Indian Journal of Science and Technology Vol. 4 No. 12 (Dec 2011) ISSN: 0974- 6846

Hydrochemical characterization of groundwater in the proximity of river Noyyal, Tiruppur, South India

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Abstract

Hydrochemical investigations of the groundwater and the seasonal effect on the chemical budget of ions in the proximity of river Noyyal were carried out. Geochemical results show that the seasonal effect does not change the order of abundance of ions. Trend line diagram depicting the linear relationship among various parameters were carried out. Linear relationship is observed at almost all stations between TDS and Cl^- as well as TDS and Na^+ throughout the study area reflecting that the nature and origin of these ions would have come from the same source. In order to study the hydrogeochemical classifications, Piper-Hill diagram is used. During both the monsoon periods, Piper diagram characterizes the water types as NaCl, mixed CaMgCl and $CaHCO_3$. Most of the samples fall in the sodium-potassium zone but the dominance of chloride type of waters was observed among anions. Gibb's diagram clearly demonstrates the dominance of non-geogenic activity responsible for the chemical budget of water. During both the monsoon periods, most of the samples fall away from the three major natural factors viz., Precipitation dominance, rock dominance and evaporation-crystallization dominance indicating that the chemistry of water is decided predominantly by anthropogenic activities. In the study area, the influence of polluted river water to the adjacent aquifer dominates the change in chemical composition of groundwater.

Keywords: Groundwater, Geochemistry, River Noyyal, Water quality.

Introduction

Groundwater exploitation, awareness of its importance with regard to quality, quantity and artificial recharge has increased tremendously, particularly in the field of agricultural, industrial and domestic sectors, since many regions have only insufficient rainfall which is further worsened by the frequent failures and variability in the occurrence of monsoon. Industrial pollution has been and continues to be a major factor causing the degradation of the environment around us, affecting the water, the air and the soil. Of these, the pollution of water is arguably the most serious threat to current human welfare. Water is polluted not only by industries but also by households (Loganathan *et al.*, 2011; Ravichandran & Jayaprakash, 2011; Saravanakumar & Ranjith Kumar, 2011). Both industries and household wastewater contain chemicals and biological matter that impose high demands on the oxygen present in water. Pollution due to the above factors decreases the dissolved oxygen content in the water leading to high biological and chemical oxygen demand. In addition to low levels of dissolved oxygen in water, industrial wastes (effluents) also contain chemicals and metals that are directly harmful to human health and ecosystem.

Geochemical evolution of groundwater and the processes controlling their evolution are of continued importance in the overall study of the hydrologic cycle. Chemical compositions of groundwater reflect the different natural processes that provide chemical elements to the dissolved load, i.e. mainly from weathering of rocks and soils, atmospheric inputs and anthropogenic disturbances. In recent times on account of increase in population, urbanization and industrialization, there is a threat to the quality of water in rivers, lakes and other water bodies (Mohan Raj & Ravichandran, 2010; Dhiviyaa Pranavam *et al.*, 2011). Urban rivers have been associated with water quality problems and the practice of discharging untreated domestic and industrial waste into the water course has emerged to an alarming level (Hall, 1984). Unfortunately, the sanctity attached to rivers does not ensure a concern for the maintenance of the purity of water. In India, Planning of water quality control strategy and standards is not an easy task. The size of the work, multiplicity in agencies involved, political, economic hardship and administrative coordination are some of the major issues. However, to comprehend the extent of problem, it is necessary to control water pollution problems. Many studies were carried out keeping in view of the importance of hydrogeochemistry of groundwater (Tesoriero *et al.*, 2004; Devadas *et al.,* 2007; Möller *et al.*, 2007; Subramani *et al.,* 2010; Ayedun *et al.*, 2011).

The aim of this study is to assess the hydrochemical characteristics of groundwater near River Noyyal which passes through Tirupur, the textile town of South India where the water gets polluted due to the indiscriminate discharge of effluents from industries located in this region. In this work, in order to achieve this objective, the chemistry of groundwater in the proximity of River Noyyal is studied in detail. Such studies contribute to effective management and utilization of the groundwater resource.

Study area

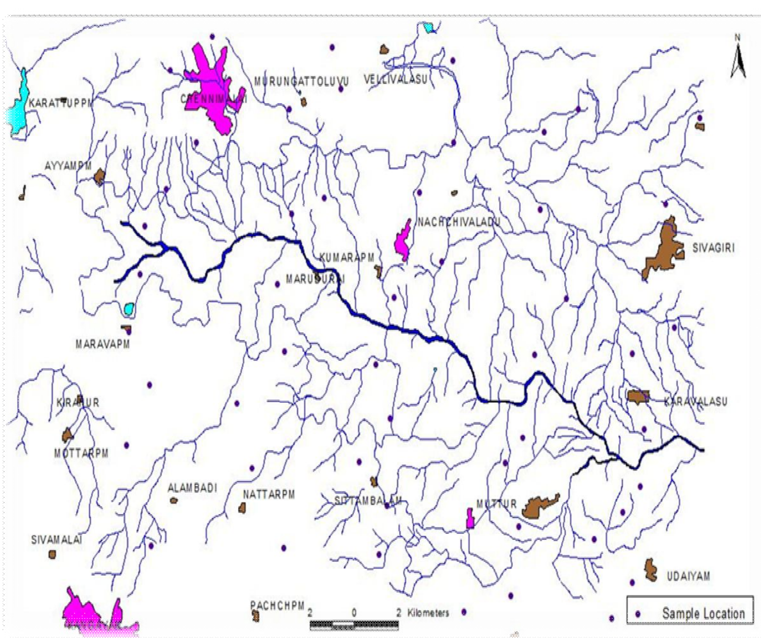
The study area is located in the central part of Tamil Nadu (lat. 11°06'19"N; long. 77°30'14"E and lat.11°03'51"N; long. 77°47'52"E). The region is basically an agricultural area with paddy as the main crop. River Noyyal is a seasonal river and it originates from

Vellingiri Hills in the Western Ghats of Coimbatore District. It flows through Coimbatore, Tiruppur, Erode and Karur districts and finally joins into Cauvery River near Noyyal village. It flows over a distance of 175 kilometers. The catchment area of the river is 3.49 lakh hectares. On both sides of the banks of river Noyyal, more than 100 villages are situated. Noyyal was the major source for irrigation, drinking water and other activities of the people living on both sides of the river and even for people living beyond 3 kms from the river. The industrial effluent released by dyeing and bleaching factories in Tiruppur, a major hosiery centre in South India has become a serious issue because it has severe impact on water bodies. At present there are 1500 Knitting units, 700 Dyeing & Bleaching Units, 500 Fabric Printing, 2500 Garmenting, 250 Embroidery, 300 Compacting and Calendaring and 500 other ancillary units are functioning (Palanivel & Rajaguru, 1999). Many dyeing units in Tiruppur are within a radius of 5 km from the Noyyal River. Dyeing units comes under Red category since they produce hazardous wastes near the natural water resources. Many of the dyeing and bleaching units have continued discharge of their effluents amounting 80 to 100 MLD per day into the River Noyyal after semi-treatment or without treatment.

Materials and method

Fifty groundwater samples were collected during pre-monsoon and post-monsoon seasons in a grid pattern at five selected zones and five samples each at northern and southern part of the river is collected at a distance of about 500m, 1000m, 1500m, 2000m and 2500m from River Noyyal in order to study the level of penetration of polluted water into the aquifer system (Fig.1). Samples were collected during July 2008 (pre-monsoon); December 2008 (post-monsoon); July' 2009 (pre-monsoon) and December' 2009 (post-monsoon). Surface water samples were collected using Aqua trap water sampler. For collection, preservation and analysis of the samples, the standard methods (APHA, 1995) were followed. Electrical conductivity and pH of water samples were measured in the field immediately after the collection of the samples using portable pH and electrical conductivity meters. Na^+ and K^+ were measured by using a flame photometer. Total dissolved solids (TDS) were measured by evaporation and calculation methods (Hem, 1991). Ca^{2+} and Mg^{2+} were determined titrimetrically using standard EDTA. Chloride was estimated by $AgNO_3$ titration. Sulphate was analysed using the turbidimetric method (Clesceri *et al.* 1998). Nitrate was analysed using UV-visible spectrophotometer (Rowell, 1994).

Fig.1. Study area map showing the sample locations



Results and discussion

The statistical parameters of the chemical composition of surface water such as minimum, maximum and mean of groundwater are presented in Table 1 for both premonsoon and postmonsoon. The salient features of the hydrochemistry of the surface water are as follows: The average pH of groundwater during pre-monsoon is 7.81 falling in the alkaline pH range. However, during post-monsoon, the pH of groundwater was also found to be alkaline with a mean value of 7.61. Average concentration of salinity is found to be 1076.97 mg/L in premonsoon and 829.37mg/L in postmonsoon. There is a considerable amount of dilution of concentration of ions during the postmonsoon due to precipitation. Higher concentration of Total Disssolved Solids (TDS) is observed in the groundwater near the polluted river in all the five zones. TDS values decrease away from River Noyyal in both northern and southern part of the river. The infiltration and percolation of river water into the groundwater would have increased the salinity of the adjacent aquifers. As per the TDS classification (Fetter, 1990) most of the groundwater samples collected during premonsoon and post-monsoon periods, upto three levels, namely, groundwater samples at 500m, 1000m and 1500m from River Noyyal belong to brackish type (TDS>1,000 mg/l). The average ionic concentrations (based on mmol/L) of Ca^{2+}, Mg^{2+}, Na^+ and K^+ during pre-monsoon are 10.7, 32.5, 53.5 and 3.2%. The order of abundance is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. During post-monsoon, the average ionic concentration of cations viz., Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions are 28.8, 45.6, 142.5 and 21.9 mg/L respectively. The ionic concentrations (based on mmol/L) are 12.2, 30.5, 53.2 and 4.1%. The order of abundance is $Na^+ > Mg^{2+} > Ca^{2+} > K^+$. Similarly, in the case of anions during pre-monsoon, the average ionic concentration of HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- are 331.2, 124.9, 325.7 and 20.4 mg/L respectively. The ionic concentrations (based on mmol/L) are 31.5, 13.5,

Indian Journal of Science and Technology Vol. 4 No. 12 (Dec 2011) ISSN: 0974- 6846

Table.1. Summary statistics of the physico-chemical parameters

Parameters (mg/L)	Premonsoon (July'2008)			Postmonsoon (Dec'2008)			Premonsoon (July'2009)			Postmonsoon (Dec'2009)		
	Mini	Maxi	Mean	Mini	Maxi	Mean	Mini	Maxi	Mean	Mini	Maxi	Mean
pH	7.40	8.90	7.87	7.30	8.00	7.61	7.40	9.60	7.75	7.40	7.80	7.61
EC (µS/Cm)	672	5975	1851	470	3340	1353	570	4280	1601	580	3690	1300
TDS	415	3693	1157	290	2064	854	362	2645	997	362	2280	805
Ca	20	80	38	13	62	29	11	85	32	10	68	30
Mg	30	338	77	9	120	47	14	160	54	14	110	43
Na	26	665	210	10	443	147	25	634	191	32	572	149
K	7	87	23	7	110	22	3	47	18	6	57	16
HCO_3	145	692	336	78	655	283	125	601	292	101	550	244
CO_3	0	0	0	0	0	0	0	0	0	0	0	0
SO_4	12	570	127	5	205	55	10	195	87	10	334	72
Cl	61	1485	331	25	693	217	28	1023	285	22	809	217
NO_3	4	115	20	5	110	19	4	45	15	7	85	19

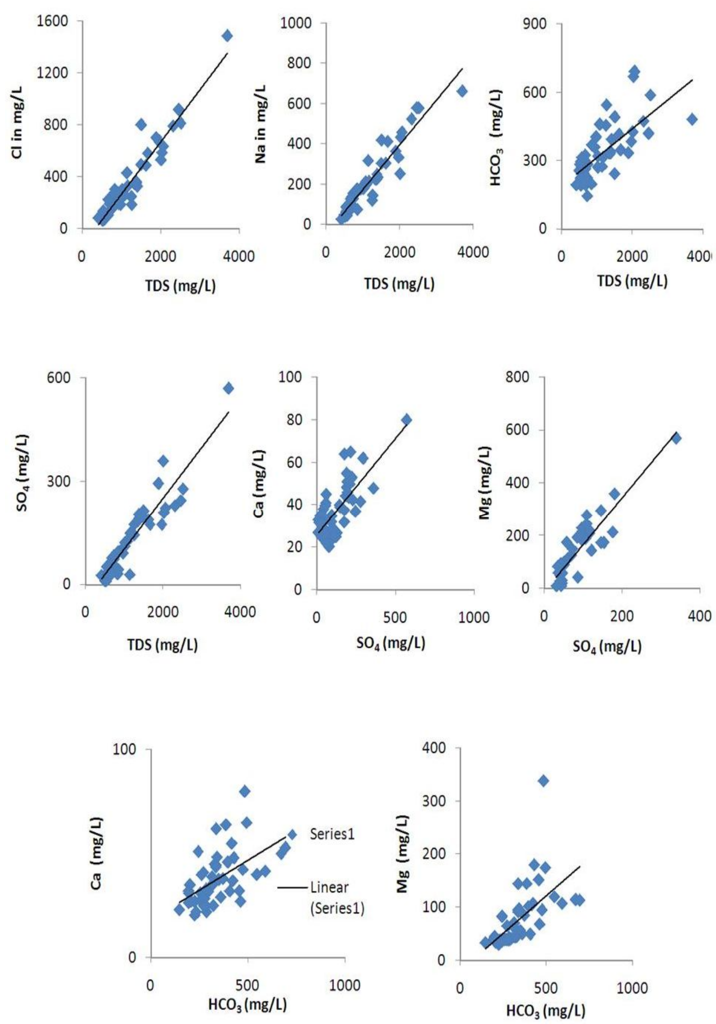
53.2 and 1.7%. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$. During post-monsoon, HCO_3^-, SO_4^{2-} Cl^-, NO_3^- the average concentration of ions are 279.3, 53.6, 210.4, 18.7 respectively. The ionic concentrations (mmol/L) are 35.9, 11.0, 50.7 and 12.5%. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^-$.

Correlation and trend line analysis

The major hydrochemical contributing ions to the groundwater chemical budget are Na^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, and SO_4^{2-}. Cross plots and trend analysis of cations and anions showed fairly good correlations. Correlation co-efficient matrix of both cations and anions with total dissolved solids (TDS) shows significant correlation with certain ions. During pre-monsoon, the average correlation coefficient of 0.85 and 0.96 was observed between TDS and Mg^{2+} and Na^+; 0.77 was observed between Ca and TDS. In the case of anions, average correlation coefficient value of 0.96 was observed between TDS and Cl^-; 0.75 and 0.78 were observed between TDS and HCO_3^- and SO_4^{2-} respectively.

Correlation of postmonsoon is found to follow similar pattern as that of pre-monsoon. Trend line diagram depicting the linear relationship between various parameters are presented in Fig.2. Linear relationship is observed at almost all stations between TDS and Cl^- irrespective of the distance from the polluted riverwater. Similarly, TDS and Na^+ also shows linear relationship throughout the study area which indicates that the nature and origin of these ions would have come from the same source. It was observed from the trend diagrams that HCO_3 does not show much linearity with regard to TDS whereas SO_4^{2-} Vs TDS shows improved linearity suggesting that in addition to hydrochemical changes, other anthropogenic activities, are also responsible for the variation in the chemical budget of the groundwater. Ca^{2+} Vs SO_4^{2-} and Mg^{2+} Vs SO_4^{2-} shows linear

Fig. 2.Trend line diagrams depicting relationship among ions



relationship whereas Ca^{2+} Vs HCO_3^- and Mg^{2+} Vs HCO_3^- shows no linear relationship which clearly indicates that HCO_3^- has different origin from that of other ions. Oxidation of carbon and other organic wastes in the river water would have also increased the HCO_3^- concentration in the groundwater through percolation from the surface water. Ca^{2+}-SO_4^{2-}, Mg^{2+}-SO_4^{2-} shows similar trend in the linear relationship suggesting that much of these ions should have originated from common source especially from rock-water interaction. (Fig.2)

Chloro-Alkaline Indices

The chemical reactions in which ion exchange between the groundwater and aquifer environment occurs during the periods of residence and movement may be understood through study of Chloro - Alkaline Indices (Schoeller, 1977).

CA I = Cl - (Na + K)/Cl and

CA II = (Na + K)/(SO_4 + HCO_3 + CO_3 + NO_3)

The Chloro - Alkaline indices may be positive or negative according to whether exchange of sodium/potassium from rock with magnesium and calcium in water or the reverse.

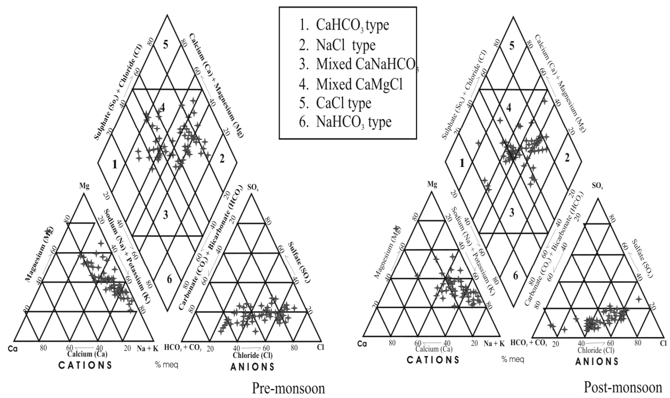
$Na^+ + K^+$ ↔ $Ca^{2+} + Mg^{2+}$
(Water) Reverse (Rocks)

Schoeller (1977) proposed a measure called "Index of Base Exchange" (IBE) to describe the metasomatism taking place in groundwater. There are some underground substances (clay minerals, glauconite, zeolites and organic substances) which can absorb and exchange their cations with cations present in the water. Cation exchange plays an important role in the chemistry of Na and K. The positive ratio of (Cl-(Na + K)/Cl) (Swaine & Schneider, 1971) in the groundwater of the study area shows the probability of exchange of Ca - Mg (water) by Na -K (mineral).

Classification of water types

Piper-Hill diagram is used to infer hydro geochemical facies (Piper, 1953). These are recognizable parts of different characters belonging to any genetically related system. Hydrochemical facies are distinct zones that possess cation and anion concentration categories. Chemical data of the study area are presented in Fig.3 by means of piper trilinear diagram for premonsoon and postmonsoon. During premonsoon (July, 2008), considerable portion of samples fall in the sodium-potassium zone of the diagrams but the dominance of chloride type of waters was observed among anions

Fig.3. Piper diagram representing hydrochemical focies



followed by bicarbonate type. Majority of the sample falls in the category of Na-Cl (52.88%) followed by Ca - Mg - Cl (26.9%), Ca - HCO_3 (21.2%) and none in the Ca - Na - HCO_3 as shown in the cation-anion graph (Fig.3). Similar pattern is observed for the pre-monsoon period of July' 2009 with regard to the cationic and anionic phase. Hydrochemical type during postmonsoon period is Na - Cl (52.14%) followed by Ca - Mg - Cl (27.85%), Ca - HCO_3 (20.17%) and none in the Ca - Na - HCO_3. (Fig.3)

Mechanism controlling groundwater chemistry

Geo-environmental conditions have a marked influence on groundwater quality. Hydrogeochemical studies relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to elucidate the factors controlling groundwater chemistry (Rengarajan & Balasubramanian, 1990). It is a generally accepted fact that there is a close relationship between water composition and aquifer (Gibbs, 1970). Gibbs proposed a method where the rock-water interaction, precipitation or evaporation are identified and quantified. The source of the dissolved ions in the groundwater can be understood by Gibbs diagram (Gibbs, 1970). It is a plot of $(Na^+ + K^+)/(Na^+ + K^+ + Ca^{2+})$ Vs TDS and Cl/(Cl + HCO_3) Vs TDS. The mechanisms responsible for controlling the groundwater chemistry of the study area by using Gibbs's ratio have been represented in Table.2.

It is interesting to note that the results show a different phenomena is responsible for the chemical budget of this water since majority of the values during both the monsoon periods concentrated away from the three major factors, namely, precipitation dominance, rock-water interaction and evaporation-crystallization Fig.4.

Table 2. Seasonal variation of indices and ratios

Parameters	Premonsoon (July'2008)			Postmonsoon (Dec'2008)			Premonsoon (July'2009)			Postmonsoon (Dec'2009)		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
CA	0.55	41.19	8.22	-2.44	18.42	4.90	-1.93	27.86	6.79	-2.51	21.70	4.87
CA II	0.34	2.72	1.08	0.24	2.01	1.05	0.29	2.71	1.19	0.41	2.12	1.14
Gibbs ratio II	0.46	0.94	0.79	0.53	0.96	0.82	0.61	0.95	0.82	0.43	0.97	0.83
Gibbs ratio II	0.26	0.84	0.56	0.16	0.77	0.52	0.16	0.84	0.56	0.16	0.77	0.56

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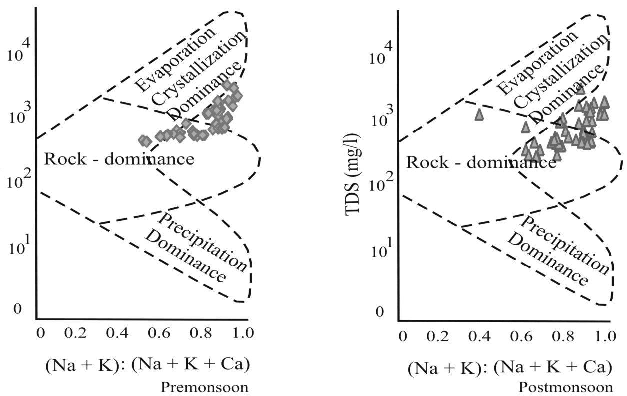
Fig.4. mechanism controlling groundwater chemistry



This clearly demonstrates that apart from the natural source, artificial factor, namely, anthropogenic activity decides and dominates the change in chemical composition of groundwater (Hem, 1991; Karanth, 1997). It could be said that rock-water interaction has some contribution to the chemical budget of this water.

Conclusions

The hydrogeochemical study of groundwater near River Noyyal provides the following conclusions: Elevated values of TDS are observed in the groundwater near the polluted river in all the five zones. TDS values were found to decrease in wells existing far away from River Noyyal in both northern and southern part of the river. Trend line analysis show that in addition to hydrochemical changes, other anthropogenic activities, are also responsible for the variation in the chemical budget of the groundwater. Non-linear relationship of HCO_3^- with alkaline metal ions reveals that it has different origin from that of other ions. Piper diagram characterizes the water types as NaCl, mixed CaMgCl and $CaHCO_3$ during both the monsoon periods. Gibb's diagram clearly reveals that the major factor affecting the chemical budget of water is due to anthropogenic activities in addition to rock-water interaction.

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