Appraisal of groundwater quality for drinking and irrigation purpose using GIS and statistical approach with special reference to nitrate contamination in a semi-arid region: A case study

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Abstract

Groundwater contamination has become an environmental issue all around the world. The specific objective of the present study is to evaluate the risk assessment of groundwater for nitrate contamination and in addition to assess the suitability of groundwater for domestic and irrigation purposes in the semi-arid region. Thirty sample locations were identified based on the more active industrial and high-densified residential regions in the study area. To evaluate the drinking and irrigation fitness of groundwater by analysed water quality parameters such as pH, Electrical conductivity, total dissolved solids, Total hardness, calcium, magnesium, sodium, potassium, chloride, sulphate, fluoride, carbonate and bicarbonate. According to World Health Organization (WHO) 2011 and Bureau of Indian Standard (BIS) 2012 standards, the GIS Spatial analysis of groundwater parameters was carried out to identify each parameter high contaminated regions in the study area. Multivariate statistical analysis, such as principal component analysis, cluster analysis, and Pearson correlation matrix, was used to understand the relationship between water quality parameters. The Results show that 40% of samples are highly affected due to the high concentration of nitrate. The total non-carcinogenic health risks for male, women, and children are 40%, 50%, and 53.33%, respectively. It reveals that, children and women are at high risk than male in the study region. The major sources of contamination are discharges from the household, uncovered septic tanks, leachate from the waste dump, and excess utilization of fertilizers in the agriculture field.

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The Results show that 40% of samples are highly affected due to the high concentration of nitrate. The total non-carcinogenic health risks for male, women, and children are 40%, 50%, and 53.33%, respectively. It reveals that, children and women are at high risk than male in the study region. The major sources of contamination are discharges from the household, uncovered septic tanks, leachate from the waste dump, and excess utilization of fertilizers in the agriculture field.

Keywords: Groundwater, GIS, Statistical analysis, Nitrate contamination, Risk assessment

Introduction

In the arid and semi-arid regions, groundwater is the most significant water sources for agriculture, domestic, and industrial activities. Natural and artificial source of groundwater contamination can be identified with human health, which are the most across the broad issues in arid and semi-arid regions in the world (Abbasnia et al., 2019 Busico et al., 2020 Balamurugan et al., 2020a, Shankar et al., 2019, Patil et al., 2020). It is essential to monitoring the human health, quality and amount of grains since it affects soils, crops, and the natural condition of ecosystem (Balamurugan et al., 2020b). About 80% of the health issues and diseases around the world are due to the consumption of contaminated water for domestic purposes (Adimalla et al., 2019a, Karunanidhi et al., 2019, Kavurmacı et al., 2020). Geogenic and human activities are the major sources of groundwater contamination in arid and semi-arid region. Among the many contaminants, nitrate contamination is the serious issue to monitor and evaluate its impact on human health. As it is highly soluble in water and easily spread groundwater contaminants all around the world (Adimalla et al., 2019c, Ahada and Suthar 2017, Mohanakavitha et al., 2019a, Mohanakavitha et al., 2019b, Nadikatla et al., 2020, Nhu et al., 2020, Ohwoghere-Asuma et al., 2019). In the southern part of India, rural and local residents are directly drawn from bore wells or open wells for drinking and agriculture uses. Their continuous consumption of groundwater with a high concentration of nitrate has seriously increased health issues. In recent years, numerous of research carried out the impact of nitrate contamination in drinking water and environmental issues. The elevated concentration of nitrate in drinking water can cause liver damage, blue baby syndrome for infants and cancers (Kaur et al., 2020, Khurshid et al., 2019, Taneja et al., 2019 and Thapa et al., 2019).

Adimalla (2020) carried out the study on nitrate contamination in drinking water from the semi-arid region of south India and found that agricultural activities and animal waste disposal are the significant factors that deteriorate groundwater's nature in the study region. Karunanidhi et al., (2019) investigated the potential health risk assessment in hard rock regions due to fluoride and nitration contamination. It also reveals that excess usage of synthetic fertilizers, cow dung used for fertilizer in the agriculture field is the source of groundwater contamination. Tian et al., (2019) studied the risk assessment of nitrate contamination in shallow groundwater. They stated that waste disposal from residential areas and modern agricultural activities are major sources of nitrate contamination in groundwater. Wagh et al., (2020) conducted a study on risk assessment of groundwater due to high nitrate contamination in kadava river basin, India and found that disposal of waste from resident area near river basin and modern agriculture activities are highly deteriorated the groundwater nature. Saurabh Shukla and Abhishek Saxena (2020) reviewed the sources and leaching of nitrate contamination in groundwater. They stated that isotopic studied with the help of statistical tools reveal a better result in the determination and identification of nitrate contamination than the geogenic factors studies. Nadikatla et al., (2019) evaluated the groundwater quality using the water quality index method in Srikakulam district, Andhra Pradesh, India. They found that, the entire groundwater quality is affected due to lack of improper sanitation facilities, sewage disposal and seepage runoffs.

Statistical analysis was used to identify the major ions that contribute to deteriorate the nature of groundwater in the study region. In this domain, the correlation coefficient, principal component analysis (PCA), and hierarchical cluster analysis (HCA) are the most efficient methods to evaluate and gives a clear idea about the chemical composition of groundwater. Su et al., (2020) evaluated the impact of natural and anthropogenic activities of the groundwater using multivariate statistical techniques in Baotou city, china and found that, three cluster values reveal rock water interaction, sewage intrusion and evaporation are the factors that affect the nature of groundwater. Singh et al., (2020) conducted a study on multivariate analysis of groundwater in the agricultural dominates taluks in Punjab, India, and found that PCA analysis suggested that the chemical composition of groundwater gets disturbed by the process of rock water interactions and high impacts of anthropogenic activities. Sajil (2020) investigated the hydrogeochemical and multivariate statistical analysis of pollution sources in the groundwater near the Bhavani river basin, Tamilnadu and stated that, higher factor loadings for major ions indicate mixed influenced of natural and anthropogenic activities destroyed the quality of groundwater in the study region.

From the above context, the specific objectives of the present study is (1) to evaluate the physio-chemical characterises of groundwater and compared with World Health Organisation (WHO) and Bureau of Indian Standards (BIS) (2) To determine the nitrate contamination in study area (3) To ascertain the vulnerable regions based on WQI index value (4) To identify the sources of contamination using statistical analysis. The present study's results are useful for change effective approaches for enhancing the rural drinking water system in a nitrate prone zone.

2 Material and methodology

2.1 Study area

Palani is a famous religious tourist place in the southern part of India and a prominent taluk in Dindigul district. It lies between 10.45°N latitude and 77.51°E longitude covering an area of 666.95 sq.km excludes the hilly terrain. A study boundary covered by Coimbatore in the south-east, Madurai by north-west. A subdivision of the Western Ghats borders the background to the town, the Palani Hills, where on lies the slope station of Kodaikanal. The view inside the town is ruled by the two slopes, Sivagiri and Sakthigiri, on the previous of which lies the sanctuary. At the foot of the slopes lie a few lakes which drain to the Shanmuga river, a tributary of the Amaravathi River, which takes its source on the inclines of the Palani Hills. A study area located above the sea level at an elevation of 315m, an average annual temperature of 27.2°C, and annual rainfall is 630mm. The highest temperature was recorded about 29.6°C during April and May month.

2.2 Geological Setting

Hard rocks cover more than 95% of the study area. The gneissic rock type is the parent rock seen commonly in the entire study area. Charnockite rock is covered in the southern part of the study area. The pyroxene granulite is grey in colour and granulitic rock with mineral seen on the weathered surface. It consists of diopside, hypersthene, plagioclase, hornblende, biotite, and quartz (Sujatha 2020, Chandra Mohan et al., 2017, Jawahar raj and Prabhakaran 2018). An elevation of the Palani hills ranges from 1163 to 2502m, and Sirumalai hill located in the southeast part of the study area. The plains are dominant in between these hill ranges. Red soil and black cotton soil are highly observed soil types in the study region. In the view of geotechnical properties of soil in the study area are high permeability and fractured rock types.

2.3 Sampling and analysis

Thirty sample locations are identified based on the high densified resident, agricultural activities, and waste disposal site in the study area. The samples were collected in the prewashed polyethylene bottles and followed preservatives techniques to improve the accuracy of the results. A physical characteristic such as pH, electrical conductivity, and total dissolved solids are measured during the sample collection. Major cations such as calcium, magnesium, sodium, and potassium, major anions such as chloride, sulphate, nitrate, fluoride, carbonate, and bicarbonate are measured in the laboratory methods recommended by American Public Health Association (APHA, 1995).

2.4 Quality assurance and quality control

Quality assurance and quality control is an efficient method to get a more accurate result during the sampling and testing of groundwater. One of the most important activities associated with sampling site selection satisfies the objective of the present research. Once well selected, sampling documentation and collection was carried out. All the samples were collected in the 1 litre polyethylene bottle washed with a 10% HNO_3

solution. An ionic balance error (IBE) equation is used to get an accuracy of analytical results between the concentration of major cation and anion in milliequivalent per litre (meq/L) for all collected samples (Eqn.2). The value of IBE should not exceed the acceptable limit of ± 10%.

$$IBE = \frac{\sum Cations- \sum \text{Anions}}{\sum Cations+ \sum \text{Anions}} \times 100$$

(1)

2.5 Water quality index (WQI)

WQI is the most significant tool to estimate the drinking water quality in rural, urban, and industrial regions. WQI indicates the nature of water in terms of numbers that reveal the present nature of water for any intended use (Adimalla et al., 2019b, Kirubakaran et al., 2015). The index values are calculated followed by (1) selecting and assigned weightage(wi) of each water quality parameter based its importance in the overall quality for drinking uses (2) relative weightage(Wi) is calculated from the Eqn.2 (3) calculating the quality rating(qi) for each parameter from the Eqn.3. (4) calculating the sub-index (SIi) and summation of sub-index value to estimate the overall quality of water.

$$Wi = \frac{w_i}{\sum_{i=1}^{n} w_i}$$ **(2)**

$$q_i = \frac{C_i}{S_i} \times 100$$ **(3)**

$$\mathrm{SI}_i = W_i \times q_i$$ **(4)**

$$WQI = \sum \mathrm{SI}_i$$ **(5)**

2.6 Hydro facial analysis

Piper (1994) proposed a graphical representation of analytical data to understand the major ions influencing groundwater's nature. The diagram suggested that, two triangles of cations and anions, respectively, and one diamond-shaped reveal that summarize both triangles. This pictorial graph is drawn based on the water cations and anions in chemical equilibrium. The piper diagram results show that alkaline earths exceed alkaline, major other sources of contamination and problems need to be answered by exhaustive studies of critical water quality in specific sample locations.

2.7 Geochemical mechanics

Gibbs (1970) proposed a plot to identify groundwater geochemical characteristics and evolution. It was widely used for groundwater studies to establish the relationship of water composition and effects of aquifer lithology in the nature of groundwater chemistry (Muniraj et al., 2019 Umamaheswari et al., 2015). It gives an exact mechanism for controlling the groundwater chemistry of a region. Precipitation, evaporation, and rock water interaction are the three distinct fields in a plot.

2.8 Health risk assessment (HRA)

HRA is the most important process of measuring human exposure to contaminants by consuming the elevated concentration of chemical parameters in groundwater for drinking purposes (Shukla et al., 2020). It includes major components such as exposure media, time, concentration, receptor exposure, and nature of the environment. Elevated concentration of nitrate was categories as non-carcinogenic risk according to the international agency for research on cancer (IARC). The present study considered the health effects of nitrate contamination through drinking water intake on high densified residents of the study area. The impact of a high concentration of nitrate on the human body was calculated in two steps (Soleimani et al., 2020). In the first step, chronic daily intake was estimated (Eqn.6), and in the second step, the hazard quotient was calculated with reference doses (Eqn.7).

$$CDI = \frac{CPW \times IR \times ED \times EF}{ABW \times AET}$$

(6)

$HQ = \frac{\text{CDI}}{\text{RfD}}$ **(7)**

Where,

E - Chronic daily intake, it is expressed in mg per kg/day,

CPW - Concentration of specific pollutant in groundwater in mg per day,

IR-Rate of human ingestion in Litres per day,

ED -Duration of exposure and expressed in years,

EF -Frequency of exposure and expressed in no. of days per years,

ABW - Average body weight in Kilogram.

AET -Average time in days,

HQ -Non-carcinogenic for Hazard Quotient,

RfD - Reference dose of nitrate and expressed in mg/kg/day.

2.9 Irrigation indices

It was observed that majority of people in a study area depends on agriculture of their daily income. Consequently, it is necessary to evaluate the suitability of groundwater for irrigation uses (Kumar et al., 2019). Various irrigation indices such as sodium absorption ratio (SAR), residual sodium carbonate (RSC), percentage sodium (%Na), magnesium hazards (MH), permeability index (PI), potential salinity (PS), residual sodium bicarbonate (RBSC), kelly ratio (KR), synthetic harmful coefficient (K), and exchangeable sodium percentage (ESP) are calculated using following formulas,

Sodium Absorption Ratio:

$SAR = \frac{\text{Na}}{\sqrt{(Ca+Mg)/2}}$ **(8)**

Residual Sodium Carbonate:

$RSC = \frac{\text{HCO3 } + \ CO3}{Ca \ + \ Mg}$ **(9)**

Percentage Sodium:

$\%Na = \frac{(Na+K)\times 100}{Ca+Mg+Na+K}$ **(10)**

Magnesium Hazards:

$MH = \frac{Mg \ \times 100}{Ca+Mg}$ **(11)**

Permeability Index:

$PI = \frac{\sqrt{\text{HCO3}} \ + \ Na}{\sqrt{(Na+Mg+Ca}}$

(12)

Potential salinity:

$\text{PS} = \text{Cl}^{-} + \frac{1}{2} \times \text{SO}_4^{2-}$

(13)

Residual sodium bicarbonate:

$RBSC = \text{HCO}_3^{-} - \text{Ca}^{2+}$ **(14)**

Kelly ratio:

$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$

(15)

Synthetic harmful coefficient

$K = 12.4\ M + SAR$ **(16)**

Exchangeable sodium percentage

$ESP = \frac{100\ (-0.0126+0.01475SAR)}{1+(-0.0126+0.01475\ SAR)}$

(17)

2.10 Spatial analysis

Inverse distance weighted (IDW) interpolation is an efficient method to determines cell values using a linearly weighted combination of a set of sample locations in the study region (Jesudhas et al., 2017 and Johnny et al., 2018). The surface of the study region is interpolated using latitude and longitude of the sample locations (Rostami et al., 2019). The weight is a function of inverse distance and assigned to each location based on distance. The concentration of each water quality parameter is represented in spatial maps using Arc GIS 10.4.

Result and discussion

Hydro geochemistry of the study area

pH

The concentration of hydrogen ion present in the water is more important, and it helps to identify the nature of groundwater whether the water is acidic or alkaline (Aravindan et al., 2010). However, the pH of groundwater in the study area ranges from 7.3 to 8.2, with an average of 7.8. It shows that the pH value for all the sample locations is most suitable for drinking purposes recommended by WHO (2011) and BIS (2012) standards. In the spatial analysis, an acceptable level of pH covers 666.95 Sq.km (Fig.3a).

Electrical conductivity (EC)

The EC is the most important parameter to estimate the total ionic concentration of groundwater and an elevated concentration of EC value reflects in total dissolved solids present in the groundwater (Azhdarpoor et al., 2019). It gives a proportion of water acceptability to transmit the electrons. In a study area, EC range from 650 to 6330 µS/cm with a mean of 2236.5 µS/cm. Handa (1969) proposed a classification of EC value is given in table.3. About 1.06 Sq. Km area falls under medium, 362.48 Sq.km area falls under high, 302.51 Sq.km area falls under very high, and 0.89 Sq.km area falls in extensively high (Fig.3b) for drinking purpose.Elevated concentration of EC reveals that nature of aquifer, rock water interaction and anthropogenic activities are highly influenced the nature of groundwater

Total dissolved solids (TDS)

Total Dissolved Solids (TDS) comprise major ions such as calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate, carbonate, and bicarbonate are dissolved in groundwater (Paul et al., 2019). TDS ranges from 358 to 3716 mg/L, with an average of 1316.55 mg/L in the study area. As per WHO and BIS standards, 3.59 Sq.km area fall in acceptable, 444.08 Sq.km area falls in most permissible, and 219.28 Sq.km area (Fig.3c) falls under the undesirable limit of TDS. A higher value of TDS causes major health issues such as stones in the kidney, heart diseases, and stomach problems.

Total Hardness (TH)

TH is mainly caused by the concentration of calcium and magnesium dissolved in groundwater (Marko et al., 2014). In a study area, TH range between 240 to 1600 mg/L with a mean of 653.16 mg/L as $CaCO_3$. About 60% of the sample locations exceed the desirable limit recommended by WHO (2011) and BIS (2012). Higher concentrations of calcium and magnesium could cause the undesirable limit of hardness in groundwater. In a study area, 2.79 Sq.km area was recorded as acceptable, 297.91 Sq.km area most permissible and 366.25 Sq.km area (Fig.3d) highly affected due to excess concentration of hardness in groundwater for drinking purpose.

Major cations

The order of cation dominance is calcium > magnesium>potassium > sodium in the study area. In a study area, sodium range between 12 to 122 mg/L with an average of 51.4 mg/L. All the sample locations fall under the permissible level of sodium for drinking purposes (Fig.3e). Calcium and magnesium are major cations that are highly influencing the quality of groundwater (Kawo et al., 2018). In a study area, calcium ranges from 20 to 400 mg/L, with an average of 135.93 mg/L. In the spatial analysis, 16.97 sq.km area falls under acceptable, 599.58sq.km area falls under permissible, and 50.40 sq.km area (Fig.3f) falls under the undesirable limit recommended by WHO (2011) and BIS (2012). A concentration of magnesium ion ranges from 6.07 mg/L to 194.4 mg/L, with a mean of 76.14 mg/L. About 3.22 sq.km area is acceptable, 599.46 sq.km area is permissible, and 64.27 sq.km area (Fig.4a) is recorded as an undesirable limit as per standards. An excess concentration of calcium and magnesium causes severe health issues on human and water used for irrigation purposes (Aravinthasamy et al., 2019). Potassium range between 2 to 18 mg/L with a mean of 9.66 mg/L and 26.67 % of the sample locations (Fig.4b) are highly affected due to the presence of higher concentration. The weathering of feldspars, microcline, orthoclase, and biotite are the major mineral causes the excess concentration of potassium in groundwater.

Major anions

In a study area, major dominance of anions is in the order of nitrate> chloride> sulphate> bicarbonate> fluoride > carbonate. The concentration of chloride ranges between 25 to 893 mg/L with a mean of 282.73 mg/L. The spatial analysis reveals that, 268.29 sq.km is acceptable and 398.66 sq.km (Fig.4c) is permissible as per WHO (2011) and BIS (2012). The sulphate concentration varies from 15 to 322 mg/L, with an average of 100.01 mg/L, and 659.94 sq.km area (Fig.4d) is an acceptable limit for drinking purposes. Both the chloride and sulphate ions in the study region was observed that within the permissible limit and doesn't affect the nature of groundwater for drinking purpose. Bicarbonate concentration varies from 195.2 to 732 mg/L, with an average of 41.35 mg/L. The high concentration of bicarbonate is due to weathering of rock and rock water interaction. Nitrate is the most significant pollutant of groundwater for both drinking and agriculture uses. The concentration of nitrate varies from 5 to 73 mg/L, with a mean of 34.16 mg/L. One-third of the sample locations are highly affected due to a higher concentration of nitrate ions. In the study area, dumping of waste in open land from residents, sewage disposal, utilization of chemical fertilizers are the major factors that cause the nitrate contamination in groundwater. The spatial analysis reveals that 101.14 sq.km area (Fig.4e) is undesirable for drinking uses. Continuous consumption of nitrate contaminated water leads the major diseases such as heart problems and blue baby syndrome (Tian et al., 2019). The concentration of fluoride ion range between 0.12 to 1.79 mg/L with an average of 0.58 mg/L. about 10% of the sample locations (9.05 sq.km) exceeds the permissible limit of fluoride for drinking purposes (Fig.4f).

Piper diagram

Piper plot of groundwater in the study area shown in Fig. 5. It reveals that, partial number of sample locations is mixed Ca-Mg-Cl type, 26.66% of the sample locations are Ca-Cl type, and 23.34% of the sample locations are Ca-HCO3 type of groundwater. The results indicate alkalis earth metals, weathering, rock water interaction, inadequate rainfall, evaporation, and anthropogenic activities are major factors that influence the nature of groundwater in the study area. The major ions such as Ca^{2+}, Mg^{2+}, Cl^- and HCO_3^- are highly dominate the quality of groundwater.

Gibbs plot

The groundwater chemistry and evolution mechanisms in the study area are shown in Fig.6. The Gibbs plot of the study area shows that 90% of the sample locations are highly influenced by rock water interaction, and the remaining 10% of the sample locations are evaporation dominance. The increasing action of weathering of parent rock, oxidation-reduction, ion exchange, mineral dissolution, such as calcite and dolomite dissolution are the major factor that deteriorate the quality of groundwater. Twenty-eight samples fall under the calcite dissolution, and two samples fall in dolomite dissolution (Fig.7).

Water quality index (WQI)

WQI was calculated to assess the present nature of groundwater for drinking purposes in the study region. The classification of groundwater based on WQI value is less than 25 is excellent, 26-50 is good, 51-75 is moderate, 76-100 is doubtful, and greater than 100 is unsuitable for drinking water purpose. In the study area, WQI ranges from, 28.70 to 117.15, with an average of 53.59. About 53.33 % of the sample location is good, 26.67% of sample location is moderate, 13.33% of sample location is doubtful and 6.67% of sample locations (2 Stations) are unsuitable class of water (Table.5). In 3D spatial analysis (contour lines), the study area was carried out to visualize the highly contaminated zone (Fig.8). It indicates the higher value of WQI was recorded in the footpath of hilly terrain areas. A larger amount of waste disposal from households, sewage disposal, excess utilization of fertilizers, and pesticides for agriculture are the major factors that influence groundwater quality for drinking purposes.

Human health risk assessment

Nitrate (NO_3^-) is one of the world's largest sources of groundwater contamination. The specific objective of this study is to assess the impact on human health of the continuous consumption of high nitrate water. Higher concentration of nitrate leads the adverse health effects and its category as non-carcinogenic risk for human (Gao et al., 2020). In the study area, hazards index for male varied from 1.20E-01 to 1.75E+00 with an average of 8.21E-01, for female varied from 1.42E-01 to 2.07E+00 with a mean of 9.71E-01, for children ranged from 1.63E-01 to 2.37E+00 with a mean of 1.11E+00. About 40 %, 50% and 53.33% of the sample location exceed the HQ value of greater than one for male, female, and children, respectively (Fig.9). It indicates children and women are at higher risk than male through drinking water ingestion. However, nature of groundwater is the major source for drinking water sources; especially children, have adverse health risk through the intake of contaminated groundwater. The conception diagram (Fig.10 a, b) shows that the aquifer lithological system and source of nitrate contamination in the study area. The major source for elevated concentration of nitrate in the study area is excess utilization of fertilizer, pesticides leaching of dumping waste and sewage disposal.

Irrigation indices

Sodium absorption ratio (SAR)

The SAR value indicates the impact of sodium hazards combination with calcium and magnesium ion for agricultural purposes. A high concentration of sodium ions can reduce the physical properties of soil, such as soil texture, size, voids, porosity, and permeability (Abbasnia et al., 2019). In the study area, the SAR value range from 0.26 to 2.68, with an average of 0.93 (Table.4). Richards (1954) classifications of groundwater based on SAR are tabulated in table.5. All the sample locations fall under the excellent class of water for irrigation uses. The spatial distribution of the SAR value indicates 666.95sq.km area is an excellent category (Fig.11a). It shows that groundwater's present nature is suitable for all types of soils and crops for irrigation. Besides, the US Salinity classification (1954) of groundwater based on the relationship between SAR versus EC is shown in Fig.13. About 80% of the sample locations fall in C3-S1, 10% of the sample locations fall in C2-S1, and 10% of the sample locations fall in the C4-S1 category. It indicates that the majority of the sample locations are high salinity with low sodium type of groundwater in the study area.

Percentage of sodium (%Na)

Excess sodium concentration causes damage to soil structure, aeration, infiltration, and permeability due to the process of deflocculation. Further, it reduces the plant's growth. The combination of sodium and carbonate causes alkaline soil, and sodium with chlorides leads the saline soil (Adimalla et al., 2019c). In the study area, percentage of sodium ranges from 5.54 to 42.13 % with a mean value of 17.78% (Table.4).

About 76.67% of samples fall in excellent (514.57sq.km), 20% of samples fall in good (151.52 sq.km) and 3.33% of samples fall in permissible (0.85 sq.km). The spatial distribution of percentage sodium is shown in Fig. (11b). Moreover, Wilcox (1954) classification of groundwater was carried and it indicates the nature of groundwater is suitable for irrigation uses without the treatment process (Fig.14).

Residual sodium carbonate (RSC)

Carbonate and bicarbonate are an important parameter for assessing the suitability of groundwater for irrigation uses. The RSC value indicates the alkalinity hazards of earth metals. An excessive concentration of the sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influence the fitness of groundwater (Balamurugan et al., 2020a). In the study region, the RSC value ranges from -23.96 to 3.01, with a mean of -6.31 (Table.4). The negative value of RSC reveals that concentration calcium and magnesium are higher than those of carbonate and bicarbonate in groundwater. The value of RSC less than 1.25 meq/L is suitable, 1.26 to 2.5 meq/L is marginal, and greater than 2.5 meq/L is unsuitable for irrigation (Table.6). The spatial distribution of RSC value in the study region, 664.91 sq.km areas, is suitable, 1.94 sq.km areas is marginal, and 0.57 sq.km area falls under the unsuitable classes of groundwater (Fig.11c). It indicates that one sample location has a distribution of calcite- and dolomite-rich sediments and large amounts of bicarbonate.

Magnesium hazards (MH)

High magnesium concentration leads to an adverse effect on the soil structure and reduces the crop yield (Kuvurmaci and Karakus 2020). In the study area, MH ranges from 8.08 to 79.20%, with an average of 48.75%. The value of MH is less than 50%, thus being suitable for irrigation. About 46.67% of samples are found to be suitable, and 53.33% of samples are found to be unsuitable for irrigation uses. In the spatial analysis, 351.49 sq.km area falls under the suitable and 315.46 sq.km areas fall under the unsuitable of groundwater for agriculture purposes (Fig.11d). Excessive concentration of magnesium is due to the process of exchangeable sodium ions in groundwater. A weathering of parent rock, dissolution of calcite, and dolomite are the factors that influence the concentration of magnesium ions.

Residual sodium bicarbonate (RBSC)

Gupta (1983) classified the groundwater for irrigation use based on the relation between the bicarbonate and calcium ions. The excess concentration of sodium bicarbonate leads to a harmful effect on soil (Rahman et al., 2017). In the study area, the RBSC value ranges from -11.96 to 7.21 meq/L, with an average of -0.05 meq/L (Table.4). About 90% of the sample locations are suitable, and 10% of samples are the marginal state of contamination (Table.6). The spatial distribution of RBCS 660.00 sq.km area falls under suitable, and 6.95 sq.km area is a marginally contaminated type of groundwater (Fig.11e). A higher value of RBSC indicates the dissolution of organic matter in the soil.

Potential salinity (PS)

It is defined as the sum of chloride and half of the sulphate ion concentration in groundwater (Ahmed et al., 2020). In the study area, PS ranges from 0.86 to 28.07 meq/L with a mean of 9.01 meq/L. About 23.33 % of groundwater samples are found to be less than 5, 43.33 % of samples are found to be marginal and 33.33 % of samples are found to be unsuitable for irrigation uses (Table.6). The spatial distribution of PS observed that 33.45 sq.km is suitable, 377.56 sq.km is marginal, and 255.93 sq.km is injurious to unsatisfactory (Fig.11f).

Kelly ratio (KR)

Kelly ratio is an important index to assess the groundwater for irrigation purposes (Merouche et al., 2019). The value of KR less than one indicates the insufficiency of sodium ion (good for irrigation), and greater than one indicates an excessive amount of sodium ion in groundwater (unsuitable for irrigation). KR values in the groundwater varied from 0.05 to 0.69, with a mean of 0.21. All the sample locations are suitable for irrigation uses in the study area (Fig.11g).

Permeability index (PI)

PI is also one of the important indices to evaluate the fitness of groundwater for irrigation purposes. Continuous usage of rich minerals such as calcium, magnesium, sodium, and bicarbonate ions in groundwater causes the low permeability of the soil and reduces the crop yield (Rufino et al., 2019). According to PI classification, classes I and II are suitable, and class III is unsuitable for irrigation. The PI varied from 13.11 to 70.33 %, with a mean of 36.87% in the study area (Table.4). About 76.67 % of groundwater samples fall under class II, and 23.33 % of groundwater found to be class III (Table.6). The spatial distribution of PI observed that 642.02 sq.km areas are suitable, and 24.93 sq.km is unsuitable for irrigation purposes (Fig.11h). Excess value of PI is associated to sodium and bicarbonate ions, which may be due to the ion exchange, calcite and dolomite dissolution.

Synthetic harmful coefficient (K)

A value of K can broadly reflect the salt and alkalis hazards (Xu et al., 2016). The classification of groundwater based on K values is less than 25 is excellent, 26 – 36 is good, 37-44 is injurious, and greater than 44 is unsuitable. In the study area, K value ranges from 4.81 to 44.98 %, with an average of 16.73%. The spatial analysis reveals, 621.20 sq.km area is excellent (83.33% of sample locations), 40.07 sq.km area is good (6.67% of sample locations), 5.30 sq.km area is injurious (6.67% of sample locations) and 0.36 sq.km area is unsuitable (3.33% of sample locations). The higher value of K indicates the surplus concentration of sodium ion in groundwater.

Exchangeable sodium percentage (ESP)

The proximity of higher concentration of exchangeable sodium turns around the process of aggregation and causes soil aggregates to sprinkle into their constituent individual soil particles. The significant issues emerging from high sodium levels compared with the other replaceable cations are soil's physical properties. The higher value of ESP, the collapse of the soil structure and convert to slump, reduce porosity, permeability, become denser, and to confine the root growth of plants (Sarani et al., 2016). The ESP classification of groundwater is less than 15 is suitable, and greater than 15 are unsuitable for the agricultural process. In the study area, ESP varied from -0.87 to 2.62, with an average of 0.10 (Table.4). All the sample locations are suitable for irrigation purposes.

Statistical analysis

Correlation analysis

Pearson's correlation matrix is widely used to identify the role of each water quality parameter and its impact on the deterioration of groundwater chemistry. The value of "R" varied from -1 to +1, and it indicates the positive value is a high correlation, and negative values are less correlation with each other (Umarani et al., 2019, Wagh et al., 2020, Yidana et al., 2018). In a study area, correlation coefficient analysis (Table.7) and scatter matrix plot (Fig.15) are reveals that, the pH has a negative correlation with EC, TDS, TH, Na, Ca, Mg, K Cl, SO4, NO3 and F, and positive correlation with CO_3^{2-} (r^2=0.31), HCO_3^- (r^2=0.11) which indicates moderate correlation with each other parameters. The EC has a high positive correlation with TDS (r^2=1.00), TH (r^2=0.93), Ca^{2+}(r^2=0.88), Mg^{2+}(r^2=0.85), SO_4^{2-}(r^2=0.80) and NO_3^-(r^2=0.74) and low positive correlate with Na^+(r^2=0.17), K^+(r^2=0.32), HCO_3^-(r^2=0.59) and Cl^-(r^2=0.36). TDS has a positive correlation with TH, Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^- and negative correlation with CO_3^{2-} (r^2=0.33). TH has a high positive correlation with Ca^{2+}(r^2=0.94), Mg^{2+} (r^2=0.92) and SO_4^{2+}(r^2=0.83) and negative correlation with CO_3^{2-}(r^2=0.29). It indicates the reverse ion exchange and weathering process dominating the nature of groundwater. Since NO3- positive correlate with Ca(r^2=0.70) and Mg (r^2=0.69), it shows that agriculture activities highly influence groundwater's nature. SO_4^{2-}has a high positive correlation with Mg (r^2=0.86), indicating anthropogenic influence.

Principal component analysis (PCA)

SPSS 21.0 version was used to carry out the principle component analysis of groundwater in the study area. The result of PCA shows that more significant water quality parameters to deteriorate the natural characteristics of groundwater. The varimax method was adopted to rotate the parameters in PCA and extraction limitation of the eigen value greater than one (Pande et al., 2019, Paul et al., 2019). In the study region, PCA illustrates four factors responsible for the data structure (Fig.16a and Table.8), with 76.635 % of cumulative variance. Factor 1 comprises of 49.902% of total variance with high loadings for EC, TDS, TH, Ca^{2+}, Mg^{2+}, SO_4^{2-} and NO_3^- (Fig.16b). It represents the anthropogenic activities such as disposal of waste from residents, sewage intrusion; chemical synthetic fertilizers used for high crop yield are the major reason for the excess concentration of salt and other ions.

Factor 2 responsible for 9.618% of total variance with high factor loadings for pH, HCO_3^-, weak positive loadings of EC, TDS, Na^+, Mg^{2+}, and SO_4^{2-}. It shows that the high value of hydrogen ions is due to weathering of parent rock, rock water interaction, and ion exchange process. These are highly influencing factor in the degradation of groundwater quality. Factor 3 comprises a total variance of 8.739% with high factor loadings of K^+, CO_3^{2-} and weak positive loading of HCO_3^-. It indicates that potassium-rich minerals such as feldspars, calcite, and dolomite weathering are the major reasons. In specifically, farmers are used 15.5% of nitrogen, and 18.8% of calcium content and easily water-soluble fertilizers are widely used in the study area. The impact of these kinds of fertilizers are initially enhanced the growth of the plant in two to three weeks and gets dissolved into water, finally leachates are diluted with the groundwater. In Factor 4, total variance is 8.376% with high loadings factor of sodium and chloride ions. Due to the action of the ion exchange process, rock water interaction and anthropogenic activities are highly affecting the quality of groundwater in the study region (Fig.16c).

Hierarchical cluster analysis (HCA)

A Q-mode HCA was performed in the study area to understand the chemical composition of groundwater. It is the most efficient tool for data classification and useful graphical methods to identifying the source of contamination in groundwater (Marín Celestino et al., 2018). HCA analysis was carried out in the study area based on the water quality parameters and sample stations. Also, the Wards linkage method with a square Euclidean distance classification method for comparison measurement is used to produces the most distinctive groups in the dendrogram (Prajapati et al., 2020). The result of HCA in the study area, cluster 1, comprises CO_3^{2-}, F^-, pH, K^+, Na^+, NO_3^-, Mg^{2+}, SO_4^{2-}, Ca^{2+}, HCO_3^-, and Cl^- are jointly associated with together. Cluster 2 shows that TH associated with cluster 1, and it indicates geogenic source, weathering of calcite and dolomite rocks, and anthropogenic activities. Cluster 3 represents the EC and TDS associated with clusters 1 and 2 (Fig.17a). It shows that the reverse ion exchange process is highly influencing the nature of groundwater in the study area (Table.9a). In addition, HCA was performed based on the sample location and shown in fig. 16b. It shows that, three different types of groups are group1 comprises sample locations 1,3,17,18 and 20, group 2 represents 4,5,7,10,14,22,24 and 27 and group 3 comprises 2,6,8,9,11,12,13,15, 16,19,21,23,25,26,28,29 and 30 (Table.9b). A partial number of sample locations are having the same characteristic of groundwater and less contamination (Fig.17b). The results of the HCA variable and sample locations are reveals that geogenic and reverse ion exchange and anthropogenic activities such as waste disposal, sewage intrusion and excess utilization of synthetic fertilizers are high influencing the nature of groundwater.

Conclusion

The result of this study is to increase the credibility of the integrated GIS and statistical methodology to examine the groundwater health risk assessment of nitrate contamination and also assess its appropriateness for drinking as well as irrigation purposes.

Piper and Gibbs plot of the study area shows that the increasing action of weathering of parent rock, oxidation-reduction, ion exchange, mineral dissolution, such as calcite and dolomite dissolution, is the major factor that deteriorates the quality of groundwater.

Based on WQI value, about 53.33 % of the sample location is good, 26.67% of sample location is moderate, 13.33% of sample location is doubtful and 6.67% of sample locations (2 Stations) is an unsuitable class of water.

The results of the risk assessment 40 %, 50% and 53.33% of the sample location exceed the HQ value of greater than one for male, female, and children respectively. It indicates children and women are at higher risk than male through drinking water consumption.

All the irrigation indices show that most of the sample locations are suitable for irrigation, and few locations need monitoring before use. Statistical analysis of the study reveals that calcium, magnesium, chloride, and nitrate ions are highly influencing groundwater's nature.

The result of the study provides the present nature and source of contamination in the study area. Local authority and people who work in water resources management need to conduct awareness programs to the farmer using organic fertilizers instead of synthetic fertilizers. This work will be very much helpful to future researchers in the field of human health risk assessment and artificial recharge management plan that ensures sustainable and non-carcinogenic appraisal of groundwater quality.

Data Availability Statement

Data available in article supplementary material- The data that supports the findings of this study are available in the supplementary material of this article.

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Table.1 Relative weight of each parameters

Parameters	WHO	Weight (wi)	Relative Weight (Wi)
pH	6.5-8.5	4	0.108
TDS	500	4	0.108
TH	300	2	0.054
Ca^{2+}	75	2	0.054
Mg^{2+}	30	2	0.054
Na^{+}	200	2	0.054
K^{+}	12	2	0.054
Cl^{2-}	250	3	0.081
SO_4^{2-}	200	4	0.108
HCO_3^{2-}	500	3	0.081
NO_3^{-}	45	5	0.135
F^{-}	1.2	4	0.108
		[?]wi=37	[?]Wi=1.000

Table.2 USEPA standards for nitrate contamination

Parameter	Children	Male	Women
IR (L/Day)	0.78	2.5	2.5
ED (Years)	12	64	67
EF (days/years)	365	365	365
ABW (Kg)	15	65	55
AET (days)	4380	23360	24455

Table.3 Handa Classification of groundwater based on EC value

E (μΣ/ςμ)	Water type	Classification	No. of samples	% of Samples
0 - 250	Low	Excellent	0	0.00
251 – 750	Medium	Good	2	6.67
751 – 2,250	High	Permissible	14	46.67
2,251 – 6000	Very high	Doubtful	13	43.33
6,001 – 10,000	Extensively high	Poor	1	3.33
10,0001 – 20,000	Brines weakly conc.	Very poor	-	-

Table.4 Descriptive statistical analysis of groundwater in study area

Parameter	Min	Max	Avg.	SD	Kurtosis	Skewness	WHO 2011	BIS 2012
pH	7.30	8.20	7.80	0.26	-0.66	-0.17	6.5-8.5	6.5-8.5
EC	650	6330	2236.5	1458.77	1.80	1.53	1500	-
TDS	358	3716	1316.5	875.94	1.63	1.48	500	500
TH	240	1600	653.17	384.04	0.33	1.19	200	200
Na^+	12	122	51.40	28.84	0.52	1.07	200	200
Ca^{2+}	20	400	135.93	88.60	1.42	1.30	200	75
Mg^{2+}	6.08	194.4	76.14	46.52	0.76	1.17	150	30
K^+	2	18	9.67	4.25	-0.90	0.13	12	-
HCO_3^-	195.2	732	410.35	128.52	0.07	0.39	-	-
Cl^-	25	893	282.73	221.88	1.64	1.38	200	250
SO_4^{2-}	15	322	100.02	90.59	1.58	1.59	200	200
NO_3^-	5	73	34.17	21.81	-1.40	0.20	50	45
F^-	0.12	1.79	0.58	0.41	2.46	1.60	1.5	1.5
SAR	0.26	2.68	0.93	0.53	2.72	1.56	-	-
%NA	5.54	42.13	17.78	8.55	0.88	1.08	-	-
RSC	-23.96	3.01	-6.31	7.15	0.27	-1.03	-	-
MH	8.08	79.20	48.75	13.45	2.01	-0.60	-	-
PI	13.11	70.33	36.87	14.39	-0.43	0.41	-	-
RBSC	-11.96	7.21	-0.05	4.27	0.89	-0.72	-	-
PS	0.86	28.07	9.01	6.70	2.53	1.56	-	-
KR	0.05	0.69	0.21	0.14	3.40	1.69	-	-
SHC	4.81	44.98	16.73	10.41	1.56	1.45	-	-

Table.5 WQI classification of groundwater in study area

WQI value	Water class	No. of samples	% of samples	Remarks
0-25	**Excellent**	**0**	**0.00**	Fit for drinking and irrigation uses
26-50	**Good**	**16**	**53.33**	
51-75	**Moderate**	**8**	**26.67**	Treatment needed for drinking and fit for irrigation use
76-100	**Doubtful**	**4**	**13.33**	Irrigation uses
> 100	**Unsuitable**	**2**	**6.67**	Need to treat for irrigation uses

Table.6 Irrigation indices of groundwater in study area

SAR	Range	No of samples	% of samples	Class of water	Area covered
	< 10	30	100	Excellent	666.95
	10 - 18	0	-	Good	-
	18 - 26	0	-	Doubtful	-
	> 26	0	-	Unsuitable	-
RSC	< 1.25	28	93.33	Satisfactory	664.91
	1.25 - 2.5	1	3.33	Marginal	1.94
	> 2.5	1	3.33	Unsatisfactory	0.58
MH	< 50	14	46.67	Suitable	351.49
	> 50	16	53.33	Unsuitable	315.46
PI	> 75	0	-	Class I	-

SAR	Range	No of samples	% of samples	Class of water	Area covered
	75 - 25	23	76.67	Class II	642.02
	< 25	7	23.33	Class III	24.93
RBSC	< 5	27	90.00	Satisfactory	660.00
	5 - 10	3	10.00	Marginal	6.95
	> 10	0	-	Unsatisfactory	-
PS	< 5	7	23.33	Satisfactory	33.45
	5 - 10	13	43.33	Marginal	377.56
	> 10	10	33.33	Unsatisfactory	255.93
KR	< 1	30	100	Good	666.95
	1-2	0	-	Doubtful	-
	> 2	0	-	Unsuitable	-
%Na	0-20	23	76.67	Excellent	514.57
	20-40	6	20.00	Good	151.52
	40-60	1	3.33	Permissible	0.85
	60-80	0	-	Doubtful	-
	>80	0	-	Unsuitable	-
SHC	< 25	25	83.33	Excellent	621.20
	25-36	2	6.67	Good	40.07
	36-44	2	6.67	Injurious	5.30
	> 44	1	3.33	Unsuitable	0.36
ESP	< 15	30	100	Sodic	666.95
	>15	0	-	Non sodic	-

Table.7 Correlation analysis of water quality parameters

Parameters	pH	EC	TDS	TH	Na^{+}	Ca^{2+}	Mg^{2+}	K^{+}	$CO3^{2-}$	HCO_3^{-}	Cl^{-}	SO_4^{2-}	NO_3^{-}
pH	**1.00**	-0.41	-0.42	-0.48	-0.06	-0.50	-0.37	-0.03	0.31	0.11	-0.28	-0.30	-0.67
EC		**1.00**	**1.00**	**0.93**	0.17	**0.88**	**0.85**	0.32	-0.32	0.59	0.36	**0.80**	0.74
TDS			**1.00**	**0.93**	0.17	**0.88**	**0.85**	0.32	-0.33	0.59	0.37	**0.80**	0.77
TH				**1.00**	0.28	**0.94**	**0.92**	0.30	-0.29	0.38	0.48	**0.83**	0.74
Na^{+}					**1.00**	0.25	0.26	0.03	-0.27	0.22	0.21	0.30	0.23
Ca^{2+}						**1.00**	0.73	0.29	-0.30	0.31	0.48	0.70	0.70
Mg^{2+}							**1.00**	0.27	-0.23	0.41	0.42	**0.86**	0.69
K^{+}								**1.00**	0.04	0.16	0.48	0.25	0.27
CO_3^{2-}									**1.00**	-0.38	-0.33	-0.27	-0.36
HCO_3^{-}										**1.00**	0.10	0.42	0.31
Cl^{-}											**1.00**	0.41	0.38
SO_4^{2-}												**1.00**	0.55
NO_3^{-}													**1.00**
F^{-}													

Table.8 Component value of water quality parameter

Parameter	Component 1	Component 2	Component 3	Component 4
pH	-0.519	**0.658**	0.318	0.261
EC	**0.953**	0.149	0.079	-0.147

TDS	**0.958**	0.137	0.070	-0.151
TH	**0.967**	-0.025	0.069	-0.107
Na^{+}	0.314	0.163	-0.413	0.497
Ca^{2+}	**0.903**	-0.126	0.036	-0.076
Mg^{2+}	**0.895**	0.097	0.096	-0.126
K^{+}	0.363	-0.112	**0.675**	0.436
CO_3^{2-}	-0.417	-0.049	**0.634**	-0.304
HCO_3^{-}	0.504	**0.692**	-0.098	0.175
CL^{-}	0.536	-0.333	0.176	**0.519**
SO_4^{2-}	**0.846**	0.163	0.069	-0.023
NO_3^{-}	**0.817**	-0.227	-0.136	-0.147
F^{-}	0.091	-0.371	-0.066	0.418
Eigen value	6.986	1.347	1.223	1.173
Total % variance	**49.902**	**9.618**	**8.739**	**8.376**
Cumulative % variance	**49.902**	**59.520**	**68.259**	**76.635**

Table.9a Cluster analysis of groundwater in study area

Cluster	Groundwater parameter
I	EC, TDS
II	TH
III	CO_3^{2-}, F^{-}, pH, K^{+}, Na^{+}, NO_3^{-}, Mg^{2+}, SO_4^{2-}, Ca^{2+}, HCO_3^{-}, and Cl^{-}

Table.9b Groups of groundwater sample in study area

Group	Groundwater parameter	No. of sample	% of samples
I	1,3,17,18 and 20	5	16.67
II	4,5,7,10,14,22,24 and 27	8	26.66
III	2,6,8,9,11,12,13,15,16,19,21,23,25,26,28,29 and 30	17	56.67

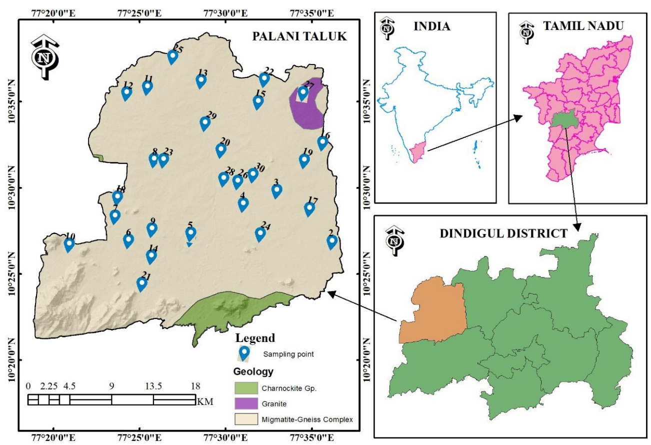

Fig.1 Study area

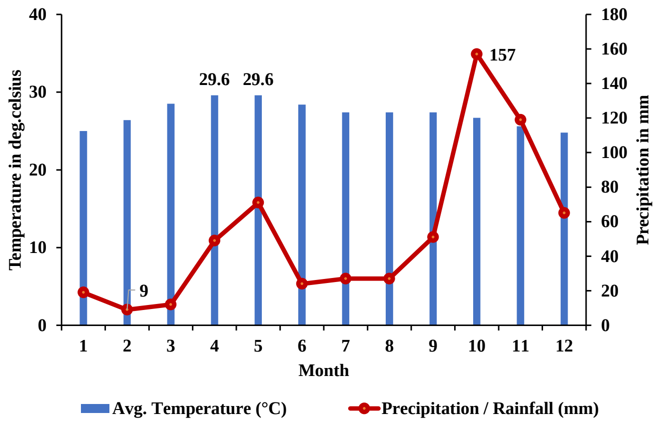

Fig.2 Climatic variation in study area

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