Groundwater quality in the Niva River basin, Chittoor district, Andhra Pradesh, India

Y. Srinivasa Rao · T. V. K. Reddy · P. T. Nayudu

Abstract This study was made to assess the groundwater quality in relation to agricultural and domestic uses in a part of the Peninsular Archean granite and gneissic complex of India. Water samples were collected from the existing wells in the Niva River basin, Chittoor district, Andhra Pradesh, India and analysed for major ions. The analytical data, processed and interpreted acoording to the WHO standards, reveal that, in general, the groundwater is suitable for both agricultural and domestic uses, exept in a few locations. High concentration of nitrates were observed in some of the wells (both agricultural and domestic) that are affected by the impact of industrial effluents. Multiple regression analysis was performed and used as a positive predictive tool in understanding the chemistry of the groundwater.

Key words Groundwater quality · Pollution · Nitrates · Total dissolved solids · Regression analysis

Introduction

The quality of water plays a prominent role in promoting both the standard of agricultural production and human health. If deterioration starts in water quality it will naturally affect the soil-crop-water system and human health conditions. In the initial period of water quality deterioration the damage may be low, but if it is not controlled at the right time, this water will not be suitable for any purpose. Water quality may vary depending upon variation in geological formations. Human activity such as industrialization, mining and urbanization may also produce effluents which pollute the environment. Keeping these points in mind, an attempt was made to study the qualitative analyses of groundwater and also to detect the causes for the deterioration of water quality, by collecting 59 groundwater samples in the Niva River basin, Chittoor district, Andhra Pradesh, India. The Niva River basin lies between the latitudes 13°02′–13°16′ N and longitudes 78°53′3″–79°09′4″ E with a catchment area of 359 km^2. Geologically, the basin is underlain by rocks of Archean age consisting of granites, granite-gneisses, recent alluvium and soils. Numerous dolerite dykes occur as intrusions in the granites and gneisses (Central Ground Water Board 1975; Geological Survey of India 1980).

The Niva River rises from the Paradarami hill ranges in Chittoor district and flows through the town of Chittoor (the headquarters of Chittoor district) and finally joins the Ponnai River as a tributary near the village of Kotrakona in the Chittoor district of Andhra Pradesh. The groundwater occurs both under unconfined and semiconfined conditions and the aquifers are mainly weathered and fractured granites, gneisses, and contact zones of crushed dykes with the granites and gneisses. The depth to the water table varies from 3.5 m to 22 m.

Chittoor is a fast growing town with a population of 1.3 lakhs [130,000 (Census of India 1991)]. Sugar, distillery, dairy and other industries in and around the town of Chittoor discharge their effluents into the nearby streams and ponds without proper treatment. Against this background, the authors undertook further studies of groundwater to determine its quality and classify the quality of water used for different purposes.

Materials and methods

A total of 59 groundwater samples from the working dug, dug-cum-bore and bore wells of the basin area were collected during July 1991. The locations of the collected groundwater samples are shown in Fig. 1. The samples were analyzed for different ions and interpreted by standard methods [American Water Work Assocation (AWWA) 1950; Rainwater and Thatcher 1960; Brown et al. 1970] in order to study the quality of water for various purposes. Electrical conductivity (EC) and concentration of nitrates contour maps were prepared.

The minimum and maximum values of major ions of

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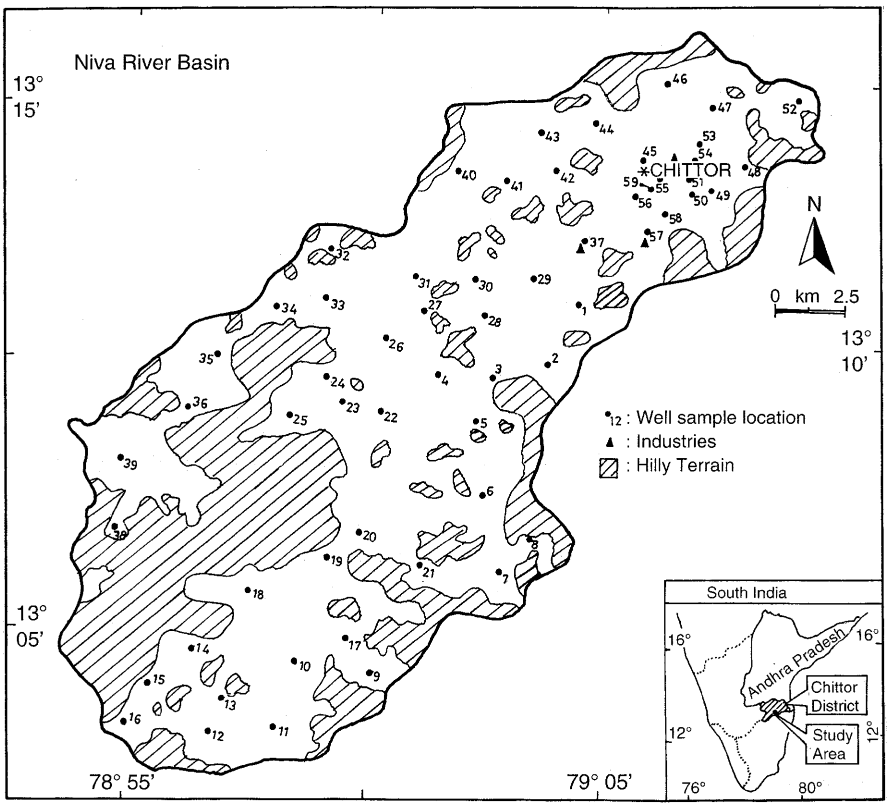

Fig. 1
Groundwater sampling locations in the Niva River basin, Chittoor district, Andhra Pradesh, India

Table 1
Range of chemical parameters in groundwater of Niva River basin, Chittoor district, Andhra Pradesh, India (measured in mg l^{-1})

Chemical parameters	Min	Max	Sample which exceed permissible limits of WHO standard
Silica	5.0	45	
Sodium	19.0	308	
Potassium	1.4	37	
Calcium	5.0	240	37
Magnesium	7.6	151	37, 50, 54, 59
Carbonate	0.0	21	
Bicarbonate	75.0	450	
Sulphate	10.0	100	
Chloride	10.0	1090	37
Nitrate	1.3	377	3, 13, 19, 22, 23, 29, 34, 37, 43, 48, 51, 54, 55, 56, 57, 58
TDS	230	2500	3, 37, 53, 54, 57
Electrical conductivity (μS cm^{-1} 25 °C)	290	4900	

groundwaters in the study area are presented in Table 1. Multiple regression analysis was utilized (Davis 1973) to determine the significance among the various ions, and regression coefficiency data matrix was used to develop a model.

Classification of groundwater and water types

Various methods and graphs were used to study and interpret the water analyses data. The data obtained on major ions are classified with the help of Romani's (1975) modified diagram. The prevalent trilinear diagrams of Piper (1944), Chillinger (1956), Handa (1965) and Back (1966) have their own limitations. Romani's modified diagram (Fig. 2) is used for proper classification of water, to study its chemical behavior and related geochemical problems and also to determine its suitability for agricultural purposes. Its advantage is that the overall water character can be studied in the square field without losing any advantages of Piper's diamond shaped field. Furthermore, as one side of the square represents the percent of sodium, the diagram is supplemented with Wilcox's (1955), thereby making it more useful.

For the classification of water, only the proportions of principal cations and anions, in terms of the percentage, epm values are plotted in each triangle (Fig. 2). The triangles are further divided into seven fields, representing the following types of water: (1) **cation triangle**, *C1* calcium type, *C2* magnesium type, *C3* sodium type, *C4* sodium-calcium type, *C5* calcium-magnesium type, *C6* sodium-magnesium type, *C7* calcium-magnesium-sodium type; (2) **anion triangle**, *A1* bicarbonate type, *A2* sulphate type, *A3* chloride type, *A4* chloride-bicarbonate type, *A5*

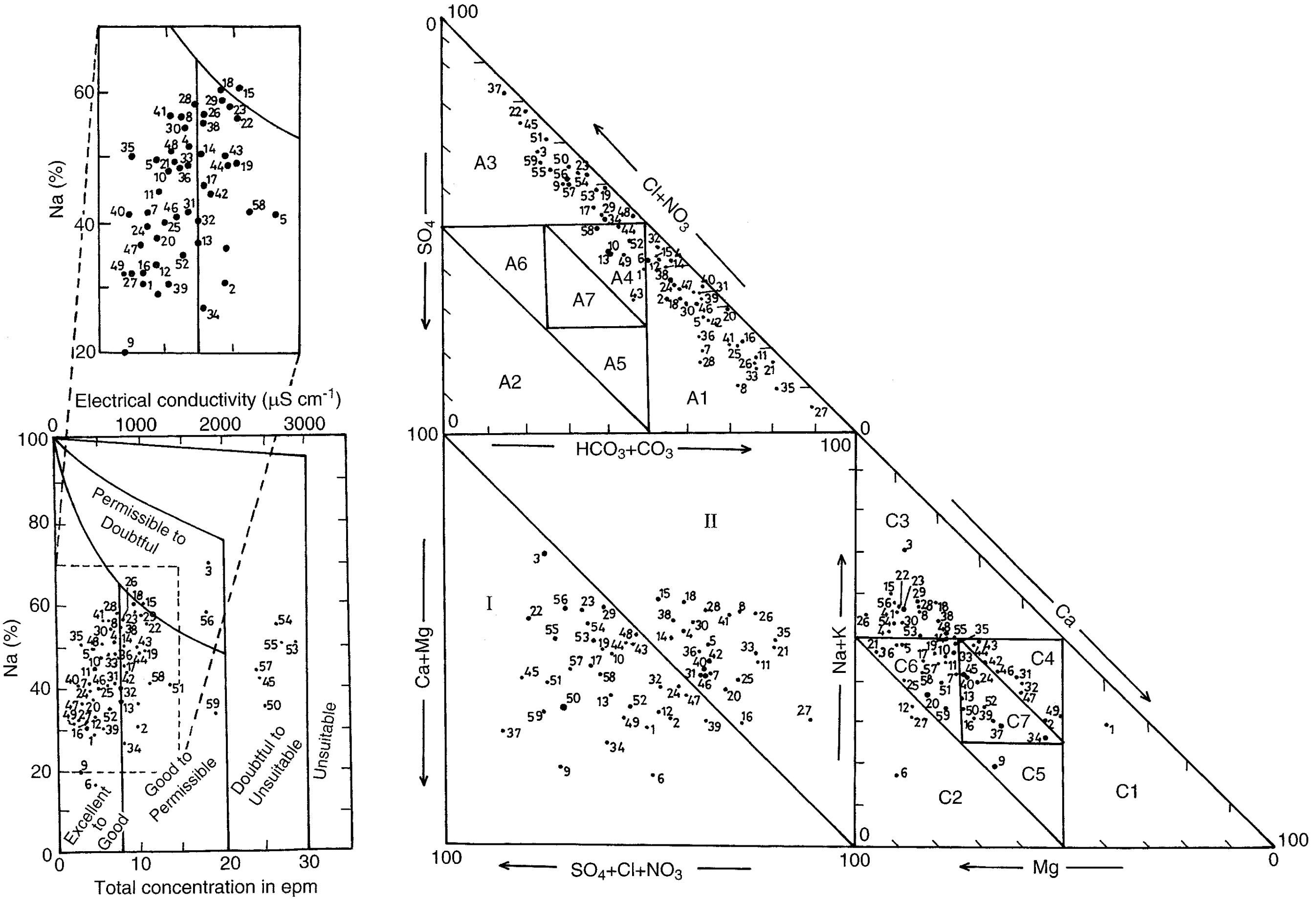

Fig. 2
Romani's (1975) diagram for geochemical classification of groundwater

bicarbonate-sulphate type, *A6* chloride-sulphate type, *A7* bicarbonate-sulphate-chloride type.

In the plotting of anions and cations, nitrate is combined with chloride according to Domenico (1972). Geochemical (Romani 1975) and quality classifications (Richards 1954; Wilcox 1955) of the analyzed waters are presented in Table 2. From this table, the waters are represented by sodium-bicarbonate type, sodium-chloride type, sodium-magnesium-bicarbonate type, calcium-magnesium-sodium-bicarbonate type, sodium-magnesium-chloride type, calcium-magnesium-sodium-chloride type, sodium-calcium-bicarbonate type, sodium-calcium-chloride-bicarbonate type, magnesium-bicarbonate type, calcium-magnesium-sodium-chloride-bicarbonate type and sodium-magnesium-chloride-bicarbonate type.

In order to study water quality, plotting in the two triangles is extended to the square field (Fig. 2). The square field is divided into group I and group II. In group I the alkaline earths (Ca, Mg) exceed the bicarbonate anions whereas in group II the reverse is true. The waters in group I have permanent hardness without residual sodium carbonate (RSC). The waters in group II have temporary hardness with RSC. Apart from showing this primary characteristic of water, the field is used to study the mixing of water and other geochemical problems similar to the diamond-shaped field of a Piper diagram. Out of 59 samples, RSC is present in 24 samples (40.7%) and absent in 35 samples (59.3%). Plotting in the square field is also extended to the supplemental percent sodium diagram and plotted according to the salinity of the water. It shows the salinity of the water and also the suitability of the water for irrigation purposes.

Classification of groundwater for irrigation purposes

Features that generally need to be considered for evaluation of the suitability of groundwater for irrigation use are RSC, salinity and sodium absorption ratio (SAR).

Residual sodium carbonate (RSC)

According to Richards (1954) by considering the presence of RSC in groundwater samples, 49 out of 59 samples are safe, 9 are marginal and 1 sample is not suitable for irrigation.

Table 2
Geochemical and quality classifications of groundwater of Niva River basin, Chittoor district, Andhra Pradesh, India. Underlining of the sample number indicates the sample is present in Group II with RSC

Water type	Sample number	Total no. of samples
Romani's classification		
C3 A1	4, 8, 15, 18, 26, 28, 30, 38, 41	9
C3 A3	3, 22, 23, 29, 48, 54, 55, 56	8
C6 A1	5, 7, 11, 20, 21, 25, 33, 35	8
C7 A1	16, 24, 36, 39, 40, 42, 46	7
C6 A3	17, 19, 51, 53, 57, 59	6
C7 A3	34, 37, 45, 50	4
C4 A1	31, 32, 47	3
C4 A4	43, 44, 49	3
C2 A1	12, 27	2
C7 A4	13, 52	2
C6 A4	10, 58	2
C1 A1	2	1
C1 A4	1	1
C2 A4	6	1
C5 A1	14	1
C5 A3	9	1
C7 A3	–	(0)
Wilcox's classification		
Excellent to good	1, 4–12, 16, 20, 21, 24, 25, 27, 28, 30, 31, 33, 35, 36, 39, 40, 41, 46 to 49, 52	31
Good to permissible	2, 13, 14, 15, 17, 18, 19, 22, 23, 26, 32, 34, 38, 42, 43, 44, 51, 58, 59	19
Permissible to doubtful	3, 56	2
Doubtful to unsuitable	45, 50, 53, 54, 55, 57	6
Unsuitable	37	1
US Salinity Laboratory's classification		
C2S1	1, 4–12, 16, 20, 21, 24, 25, 27, 28, 30, 31, 32, 33, 35, 36, 39–41, 46–49, 52	31
C3S1	2, 13–15, 17–19, 22, 23, 26, 29, 34, 38, 42–44, 49, 51, 58, 59	19
C3S2	3, 56	2
C4S1	37, 45, 50, 55, 57	5
C4S2	53, 54	2

Salinity

High concentration of salts in irrigation water renders the soil saline. This affects the salt intake capacity of the plants through their roots. According to Raghunath (1983), by considering the electrical conductivity values, 32 samples are medium, 19 are high, and 8 are very high in salinity.

According to Wilcox's (1955) diagram (which was integrated into Romani's modified diagram) 31 samples are excellent to good, 19 are good to permissible, 2 are permissible to doubtful, 6 are doubtful to unsuitable and 1 is unsuitable (Table 2).

Sodium absorption ratio (SAR)

The groundwaters of the basin are classified with respect to SAR (Richards 1954). All of the samples are excellent, except sample 56. According to the widely used diagram of Richards (1954) for evaluating waters for irrigation purposes, on the basis of sodium hazard and salinity hazard (Table 2), most of the samples (50 out of 59 samples) are C2 S1 to C3 S1 (medium to high salinity with low sodium) waters. This means they are satisfactory for irrigation use in almost all types of soils. However, 5 samples are C4 S1 (very high salinity with low sodium) waters and 4 samples are C3 S2 and C4 S2 (high to very high salinity with medium sodium) waters. From the salinity, SAR and RSC, it is found that samples 3, 26, 37, 45, 50, 53 and 57 are unsuitable for irrigation. The causes of unsuitability are due to: (1) the dumping of vegetable matter into the well (sample 3); (2) the occurrence of bedrock at shallow depth with poor drainage conditions (sample 26); and (3) the impact of industrial effluents on groundwater in the study area (samples 37, 45, 50, 53 and 57).

Classification of groundwater for domestic purposes

Drinking water should be free from color, turbidity, odor and microorganisms. However, this criteria do not fall into the realm of chemical quality (Karanth 1990). Water sample 37 is reddish yellow in color and has a foul smell. This well is situated downstream of the distillery effluent discharge site.

The presence of higher magnesium concentrations in samples 37, 50, 54 and 59 would cause a laxative effect. Based on total dissolved solids (Anon 1946; AWWA 1950; Robinnove and others 1958; Davis and DeWiest 1967) it is observed that out of 59 samples, 25 are suitable for drinking, 19 are permissible for drinking, and 15 are only useful for irrigation.

According to Voldiya (1987) excessive application of nitrogen fertilizers attributed more than 200 mg l^{-1} of nitrate into groundwaters. In the study area, out of 59 samples 16 have more than permissible limits of nitrates.

Hardness of water affects its reaction with soap and causes scale and incrustation accumulation in containers and conduits where the water is heated or transported. Chemically, the water should be soft with less dissolved solids and free from poisonous constituents. Samples are classified on the basis of hardness (mg l^{-1}) as $CaCO_3$ (Hem 1970). All the samples are hard to very hard except sample number 41 which has moderate hardness.

Interpretation of water quality

To interpret the water quality, contour maps of electrical conductivity and concentration of nitrates (Fig. 3) were

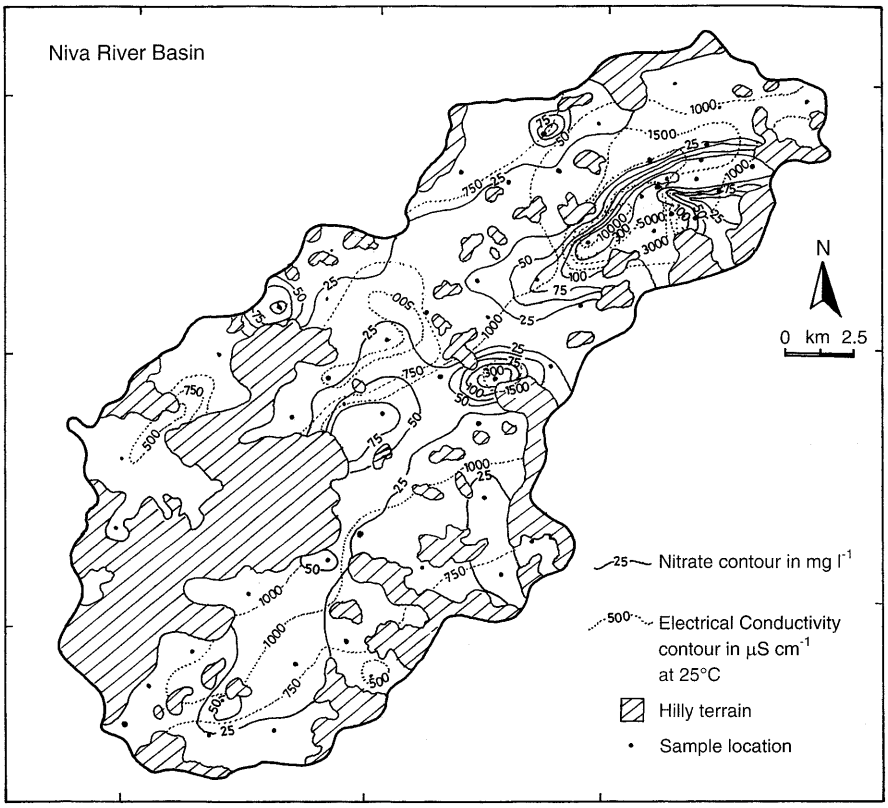

Fig. 3
Distribution of electrical conductivity and concentration of nitrates in groundwater of the study area

prepared to depict the spatial variations in the basin. Three-quarter of the basin is below 1000 μS cm^{-1} of electrical conductivity indicating that these waters have a low content of soluble salts and can be used without risk of soil salinization. However, the northeastern part of the basin (in and around Chittoor town) shows higher than 1000 μS cm^{-1}. This is largely due to the accumulation of dissolved solids from the upland areas by rainwater and leaching of dissolved solids from the effluents through the alluvial deposits.

In this basin, the concentration of nitrates ranges from 1.3 mg l^{-1} to 377 mg l^{-1}. The highest desirable and maximum permissible limit for nitrates is 45 mg l^{-1}. Twenty-seven percent of the collected samples have more than permissible limits of nitrates. The high concentration of nitrate in drinking water is toxic. Its toxicity to humans was first reported by Comly (1945). It causes blue babies or methemoglobemia disease in infants and gastric carcinomas (Gilli and others 1984). The contour map of nitrates concentration in groundwater presented in Fig. 3 shows that the increase in nitrate concentration is along flow paths of groundwater towards the lowland areas and the crowding of contours is in the northeastern part of the basin. The only source of elevated nitrate concentration in the groundwater is agricultural fertilizers in the southwestern and central parts of the basin, and the impact of industrial effluents in the northeastern parts. The high nitrate concentration in sample 3 is due to vegetable matter.

Causes for nitrates presence

Several authors (Hill 1982; Flipse and others 1984; Houzim and others 1986; Kolaja and others 1986; Vrba 1986) have related the nitrates in the groundwaters to different sources such as leaching of organic and inorganic fertilizers from agricultural land by infiltration of precipitation, irrigation water, animal waste, leakage from sewers and subsurface flow from upgradient areas. In the study area the irrigation water is mostly from the dug, dug-cum-bore and bore wells. The different sources of nitrates such as fertilizers, animal wastes and septic tanks, have been investigated by Komor and Anderson (1993) using nitrogen isotopes. Fertilizers are considered to be the principal source of nitrates in the areas under intensive agriculture. The types of fertilizers that are in use in the area under study are organic and inorganic chemicals. Organic fertilizers include solid and liquid manure, slurry and compost. Inorganic fertilizers are applied in a higher proportion than organic fertilizers. The commonly applied inorganic fertilizers in the area are urea, superphosphate and potash.

Potash from potash fertilizers and phosphates from phospate fertilizers are absorbed into the soil. But, paradoxically, neither physical nor chemical sorption of nitrate ions occurs with nitrogen fertilizers and their absorption is biological. Therefore, part of the nitrogen fertilizer is absorbed by the plants through the roots, part of which is transformed into cell walls of microorganisms. These compensatory mechanisms of nitrate removal are insignificant in the soil environment (Lance 1972) and hence nitrates percolate into the groundwater.

Groundnut, cereal and millet are cultivated in the upland area of the basin where the soil thickness is less than 1 m and rain is the only source of water. Sugarcane and rice crops are cultivated using the dug, dug-cum-bore and bore wells for irrigation in the tank pond command areas and topographical lowlands where the thickness of soil is more than two meters. Generally, people assume that crop yield increases with higher fertilizer application without considering the thickness and absorbing capacity of the soil in the study area.

The residue of fertilizers that remained insoluble due to excessive application in the upland areas drains downward by runoff and infiltrates into the subsurface waters of the lowland areas. Therefore, well water in lowland areas showed a high concentration of nitrates. In any hard rock terrain, bore wells receive groundwater from fractured zones which have interconnections. Thus the interconnections among the holes of the dug-cum-bore wells, joints, gneissic structures, weathered zones and fractures provide a passage for these dissolved residues of fertilizers to go into the deeper levels of groundwater and into the other bore wells of the area (samples 3, 13, 19, 22, 23, 29, 34, 43 and 48).

Sample 3 was collected from a temple well a few days after an Indian traditional festival "*Vinayakachavithi*". In this festival people worship the idol of *Vinayaka* with plant twigs and leaves which they dump into the nearby waters. This well was used for this purpose by the surrounding devotees. The decomposition of these materials may have added to the higher concentration of nitrates (325 mg l^{-1}).

However, in the northeastern part of the basin (samples 37, 51, 54, 55, 56, 57 and 58) industrial effluents are on additional source for the presence of nitrates. Effluents from the distillery and the sugar factory are released into the nearby stream course that flows through a fractured zone. Due to the ephemeral nature of the stream, dilution of the effluents by the stream flow is very negligible in any season. Therefore, released effluents join the base flow of the stream course and cause pollution to the wells in the surrounding alluvial zone in the downstream direction, and reach the deeper levels of groundwater flow as mentioned earlier. The highest concentration of nitrate in sample 37 is due to the proximity of that well to the distillery effluent discharge site in the downstream direction.

From the water quality study, it is concluded that the groundwater of the basin is strongly affected by the high concentration of nitrates due to the over-application of fertilizers for agricultural use. The northeastern portion of the basin is polluted due to the discharge of industrial effluents into the nearby stream course without proper treatment.

Regression analysis

A commonly used measure of the relationship between two variables is the correlation coefficient, which is simply a measure to show how well one variable predicts another (Krumbein and Graybill 1965). Multiple regression has been performed for the analyzed water samples and the correlation coefficient matrix for the major ions is presented in Table 3. This analysis is the same as the following equation:

$$Y = B_0 + B_1 X_1 + B_2 X_2 + \ldots$$

Total dissolved solids have been taken into account as a dependent variable. In general, three different sets of strong relationships exist between major cations and anions in an aqueous system (Douglas and Leo 1977). They are:

1. The highly competitive relationship between ions having the same charge but a different valence number, e.g., Ca^{2+} and Na^+.
2. The affinity between ions having different charges but the same valence number, e.g., Na^+ and Cl^-.
3. The non-competitive relationship between ions having the same charge and the same valence number, e.g., Ca^{2+} and Mg^{2+}.

1. Highly competitive ion relationship: ions such as Ca^{2+} with Na^+ and K^+; Mg^{2+} with Na^+ and K^+; and SO_4^{2-}

Table 3
Correlation matrix of chemical data for groundwater of Niva River basin, Chittoor district, Andhra Pradesh, India

Ion	SiO_2	Na^+	K^+	Ca^{2+}	Mg^{2+}	CO_3^{2-}	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	TDS
SiO_2	–	0.46	0.24	0.23	0.46	0.11	0.44	0.32	0.35	0.34	0.39
Na^+	–	–	0.50	0.40	0.76	0.23	0.70	0.61	0.77	0.56	0.76
K^+	–	–	–	0.33	0.45	0.08	0.47	0.25	0.47	0.33	0.56
Ca^{2+}	–	–	–	–	0.64	−0.11	0.32	0.30	0.80	0.49	0.79
Mg^{2+}	–	–	–	–	–	0.02	0.62	0.43	0.91	0.52	0.85
CO_3^{2-}	–	–	–	–	–	–	0.04	0.17	0.04	0.22	0.07
HCO_3^-	–	–	–	–	–	–	–	0.40	0.54	0.19	0.59
SO_4^{2-}	–	–	–	–	–	–	–	–	0.37	0.36	0.43
Cl^-	–	–	–	–	–	–	–	–	–	0.53	0.91
NO_3^-	–	–	–	–	–	–	–	–	–	–	0.64

with HCO_3^-, Cl^- and NO_3^- have positive correlation and CO_3^{2-} with HCO_3^-, Cl^- and NO_3^- have low positive correlation. However, Mg^{2+} ions have a more significant correlation with Na^+ than K^+; and SO_4^{2-} ions have more significance with HCO_3^- than with other anions.

2. Affinity ion relationship: a negative correlation exists between Ca^{2+} and CO_3^{2-}. However, Mg^{2+} ions have a very low correlation with CO_3^{2-} and low correlation SO_4^{2-}; and Na^+ ions have a significant correlation with HCO_3^-, Cl^- and NO_3^-.

3. Non-competitive ion relationship: the relationship between Ca^{2+} and Mg^{2+} ions is significant. However, among HCO_3^-, Cl^- and NO_3^- there is no significance.

TDS shows significant correlation with Cl^- (0.91), Mg^{2+} (0.85), Ca^{2+} (0.79), Na^+ (0.76), and NO_3^- (0.64). In the groundwater samples, TDS is mainly dependent on the concentration of major ions such as Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, and SiO_2. The functional relationship could be understood as:

$$\mathrm{TDS} = f/(SiO_2, Na^+, K^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-})$$

and the resulting regression coefficient of a data matrix could be used for the development of a model. A simple conversion step has been adopted in this study to compute the chemical parameters of a known value of the dependent variable TDS. Considering a known value of TDS and its component concentrations, an inverse computation could be made to determine the percentage contribution of each ion as follows:

$$\mathrm{TDS} = -135.12 + 0.58\ SiO_2 + 1.09\ Na^+ + 9.86\ K^+ + 6.53\ Ca^{2+} + 3.03\ Mg^{2+} + 4.11\ CO_3^{2-} + 1.09\ HCO_3^- + 0.54\ SO_4^{2-} + 1.33\ Cl^- + 1.62\ NO_3^-$$

Degree of fit $(r) = 0.95$

Substituting the TDS and ionic values of a sample whose constituents are nearer to the means of the constituents:

$$849 = -135.12 + 23.2 + 152.6 + 49.3 + 32.65 + 106.05 + 81.6 + 387.72 + 6.4 + 90.4 + 53.5$$

The percentages of a–j are obtained from $(849 + 135.12)$ as:

$SiO_2 = 2.36$; $Na^+ = 15.49$; $K^+ = 5.00$; $Ca^{2+} = 3.42$; $Mg^{2+} = 10.77$; $CO_3^{2-} = 8.28$; $HCO_3^- = 39.40$; $SO_4^{2-} = 0.66$; $Cl^- = 9.18$; $NO_3^- = 5.43$

Using these percentages, the ionic concentrations of any water sample in the study area could be determined, if the TDS of that sample is measured.

Results and conclusions

The hydrochemical studies conducted so far in the groundwater of the Niva River basin of Chittoor district in Andhra Pradesh, India, indicate that the groundwater is hard to very hard and represented by Na^{2+}–HCO_3^-, Na^{2+}–Cl^-, Na^+–Mg^{2+}–HCO_3^-, Ca^{2+}–Mg^{2+}–Na^+–HCO_3^- etc., types of waters. Out of the collected 59 samples 24 (40.7%) show the presence of RSC. Fifty (84.7%) samples out of 59 have medium to high salinity with low sodium waters. The northeastern part of the basin is polluted due to the impact of untreated industrial effluents. Samples 37, 55, 56 and 59 are affected by distillery effluent; 53 and 54 are affected by sugar factory effluent, while 57 and 58 are affected by dairy effluent. This statement is made on the basis of the observation of wells adjacent to the respective industrial effluent discharging sites. Samples 37, 53, 54, 56, 57, 58 and 59 are not useful for domestic purposes. These waters are unfit for human consumption, and particularly unsuitable for infants. Samples 37, 45, 50, 53 and 57 are not useful for irrigation until an appropriate treatment has been applied. The Niva River basin is to be kept under observation, especially to determine the nitrate pollution in groundwater due to the excessive use of fertilizers.

From the regression analysis, a significant relationship is observed in the highly competitive ions (Na^+ with Mg^{2+}), in the affinity ions (Na^+ with HCO_3^-, and Cl^- and NO_3^-) and in the non-competitive ions (Ca^{2+} with Mg^{2+}). Less significant correlation is observed Mg^{2+} with CO_3^{2-} and SO_4^{2-} (affinity ions). No significant correlation is observed among HCO_3^-, Cl^- and NO_3^- (non-competative ions).

The results of the multiple regression model can be used as a positive predictive tool in determining the chemistry of groundwater if the dependent variable TDS is measured at any location. However, exclusion of the abnormal samples, due to pollution effects, should be done at the time of combining all of the sample data in the multiple regression analysis. This type of model can also be developed by taking the electrical conductivity as the dependant variable.

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