0.52^{**}$	$0.27^{*}$	$0.31^{*}$	$0.59^{**}$	_			
$SO_4^{2-}$	0.01	$0.89^{**}$	0.89	0.81**	$0.83^{**}$	$0.61^{**}$	$0.40^{**}$	$0.30^*$	$0.83^{**}$	0.67**	П		
ļ.	0.03	0.00	-0.07	-0.12	-0.01	$0.27^*$	-0.07	0.11	0.05	-0.00	-0.01	1	
MQI	0.07	0.98	96.0	0.77	0.98**	$0.66^{**}$	0.46**	$0.52^{**}$	0.94	0.71**	0.89	0.01	-

\*Correlation is significant at 0.05 level (2-tailed)

\*\*Correlation is significant at 0.01 level (2-tailed)

**Table 4** Classification of WQI (after Tiwari et al. 2017)

WQI range	Category of water	Samples in this category (%)
< 50	Excellent water (EW)	25
50-100	Good water (GW)	34
100-200	Poor water (PW)	36
200-300	Very poor water (VPW)	03
>300	Unfit for drinking purpose (UDP)	02

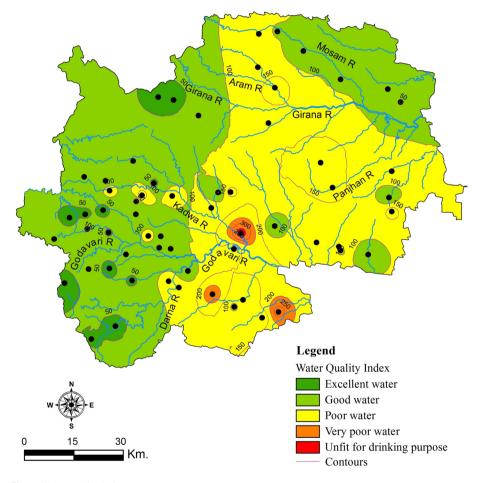


Fig. 5 Water quality Index map

with degraded water quality (Machiwal and Jha 2015). Geographically, these clusters are situated in the southeast and middle northern part of study region which performed poor water quality due to ground pollution from chemical fertilizers used in agriculture. On the other hand, groundwater quality in western and northeastern parts of the study region is observed to be good water and excellent water due to heavy rainfall, hilly topography and



**Table 5** WQI with category of water

Sample code	Latitude	Longitude	WQI	Category of water
1	19.90	73.83	116	Poor water
2	20.34	73.87	89	Good water
3	20.01	74.60	72	Good water
4	20.17	73.97	113	Poor water
5	19.83	74.00	245	Very poor water
6	20.07	74.00	328	Unfit for drinking purpose
7	19.95	73.54	73	Good water
8	20.19	73.83	114	Poor water
9			85	Good water
	20.02	74.47		
10	19.63	73.73	89	Good water
11	20.18	74.64	166	Poor water
12	20.17	73.70	37	Excellent water
13	20.25	73.59	56	Good water
14	20.10	73.38	28	Excellent water
15	20.06	73.81	84	Good water
16	19.88	73.45	34	Excellent water
17	19.89	73.71	44	Excellent water
18	19.72	73.63	45	Excellent water
19	20.26	73.51	97	Good water
20	20.37	74.46	192	Poor water
21	20.08	73.61	49	Excellent water
22	19.84	74.09	93	Good water
23	20.10	74.23	60	Good water
24	19.77	74.08	143	Poor water
25	20.04	74.47	147	Poor water
26	20.05	74.37	128	Poor water
27	20.02	73.80	83	Good water
28	19.98	73.81	65	Good water
29	20.15	73.57	33	Excellent water
30	19.96	73.61	37	Excellent water
31	19.80	74.25	269	Very poor water
32	19.91	73.91	68	Good water
33	19.84	74.11	118	Poor water
34	19.78	74.17	120	Poor water
35	19.87	73.88	111	Poor water
36	20.05	73.87	127	Poor water
37	20.05	73.74	115	Poor water
38	20.14	73.82	49	Excellent water
39	20.21	73.72	39	Excellent water
40	20.12	73.50	41	Excellent water
41	20.23	74.05	163	Poor water
42	20.60	74.64	83	Good water
43	20.28	74.66	59	Good water
44	20.28	74.69	49	Excellent water
45	20.63	74.69	63	Good water
46	20.61	74.20	182	Poor water



lable 5 (continued	Table 5 (d	continued)	١
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Sample code	Latitude	Longitude	WQI	Category of water
47	20.63	74.54	123	Poor water
48	20.08	73.67	47	Excellent water
49	20.06	73.53	103	Poor water
50	20.54	73.83	38	Excellent water
51	20.45	73.78	36	Excellent water
52	20.32	74.66	134	Poor water
53	20.26	74.43	165	Poor water
54	20.47	74.18	94	Good water
55	20.78	74.14	124	Poor water
56	20.73	74.32	61	Good water
57	20.69	74.15	106	Poor water
58	20.42	74.36	193	Poor water
59	20.63	74.44	96	Good water
60	20.79	74.20	97	Good water
61	20.51	73.94	66	Good water

less developed agriculture compared to the other sites. The results of groundwater analysis signify that most of the ground samples (22) classified as cluster 4th has good water quality (12) and cluster 5th have excellent water quality. The present studies make it clear that notable spatial analysis results of WQI are statistically significant.

#### 5 Conclusion

Groundwater is the best alternative after surface water (i.e., rivers and lakes) for drinking, agricultural and industrial purposes of Nashik district in Maharashtra, India. The hydrogeochemical parameters of groundwater play a significant role in determination of water quality. However, the groundwater resources in the study region are contaminated due to excessive use of fertilizers and chemicals, industrial wastage, domestic effluents, etc. Therefore, in order to understand the groundwater quality, sixty-one (n=61) groundwater samples were collected, analyzed and evaluated for drinking and agricultural purposes. The results of the parameters were compared to WHO (1997) and BIS (2003). Furthermore, piper trilinear and Gibbs diagram were plotted to determine the variation in hydrogeochemical facies and for understanding the functional sources of chemical constituents, respectively. These techniques have been used to achieve the objective of the present study and the following conclusions are reached.

Groundwater in Nashik District is alkaline due to industrial activities. In the southern part of the Godavari river, concentration of TDS and TH is higher as compared to those of the northern areas, but not exceeding highest permissible limit. Agriculture is a major activity in the study region, and it is particularly responsible for increasing TDS, TH, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>. In the present study, piper diagram classified out of 61 samples, 39.34% samples are plotted in piper diagram belong to Ca<sup>2+</sup>–Mg<sup>2+</sup>–Cl<sup>-</sup>–SO<sub>4</sub><sup>2-</sup> type demonstrating permanent hardness, and 57.37% samples belong to Ca<sup>2+</sup>–Mg<sup>2+</sup>–HCO<sub>3</sub> type are signifying temporary hardness. Only 3.25% samples fall under Na<sup>+</sup>–K<sup>+</sup>–Cl<sup>-</sup>–SO<sub>4</sub><sup>2-</sup> type (alkalis exceed alkaline earths). Alkaline earth exceeds alkalis in 96.72% samples



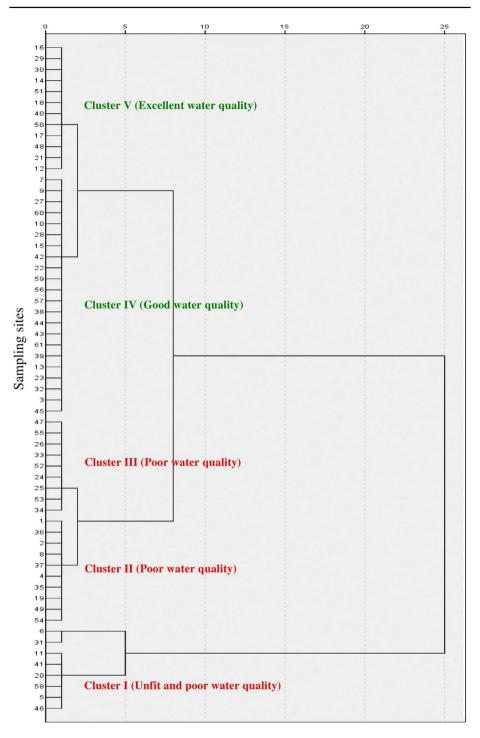


Fig. 6 Dendrogram for the groundwater grouping



and weak acid exceed strong acid in more than half (57%) of the groundwater samples. Such type of water does not create the salinity problems and it is highly suitable for drinking and agricultural purposes. Gibbs diagram shows dominance rock—water interaction in groundwater chemistry. The WQI shows that 59% groundwater samples fall in the 'excellent water' (25%) and 'good water' (34%) categories and can be used for different purposes. Remaining groundwater samples (41%) come under 'poor' to 'unfit for drinking' categories and need to be processed before its utilization. HCA confirms the spatial results of WQI. The present study can be utilized to improve the groundwater quality in Nashik district by government or the non-government planners.

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