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Evolution of Hydrochemical Parameters and Quality Assessment of Groundwater in Tirupur Region, Tamil Nadu, India

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ABSTRACT: Groundwater is the most widely distributed resource of the Earth and groundwater quality evolves rapidly as it passes through the subsurface pathways within the unsaturated zone. Increasing urbanization and anthropogenic activities have added to the problem of deficient amount of good quality groundwater. The study area is an industrial hub for textile sector. Textile production, particularly dyeing and bleaching, is essentially water intensive and so it generates large quantities of effluents and the practice of discharging untreated industrial waste into the river courses. To assess the evolution of hydrochemistry and quality, sixty two groundwater samples were collected and analyzed for the physicochemical factors such as pH, EC, TDS, TH, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, CO_3^{2-}, Cl^{-}, NO_3^{-}, SO_4^{2-} and F^{-} during the pre-monsoon period of (June-July) 2006, 2008 and 2011. By using Piper trilinear diagram, hydro chemical facies were identified. Gibb's diagram suggests that the chemical weathering of rock-forming minerals and evaporation influence the groundwater quality. The study area was evaluated for the parameters: Sodium Adsorption Ratio, Residual Sodium Carbonate, Salinity and Permeability Index. Interpretation of these hydro chemical parameters indicates that the groundwater in most of the locations in the study area is not suitable for drinking purpose and for irrigation. However, permeability index values indicate that most all the groundwater samples are suitable for irrigation purpose.

Key words: Evolution of hydrogeochemistry, Gibb's diagram, Permeability Index,Tirupur, India

INTRODUCTION

Water is the most important natural resource and it is vital for all life forms on earth. Depending on its usage and consumption, it can be a renewable or a non-renewable resource. Groundwater is an important source of water supply throughout the world. Among the various reasons, the most important is the non-availability of potable surface water. (Pichiah *et al.,* 2013). There is a general belief that groundwater is purer and safer than surface water due to the protective qualities of the soil cover. The quality of groundwater is controlled by several factors including climate, soil characteristics, rock types, topography of the area, human activities on the ground etc (Rajesh *et al.,* 2002; Cloutier et al 2008; Prasanna *et al.,* 2010). The eco-system and natural resources are faced with the twin pressure of population and industrial development, resulting in the depletion and deterioration of the natural resources at an alarmingly fast rate. Unchecked effluents and emissions from hazardous industries caused pollution of water, air and soil resulting in great health hazards to the humans. Due to rapid industrialization and subsequent contamination of surface and groundwater sources, water conservation and water quality management have a very complex shape now days.

Water quality refers to the physical, chemical and biological characteristics of water (Santhosh and Revathi 2014). The hydro chemical processes and hydrogeochemistry of the groundwater vary spatially and temporally, depending on the geology and chemical characteristics of the aquifer. Hydro geochemical processes such as dissolution, precipitation, ion exchange processes and the residence time along the flow path control the chemical composition of groundwater (Nwankwoala and Udom 2011). The time available for water-rock interactions, and hence the chemical composition of water, strongly varies depending on the flow path and storage location of the water. The flow path and residence time also

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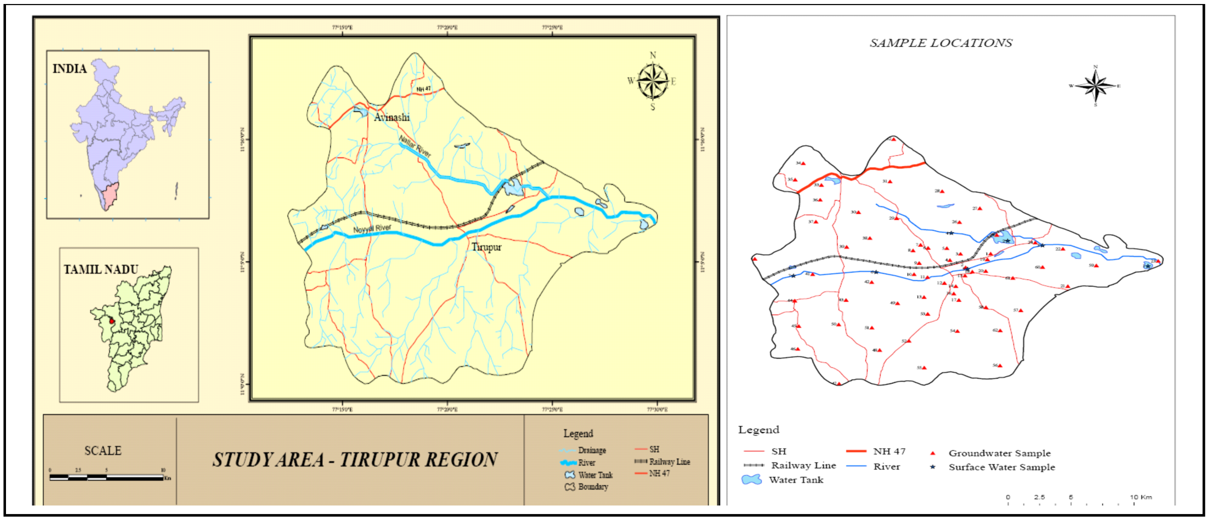

Fig. 1. Study area and the sample locations

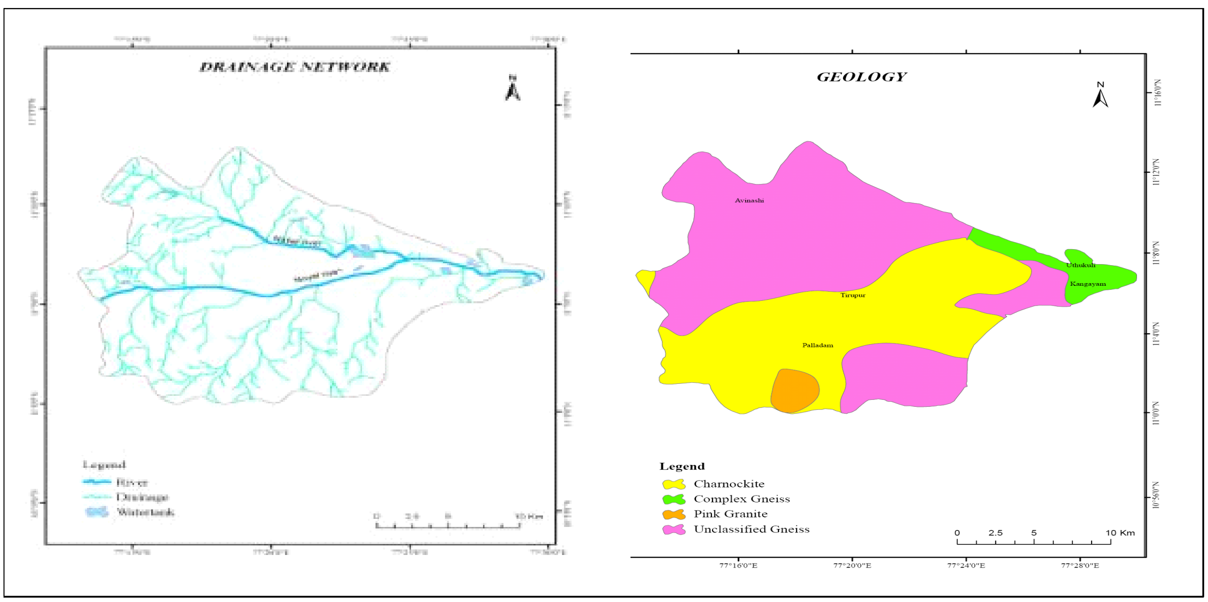

Fig. 2. Drainage network and geology of the study area

influence the contaminant fate (Sadek Younes 2012). The frequent failures of monsoon, increasing urbanization and anthropogenic activities have added to the problem for the requirement of sufficient quantum of good-quality water. Increased knowledge of geochemical processes regulating the groundwater chemical constituents will help to understand the hydrochemical systems for effective management and utilization of the groundwater resource by clarifying relations among groundwater quality and quantifying any future quality changes (Srinivasamoorthy *et al.*, 2014). The main objectives in the study are assessment of groundwater chemistry, determination of the anthropogenic factors that presently affect the water chemistry in the region and identification of the main geochemical processes controlling the groundwater in the study area in course of time. The study area lies between latitudes 11^{0}00'00"N and 11^{0}13'30"N and longitudes 77^{0}12'00"E and 77^{0}29'30"E (Fig. 1) with geographical extent of 450 km^2. The study area is characterized by an undulating terrain with the height ranging between 290 and 322 meter above the mean sea level and sloping gradually from west to east direction. Temperatures vary between 20^{0}C and 35^{0}C. The area receives scanty rains due to its location in leeward side of the Western Ghats with average annual rainfall of 640 mm. The Noyyal river runs all across the study area, almost dividing it into two halves and it passes through Tirupur, Avinashi and Palladam taluks. The river has been associating with water quality problems and the practice of discharging untreated industrial waste into the river course has been alarmed. Tirupur is an industrial hub for textile sector in India. The textile industries use synthetic organic dyes like yarn due, direct due, basic due, cat dye, sulfur dye, reactive dye and developed dye. The use of dye stuffs has become increasingly a subject of environmental concern. The large variety of chemicals used in textile process renders them very complex. The quality of groundwater in Tirupur region has been worsening rapidly during the last decade. Textile processing units in Tirupur use a number of chemical that are likely to be from the red list group which is said to be harmful and unhealthy. Groundwater quality depletion by industrial and anthropogenic activities such as urbanization is a major hitch in the study area.

Dentritic drainage network reflects the characteristic of surface as well as subsurface formation in the study area. Geologically, the area is underlain by a wide range of high-grade metamorphic rocks of peninsular gneissic complex (Fig. 2). These rocks are extensively weathered and overlain by recent valley fills and alluvium at places. The most common rock type of the area is unclassified gneiss (hornblende-biotite-gneisses), pink granite, complex gneiss charnockite and limestone deposits (Arumugam and Elangovan 2010).

MATERIALS & METHODS

Groundwater samples from sixty two locations were collected during pre-monsoon periods of 2006, 2008 and 2011 from the study area. The sample locations were selected to cover the entire study area and the attention was given to Tirupur town where pollution is expected. So, about one third of the groundwater sample locations are within Tirupur municipal area and the rest of the sampling stations are in parts of Avinashi and Palladam taluks. For analysis, all the instruments were calibrated appropriately according to the commercial grade calibration standard prior to the measurements. The samples were analyzed for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}) , bicarbonate (HCO_3^-) , chloride (Cl^-), carbonate (CO_3^{2-}), nitrate (NO_3^-), sulphate (SO_4^{2-}), and fluoride (F^-) using the standard methods given by the American Public Health Association (APHA 1995). The results were evaluated in accordance with the drinking water quality standards (Table 1) given by the World Health Organization (WHO 1993) and Indian Standard Institution (ISI 1983).

The solution should be electrically neutral. But they are seldom equal in practice. The inequality increases as the ion concentration increases (Janardhana Raju 2006). The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors are generally around 10% (Subramani *et al.*, 2005).

RESULTS & DISCUSSION

Quality of groundwater gives a clear picture about the utility of water for different purposes. The major factor which decides the quality of its groundwater in the study area is textile industrial processes and anthropogenic activities in most part of the study area. The water quality may yield information about the

Table 1. Drinking water specifications given by ISI (1983) and WHO (1993) and summary of physicochemical parameters of groundwater samples

Water quality parameters	Indian Standard Institution (1983)		WHO (1993)	
	Highest desirable	Maximum permissible	Highest desirable	Maximum permissible
pH	6.5-8.5	6.5-9.2	7-8.5	6.5-9.5
TDS (mg/l)	500	1,500	500	1,500
TH as $CaCO_3$ (mg/l)	300	600	100	500
Ca^{2+} (mg/l)	75	200	75	200
Mg^{2+} (mg/l)	30	100	50	150
Na^{+} (mg/l)	-	-	-	200
K^{+} (mg/l)	-	-	-	12
HCO_3^- (mg/l)	-	300	-	-
Cl^- (mg/l)	250	1,000	200	600
NO_3^- (mg/l)	-	-	45	-
SO_4^{2-} (mg/l)	150	400	200	400
T.Alk (mg/l)	300	600	-	-
F^- (mg/l)	0.6	1.2	-	1.5

Table 2. Physicochemical parameters of groundwater samples

Parameters	During - (2006)				During - (2008)				During - (2011)			
	Min.	**Max.**	**Mean**	**Median**	**Min.**	**Max.**	**Mean**	**Median**	**Min.**	**Max.**	**Mean**	**Median**
Turbidity (NTU)	2	18	6.65	6	0	38	7.58	6	0	18	6.40	6
EC (µS/cm)	623	5,738	2,018	1,800	309	5,950	1,809	1,410	847	9,930	2,733	2,239
pH	7.30	8.25	7.70	7.65	7.07	8.85	7.68	7.60	6.60	8.01	7.56	7.58
TDS (mg/l)	399	3,672	1,292	1,152	198	5,119	1,164	903	543	5,990	1,764	1,450
TH [&] (mg/l)	192	956	460	476	114	2,558	696	560	212	3,600	777	625
Ca^{2+} (mg/l)	35	288	106	94	15	1,023	149	109	28	913	166	122
Mg^{2+} (mg/l)	13	107	51	52	0	319	75	72	0	480	92	73
Na^{+} (mg/l)	24	720	181	136	8	220	89	88	24	1,120	224	157
K^{+} (mg/l)	7	224	67	56	1	91	23	14	7	269	67	51
HCO_3^- (mg/l)	129	733	347	353	53	650	186	266	138	787	411	396
CO_3^{2-} (mg/l)	0	312	58	42	0	243	32	27	0	280	51	27
Cl^- (mg/l)	31	1,092	334	263	18	2,249	360	226	34	3,190	546	394
NO_3^- (mg/l)	6	520	79	51	0	125	34	30	0	569	77	58
T.Alk (mg/l)	160	630	365	352	115	695	401	395	209	731	434	428
SO_4^{2-} (mg/l)	4	382	86	62	0	427	79	52	0	1,210	159	98
F^- (mg/l)	0	2	0.90	0.80	0	1.00	0.40	0.40	0	2.10	0.70	0.60
SAR*	0.87	14.36	4.72	4.49	0.34	5.8	2.09	2.18	0.6	22.1	6.6	5.2
RSC@	-8.48	5.5	-1.24	-0.96	-61.74	6.07	-46.33	-3.73	-66.7	2.8	-0.12	-4.2
Na+K (%)	12.9	71.5	48	50.9	3.8	67.7	30.3	28.9	4	72	43.60	46
PI ? (%)	34.88	80.4	63.12	65.13	7.62	84.47	45.73	43.32	5.5	73.9	49.3	52.35

& TH – Total Hardness; *SAR –Sodium Adsorption Ratio; @RSC–Residual Sodium Carbonate; PI:& Permeability Index

environments through which the water has circulated (Janadhana Raju 2006). The hydrochemistry of groundwater of the parameter analysis and the statistical parameters such as minimum, maximum, mean and median are given in Table 2. The pH values of groundwater ranges from 6.60 to 8.50 with an average value of 7.65. This reveals that the groundwater of the study area is mainly of alkaline in nature (Aarumugam and Elangovan 2009). However, in all the locations of the pH of the groundwater samples are within safe limits. EC is a good measure of salinity hazard to plants as it reflects the total dissolved solids in groundwater (Karanth 1987) and the values ranges from 309 to 9,930 µS/cm with an average value of 2,187 µS/cm. Higher values are generally noticed near the Noyyal and Nallar river courses and concentration is found to be high in down stream side of the study area. To ascertain the suitability of groundwater for any purpose, it is essential to classify the groundwater depending upon its hydrochemical properties based on Total Dissolved Solids (TDS) values (Davis and DeWiest 1966; Freeze and Cherry 1979). Total dissolved solids of groundwater samples have ranges from 399 to 3,672 mg/l with the average values of 1,292 mg/l, 198 to 5,119 mg/l with the average values of 1,164 mg/l and 543 to 5,990 mg/l with the average values of 1,764 mg/l during 2006, 2008 and 2011 respectively.

The overall assessments of mean and median values are 1,407 mg/l and 1,168 mg/l respectively. This indicates that the water in the study area is unfit for drinking purpose. The study reveals that 8.06, 33.87, 56.45 and 1.61% of the samples come under the categories desirable for drinking; permissible for drinking; useful for irrigation and unfit for drinking and irrigation respectively during 2006, while 12.9, 40.32, 43.55 and 3.23% of the samples are under the categories desirable for drinking; permissible for drinking; useful for irrigation and unfit for drinking and irrigation respectively during the year 2008. Conversely, samples of 22.58, 66.13 and 11.29% are enveloped under the categories permissible for drinking, useful for irrigation and unfit for drinking and irrigation respectively during the year 2011. 22.58 to 40.32 % of the groundwater is belonging to fresh water type (Table 3) and 46.77 to 77.42% of the sample locations represent brackish water type (Freeze and Cherry 1979). The spatial variation of TDS is represented in Fig. 3. The study points out that only 8 to 13% of the samples can be used for drinking purpose without any risk during 2006 and 2008. However, all the samples appeared above the desirable limit of 500 mg/l belong 2011. Hydrochemical facies of groundwater depends on lithology, resident time and regional flow pattern of water (Jamshidzadeh and Mirbagheri 2011).

The major ion concentration of groundwater sample had been used to classify groundwater into various types based on dominant cations and anions. Most of the graphical methods had been designed to simultaneously represent the total dissolved solid

Table 3. Groundwater classification based total dissolved solids

Groundwater classification (after Freeze and Cherry 1979)					Groundwater classification (after Davis and DeWiest 1966)				
		Percentage of samples					Percentage of samples		
TDS (mg/l)	Classification	During - (2006)	During - (2008)	During - (2011)	TDS (mg/l)	Classification	During - (2006)	During -(2008)	During -(2011)
< 1,000	Fresh water type	40.32	53.23	22.58	< 500	Desirable for drinking	08.06	12.9	-
1,000 - 10,000	Brackish water type	59.68	46.77	77.42	500 - 1,000	Permissible for drinking	33.87	40.32	22.58
> 100,000	Saline water type	-	-	-	> 1,000	Unfit for drinking	58.07	46.78	77.42

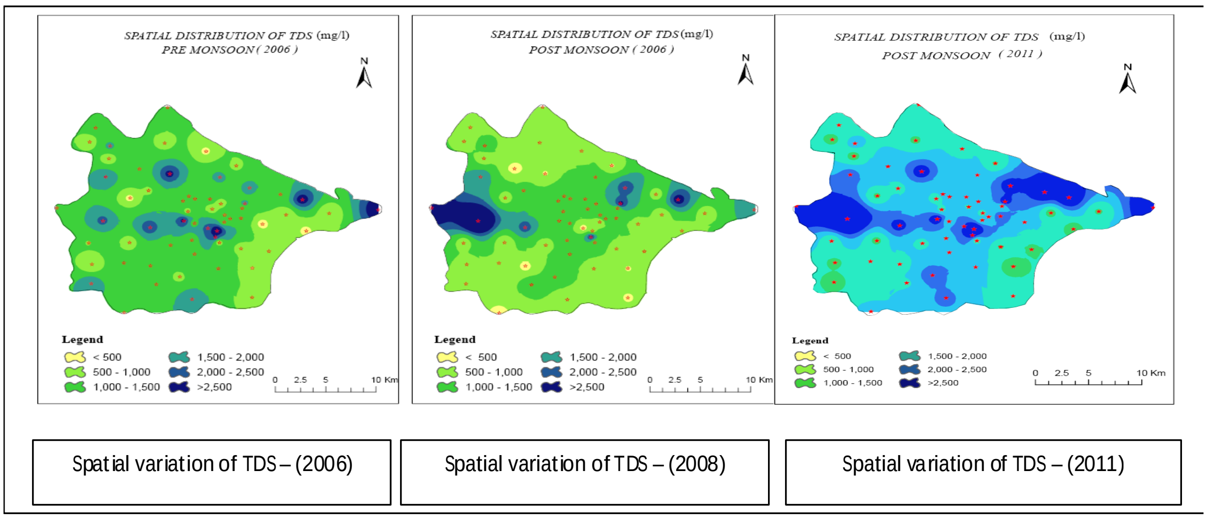

Fig. 3. Spatial variation of total dissolved solids (mg/l) of groundwater samples

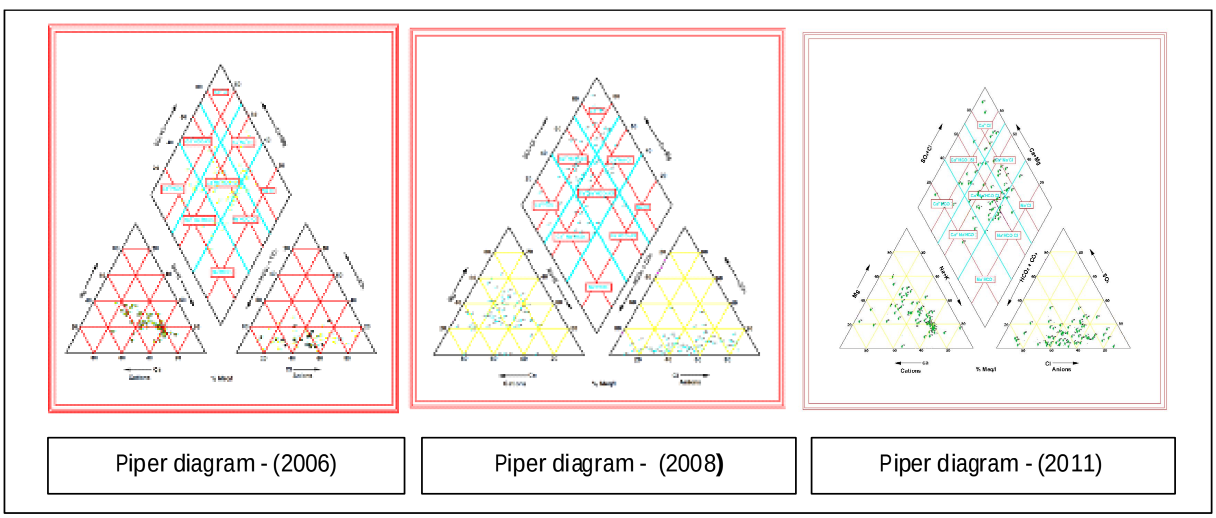

Fig. 4. Piper diagram depicting hydrochemical facies of groundwater

concentration and the relative proportions of certain major ionic species (Hem 1989). The piper diagram (Piper 1944) is the most widely used graphical form to understand the problem concerning the geochemical evolution of groundwater. It resembles in many ways the diagram proposed by Hill (Hill 1940). In that diagram, the percentage equivalents per mole (epm) values of the major ions were plotted on cation and anion triangles, and then the locations were projected to a point on a quadrilateral representing both cations

Table 4. Classification of groundwater based on chemical characteristics (Piper 1994)

Water types	Percentage of samples During - (2006)	During - (2008)	During - (2011)
Ca Na HCO_3 Cl	38.71	17.74	30.65
Na HCO_3Cl	17.74	01.61	12.90
Ca HCO_3	12.90	08.06	04.84
Ca Na Cl	11.29	08.06	14.52
Na Cl	06.45	-	04.84
Ca Na HCO_3	06.45	14.52	04.84
Ca HCO_3 Cl	03.23	30.65	14.52
Na HCO_3	03.23	-	01.61
Ca Cl	-	19.35	11.29

Table 5. Relative abundance of major cations and anions for groundwater samples

Cations	Percentage of samples During - (2006)	During - (2008)	During - (2011)	Anions	Percentage of samples During - (2006)	During - (2008)	During - (2011)
Na>Ca=K>Mg	40.32	09.68	30.65	HCO_3>Cl>SO_4> NO_3	37.10	20.97	24.19
Na>Ca>Mg=K	17.74	24.19	24.19	HCO_3>Cl>NO_3> SO_4	25.81	32.26	20.97
Ca>Na>Mg>K	14.52	30.65	11.29	Cl>HCO_3>SO_4 > NO_3	20.97	38.71	25.81
Na>K>Ca>Mg	14.52	01.61	09.68	Cl>HCO_3>NO_3>SO_4	12.90	01.61	11.29
Ca>Na>K>Mg	08.06	03.23	01.61	NO_3>HCO_3>Cl>SO_4	01.61	-	-
Ca>Mg>Na>K	04.84	25.81	12.90	HCO_3>NO_3> Cl> SO_4	01.61	01.61	01.61
Mg>Ca>Na>K	-	04.84	03.23	HCO_3>SO_4> Cl> NO_3	-	03.22	06.45
Na>Mg>Ca>K	-	-	04.84	Cl> SO_4>HCO_3> NO_3	-	01.61	08.06
Mg>Na>Ca>K	-	-	01.61	SO_4>Cl> HCO_3> NO_3	-	-	01.61

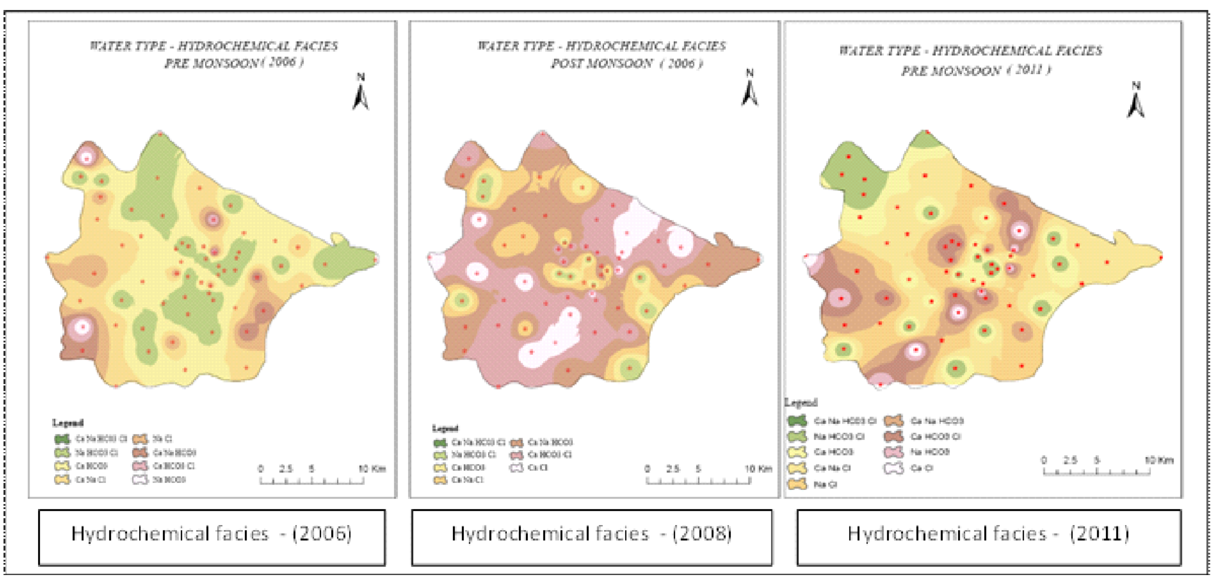

Fig. 5. Hydrochemical facies of groundwater

and anions. The central diamond-shaped field was used to show the overall chemical character of the groundwater (Deutsch 1997). Fig. 4 shows the plot for the sixty two groundwater samples on the piper diagram for 2006, 2008 and 2011. The water types with their distribution during 2006 are calcium, sodium, bicarbonate, chloride type (Ca Na HCO_3 Cl), sodium, bicarbonate, chloride type (Na HCO_3 Cl), sodium, chloride type (Na Cl), calcium, sodium, chloride type (Ca Na Cl), calcium, bicarbonate, chloride (Ca HCO_3

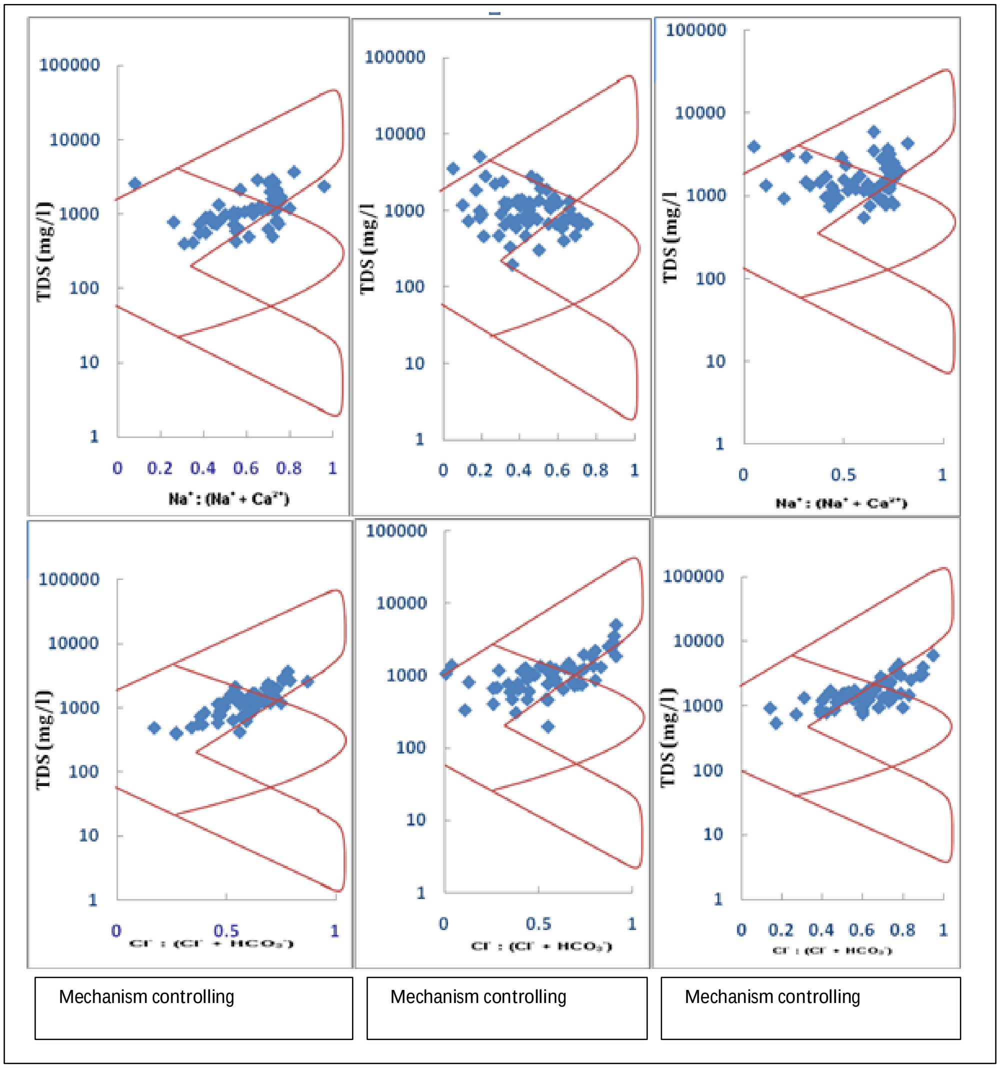

Fig. 6. Mechanism controlling groundwater quality (after Gibbs 1970)

Table 6. Groundwater classification based on total hardness (Sawyer and Mc Cartly 1967)

TH as $CaCO_3$ (mg/l)	Classification	Percentage of samples		
		During - (2006)	During - (2008)	During - (2011)
< 75	Soft	-	-	-
75 – 150	Moderately high	-	01.61	-
150 – 300	Hard	19.35	08.06	6.45
> 300	Very hard	80.65	90.32	93.55

Cl) type, calcium, bicarbonate type (Ca HCO_3), calcium, sodium, bicarbonate type (Ca Na HCO_3) and sodium, bicarbonate (Na HCO_3) type. The water types with their distributions during 2008 are calcium, sodium, bicarbonate, chloride type (Ca Na HCO_3 Cl) , sodium, bicarbonate, chloride type (Na HCO_3 Cl), calcium, sodium, chloride type (Ca Na Cl), calcium, bicarbonate, chloride (Ca HCO_3 Cl) type, calcium, bicarbonate type (Ca HCO_3), calcium, sodium, bicarbonate type (Ca Na HCO_3) and calcium, chloride type (Ca Cl). During 2011, the water types are: calcium, sodium, bicarbonate, chloride type (Ca Na HCO_3 Cl), sodium, bicarbonate, chloride type (Na HCO_3 Cl), calcium, bicarbonate type (Ca HCO_3), calcium, sodium,

Table 6. Groundwater classification based on total hardness (Sawyer and Mc Cartly 1967)

TH as $CaCO_3$ (mg/l)	Classification	Percentage of samples During - (2006)	During - (2008)	During - (2011)
< 75	Soft	-	-	-
75 – 150	Moderately high	-	01.61	-
150 – 300	Hard	19.35	08.06	6.45
> 300	Very hard	80.65	90.32	93.55

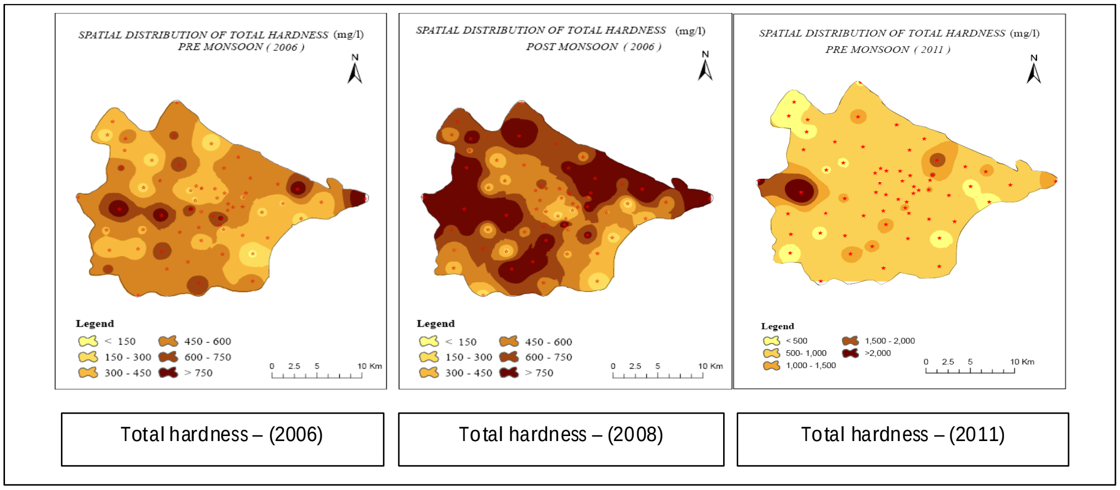

Fig. 7. Spatial distribution of total hardness

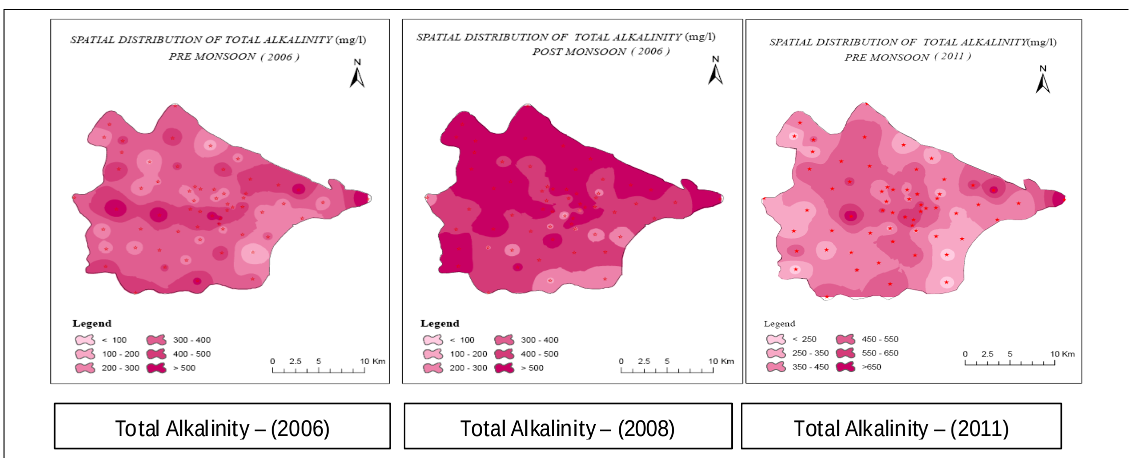

Fig. 8. Spatial distribution of total alkalinity

chloride type (Ca Na Cl), sodium, chloride type (Na Cl), calcium, sodium, bicarbonate type (Ca Na HCO_3), calcium, bicarbonate, chloride (Ca HCO_3 Cl) type, sodium, bicarbonate (Na HCO_3) type and calcium, chloride type (Ca Cl). CaCl type of water formed instead of Na HCO_3 and NaCl during 2008. However, nine water types are formed during 2011. They are illustrated in Table 4.

The spatial distribution of hydrochemical facies are shown in Fig. 5. One of the most interesting aspects of hydrochemistry is the occurrence of water bodies with different water chemistry in very close proximity to each other. This has been variously attributed to the subsurface geology (Offiong and Edet 1998). Within the study area water bodies identified on the basis of relative abundance of major cations and anions are presented in Table 5. Gibb's diagram represents the ratio of Na^+ : (Na^+ + Ca^{2+}) and Cl^- : (Cl^- + HCO_3^-) as a function of total dissolved solids. It is widely used to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation-dominance (Gibbs 1970). The chemical data of groundwater samples of the study area is plotted in Gibbs's diagram (Fig. 6). The distribution

Table 7. Groundwater samples of the study area exceeding the standard regarding total alkalinity

Total alkalinity	Percentage of samples		
	During - (2006)	During - (2008)	During - (2011)
Exceeding the desirable limit	62.90	77.42	75.81
Exceeding the maximum limit	03.22	06.45	11.29

Table 8. Groundwater samples of the study area exceeding the standard regarding fluoride

Fluoride	Percentage of samples		
	During - (2006)	During - (2008)	During - (2011)
% of samples within desirable limit (0.6-1.2 mg/l)	64.52	32.26	32.26
% of samples exceeding limit (< 0.6 mg/l)	16.13	67.74	53.23
% of samples exceeding the maximum limit (> 1.2 mg/l)	19.35	-	14.51

of sample points suggests that the chemical weathering of rock-forming minerals and evaporation influence the groundwater quality. Evaporation increases salinity by increasing sodium and chloride in relation to the increase of total dissolved solids. Semi-arid climate, gentle slope, lack of good drainage conditions and longer residence time of groundwater also contribute to the groundwater quality (Subba Rao 2006). Evaporation greatly increases the concentration of ions formed by chemical weathering, leading to higher salinity. Kankar forms from evaporation activity. As a result the water samples point moves from the zone of rock-dominance towards the zone of evaporation-dominance. Semi-arid climate also tends to evaporation-dominance of groundwater systems. The quality of groundwater in the study area is highly influenced by textile industrial activities and anthropogenic contamination. The major portion of total hardness is caused by calcium and magnesium ions and plays role in heart disease in human. The TH of the groundwater was calculated using the formula as given below (Sawyer and McCartly 1967).

$$TH\left(asCaCO_3\right) mg/l = \left(Ca^{2+} + Mg^{2+}\right) meq/l \times 50 \qquad (1)$$

For total hardness the most desirable limit is 80-100 mg/l (Freeze and Cherry 1979). Groundwater exceeding the limit of 300 mg/l is considered to be very hard (Sawyer and McCartly 1967). In the study area 6.45 to 19.35 % of the samples fall in the water type of hard and 80.65 to 93.55% belong to very hard type (Table 6). TH ranges from 114 to 3,600 mg/l with an average value of 644 mg/l. Twenty seven samples surpass the maximum allowable limit of 500 mg/l during 2006, 39 samples exceed 500 mg/l during 2008 and 46 samples exceed 500 mg/l during 2011. This study proves that the continuous discharge of untreated effluents from the textile dyeing units in the study area. The spatial distribution of TH is shown in Fig. 7.

During 2006, the concentration of cations Ca^{2+}, Mg^{2+}, Na^+, and K^+ ions ranged from 35 to 288, 13 to 107, 24 to 720 and 7 to 224 mg/l with a mean of 106, 51, 181 and 67 mg/l respectively. The order of abundance is $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$. But during 2008, the concentration of cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions ranged from 15 to 1,023, 0 to 319, 8 to 220 and 1 to 91 mg/l with a mean of 149, 75, 89 and 23 mg/l respectively. The order of abundance is $Ca^{2+} > Na^+ > Mg^{2+} > K^+$. During 2011, the concentration of cations Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions ranged from 28 to 913, 0 to 480, 24 to 1,120 and 7 to 269 mg/l with a mean of 166, 92, 224 and 67 mg/l respectively. The order of abundance is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. By the effect on monsoon, the order of abundance of cations changes all major ions. Similarly, in the case of anions during 2006, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and CO_3^{2-} ranged from 129 to 733, 4 to 382, 31 to 1,092, 6 to 520 and 0 to 312 mg/l with a mean of 398, 86, 334, 79 and 58 mg/l respectively. The order of dominance is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^- > CO_3^{2-}$. During 2011, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and CO_3^{2-} ranged from 53 to 650, 0 to 427, 18 to 2,249, 0 to 125 and 0 to 243 mg/l with a mean of 186, 79, 360, 34 and 32 mg/l respectively. The order of abundance is $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > CO_3$. During 2011, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and CO_3^{2-} ranged from 138 to 787, 0 to 1,210, 34 to 3,190, 0 to 569 and 0 to 280 mg/l with a mean of 411, 161, 546, 77 and 51 mg/l respectively. The order of dominance indicated $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > CO_3^{2-}$. Fluoride varies from 0 to 2, 0 to 1.0 and 0 to 2.10 mg/l with an average value of 0.9, 0.4 and 0.70 mg/l during 2006, 2008 and 2011 respectively.

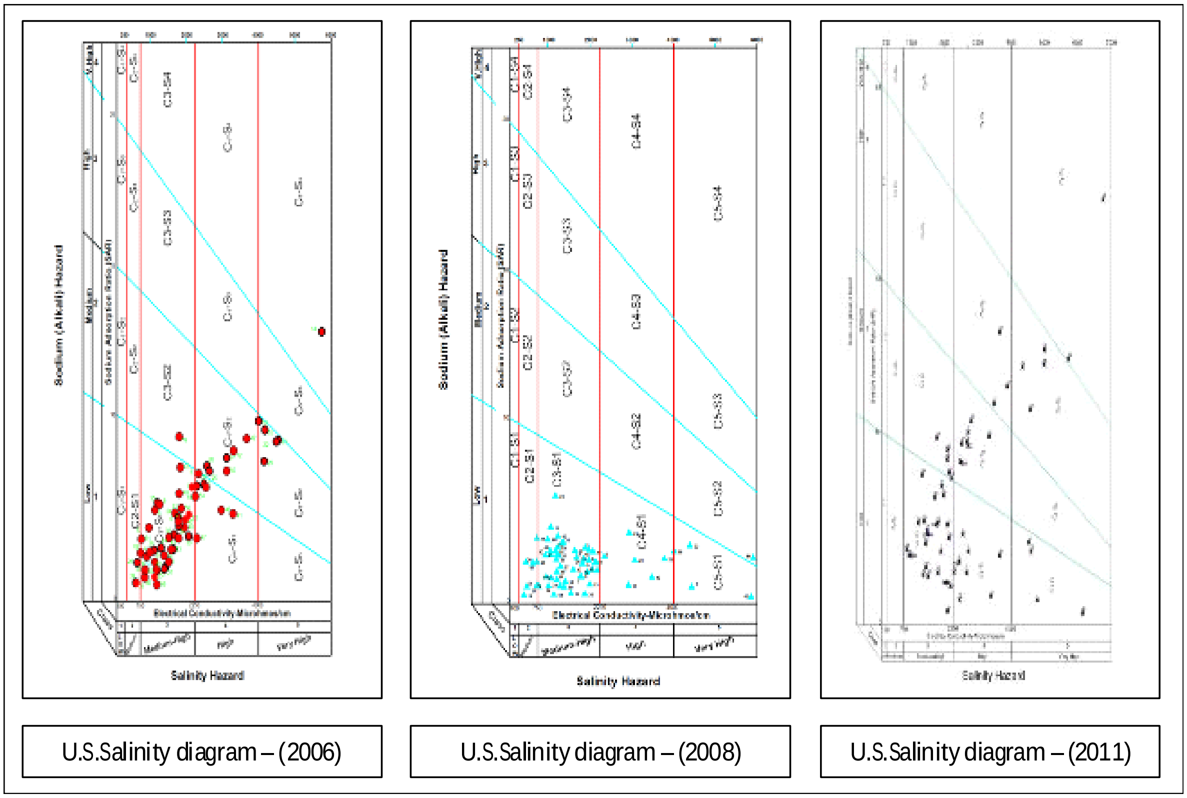

Fig. 9. Salinity and alkalinity hazard of irrigation water in US Salinity diagram (US.Salinity Laboratory Staff 1954)

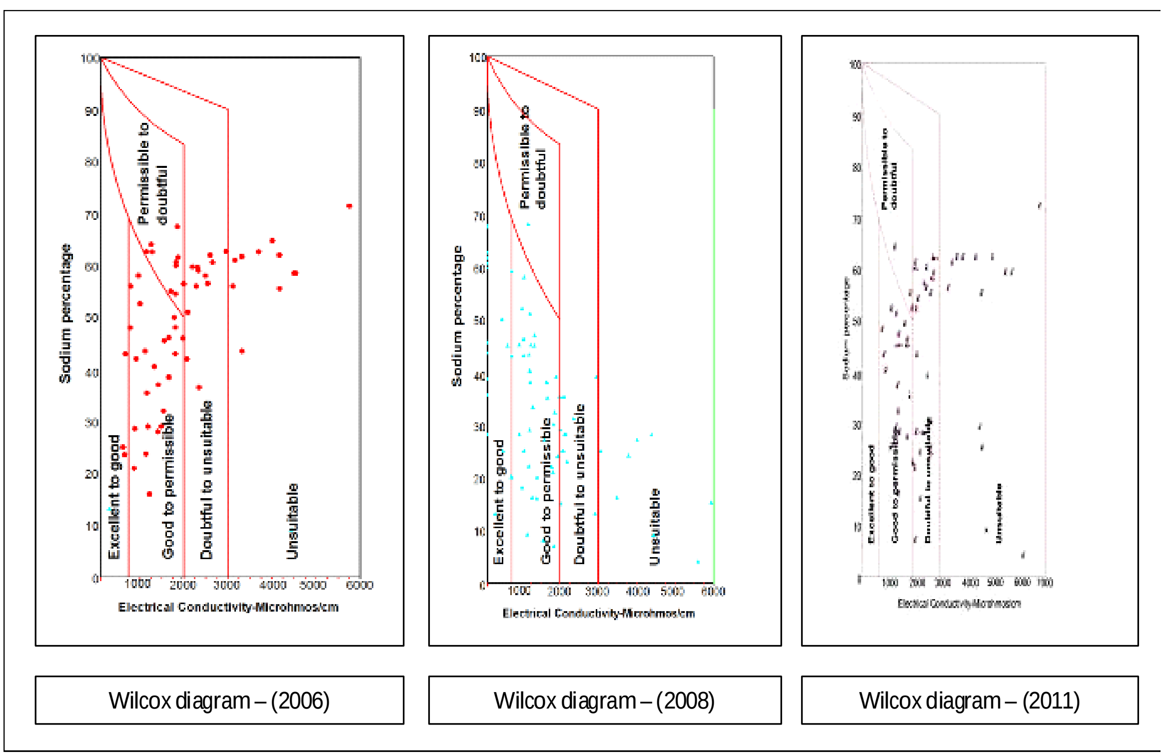

Fig. 10 .Suitability of groundwater for irrigation in Wilcox diagram

Table 9. Distribution of groundwater samples (%) for irrigation, according to U. S. Salinity Laboratory's

Classification			Percentage of samples		
			During - (2006)	During - (2008)	During - (2011)
Good waters	C2S1	a	03.23	11.29	-
	C3S1	o	62.90	70.97	41.94
Moderate waters	C3S2	đ	01.61	-	09.68
	C4S1	ě	12.90	09.68	14.52
	C4S2	©	09.68	-	12.90
	C4S3	Ö	-	-	04.84
Bad waters	C5S1	¤	-	06.45	06.45
	C5S2	?	08.06	01.61	-
	C5S3	œ	-	-	06.45
	C5S4	¤	01.61	-	03.23

Î SAR Low - EC Moderate, O SAR Low- EC Medium-High, đ SAR Medium- EC Medium-High, ě SAR Low-EC High, © SAR Medium- EC High, Ö SAR High-EC High £ SAR Low - EC Very High , :& SAR Medium-EC Very High, œ SAR High-EC Very High <& SAR Very High-EC Very High.

Table 10. Distribution of groundwater samples (%) for irrigation, according to Wilcox diagram

Classification	Percentage of samples		
	During - (2006)	During - (2008)	During - (2011)
Excellent to good	4.83	12.90	-
Good to permissible	41.93	56.45	30.65
Permissible to doubtful	14.52	01.61	4.84
Doubtful to unsuitable	20.97	16.13	40.32
Unsuitable	17.74	40.32	24.19

Table 11. Irrigation quality of groundwater based on residual sodium carbonate

RSC (meq/l)	Classification	Percentage of samples		
		During- (2006)	During - (2008)	During - (2011)
< 1.25	Good	79.03	87.1	90.32
1.25 - 2.5	Doubtful	11.29	06.45	08.06
> 2.5	Unsuitable	09.68	06.45	01.61

Total Alkalinity (T.Alk) of groundwater samples ranged from 160 to 630 mg/l with an average value of 365 mg/l during 2006 and ranged from 115 to 695 mg/l with an average value of 401 mg/l during 2008 and varied from 209 to 731 mg/l with an average value of 434 mg/l during 2011. The overall mean and median values are 400 mg/l and 392 mg/l respectively. The study shows that 62.90, 77.42 and 75.81% (Table 7) of the sample locations exceeded the desirable limit of the standard during 2006, 2008 and 2011 respectively. The spatial distribution of total alkalinity is presented in Fig. 8.

Occurrence of fluoride is quite sporadic and marked differences in concentrations occur even at very short distance. The crystalline formations are charnockite and granitic gneiss. (Mithas Ahamad Dar 2010). The gneisses of this area have quartz, feldspar (potash feldspars and albite), biotite etc. The charnockite of this area has potash feldspars, quartz and biotite which are potential sources of fluoride in the study area. The fluoride ion concentration of groundwater samples range from 0 to 2.0 mg/l during the 2006 with a mean of 0.9 mg/l, 0 to 1.0 mg/l with the average value of 0.4 mg/l during 2008 and 0 to 2.10 mg/l with an average value of 0.70 mg/l during 2011. The study indicates that 35.48 to 67.74% (Table 8) of samples are beyond the limit of the standards.

Irrigational suitability of groundwater in the study area was evaluated by Sodium Adsorption Ratio (SAR), Residual Sodium Carbonate (RSC), US Salinity Laboratory's diagram (USSL), Wilcox diagram and Permeability Index. The total dissolved content measured in terms of electric conductivity gives the salinity hazard of irrigation. The salt present in the water, besides affecting the growth of plants directly affects soil structure permeability and aeration, which indirectly affects plant growth (Umar *et al.*,

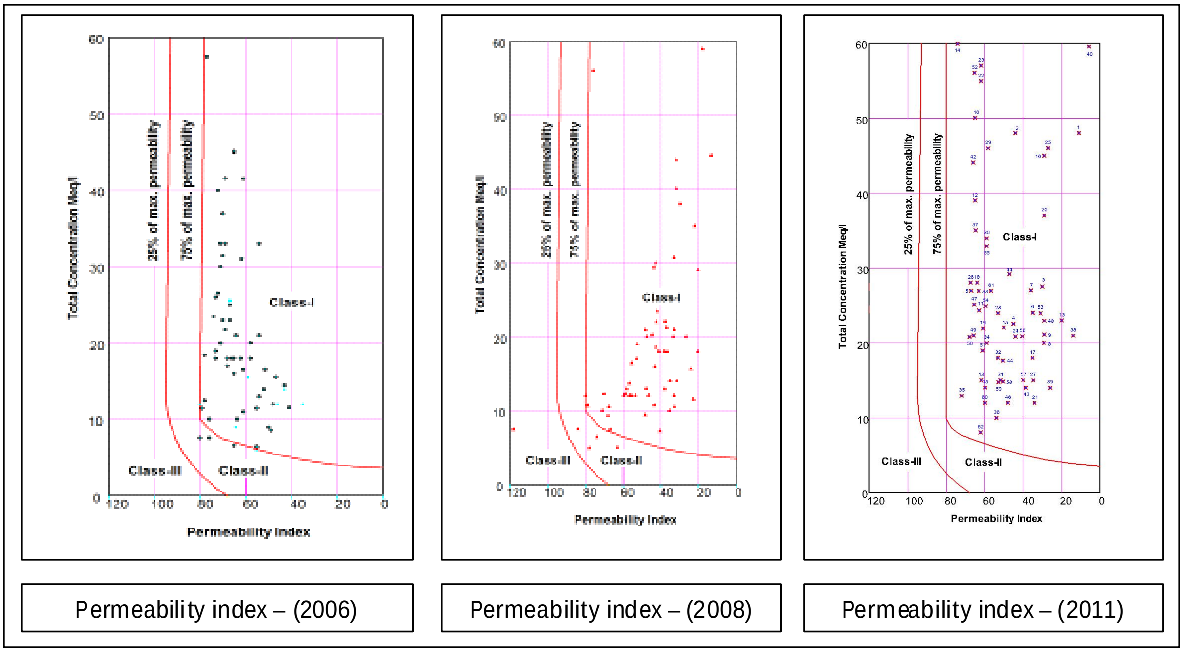

Fig. 11. Suitability of groundwater for irrigation based on permeability index

2001). SAR is an important parameter for determining the suitability of groundwater for irrigation purpose because it is a measure of alkali hazard to crops. The SAR is calculated as follows:

$$SAR = \frac{Na^{+}}{(Ca^{2+} + Mg^{2+})^{1/2}/2} \quad (2)$$

Where all the concentrations are expressed in meq/l. According to Richard's classification (Richard 1954), based on SAR, 98.39% of the samples were excellent and 1.61% was good during 2006. All the groundwater samples came under excellent category during 2008. However, 80.65, 17.74 and 1.61% of the samples belonged to excellent, good and fair category during 2011. The analysitical data plotted on US salinity diagram (US Salinity Laboratory Staff 1954). The study (Fig. 9) illustrates that 66.13, 1.61 and 32.26% of groundwater samples fall into the categories of good waters (C2S1 and C3S1), moderate water (C3S2) and bad water (C4S1, C4S2, C4S3, C5S1, C5S2, C5S3 and C5S4) respectively during 2006. About 82.26 and 17.74% of groundwater samples had fallen into the categories of good water (C2S1 and C3S1) and bad water (C4S1, C4S2, C4S3, C5S1, C5S2, C5S3 and C5S4) respectively during 2008. 41.94, 9.68 and 48.38 % of groundwater samples had fallen into the categories of good waters (C2S1 and C3S1), moderate water (C3S2) and bad water (C4S1, C4S2, C4S3, C5S1, C5S2, C5S3 and C5S4) respectively during 2011. The details are given in Table 9. It indicates groundwater of medium high salinity and low sodium, which can be used for irrigation in almost all types of soil with little danger of exchangeable sodium.

Sodium percentage (Na%) is widely used to assess the suitability of water for irrigation (Wilcox 1955). It defined as follows:

$$Na\% = \frac{(Na^{+} + K^{+}) \times 100}{(Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})} \quad (3)$$

where all the ionic concentrations are expressed in meq/l. Based on the classification of Na%, 76.61, 98.38, and 83.87% of the samples had fallen under categories of excellent to permissible during 2006, 2008 and 2011 respectively. During 2006, 24.19% of samples had fallen under doubtful category.

But only one sample is under doubtful category during 2008. However, ten samples were under doubtful category during 2011. The percentage of sodium (Na %) is widely used to assess the suitability of water quality for irrigation (Wilcox 1955). All the sampling points on the Wilcox diagram are displayed (Fig. 10) except a sample belong to 2011 due to abnormal electrical conductivity (9,930 µS/cm). According to Wilcox diagram, 4.83 to 12.90 %, 30.65 to 56.45%, 01.61 to 14.52%, 16.13 to 40.32% and 17.74 to 40.32% of the groundwater samples are excellent to good, good to permissible, Permissible to doubtful, Doubtful to unsuitable and

Unsuitable respectively The details are summarized (Table 10).

RSC influences the suitability of groundwater for irrigation. It has been calculated to determine the hazardous effect of carbonate and bicarbonate on the quality of water for agricultural purpose (Eaton 1950) and has been determined by the formula

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+}) \quad (4)$$

where all the concentrations are reported in meq/l. Based on RSC values (Table 11), 79.03, 11.29 and 9.68% of the groundwater samples had fallen into the categories of good, doubtful and unsuitable respectively during 2006, 87.1, 6.45 and 6.45% of the groundwater samples fall into the categories of good, doubtful and unsuitable during 2008 and 90.32, 8.06 and 1.61 % of the samples fall into the categories of good, doubtful and unsuitable during 2011 respectively. The permeability of soil is affected by long-term use of irrigation water and is influenced by sodium, calcium, magnesium and bicarbonate contents of the soil. Doneen (1964) evolved a criterion for the suitability of groundwater based on Permeability Index (PI). The analytical data are plotted in the charts (Fig. 11). According to PI values, the groundwater of the study area can be designated as class I except three samples during 2006 and five samples during 2008. The PI ranged from 35 to 80% with a mean of 63%, 8 to 64% with a mean of 46% and 6 to 74% with a mean of 49% during 2006, 2008 and 2011respectively. It is noted that all the groundwater samples of the PI values fall under class I during 2011. The overall average value (53%) of the PI also comes under class I (< 75%) of Doneen's chart (Domenico and Schwartz 1990).

CONCLUSIONS

The hydro-geochemical investigation reveals that the groundwater is alkaline in nature. Higher EC values are noticed near the Noyyal and Nallar river courses and concentration is found to be high in down stream. Nine water types are formed during 2011. On the basis of TDS, 8 to 13% of the samples can be used for drinking purpose without any risk during 2006 and 2008. However, during 2011 period all the samples show desirable limit for TDS. Piper diagram concludes that the alkalis significantly exceed the alkaline earths and strong acids exceed the weak acids. This leads to a NaCl type of groundwater. The study proves that the chemical weathering of rock-forming minerals and evaporation influence the poor quality of groundwater. Groundwater of the study area belongs to hard to very hard water types. Regarding total alkalinity 62.90 to 77.42 % of the groundwater of the area exceeded the desirable limit of the standards. 35.48 to 67.74% of the samples is beyond the limit of the standards of fluoride. US salinity diagram indicates that groundwater of medium high salinity and low sodium, which can be used for irrigation in almost all types of soil with little danger of exchangeable sodium. Based on sodium percentage, 76.61 to 98.38% of the samples fall under categories of excellent to permissible. Wilcox diagram reveals that 4.83 to 12.90 %, 30.65 to 56.45%, 01.61 to 14.52%, 16.13 to 40.32% and 17.74 to 40.32% of the groundwater samples are excellent to good, good to permissible, Permissible to doubtful, Doubtful to unsuitable and Unsuitable. Based on RS, 79.03 to 90.32% 6.45 to 11.29% and 1.61 to 9.68% of the groundwater samples fall into the categories of good, doubtful and unsuitable for irrigation. The overall value of the PI comes under class I which reveals that most of the groundwater samples are suitable for irrigation. It is suggested that all the bleaching and dyeing units in Tirupur should install latest Zero Liquid Discharge plant with Reverse Osmosis plant and rejection systems. All the reject waters should be evaporated using latest solar based systems so that the effluent discharge into the Noyyal river basin will be totally avoided and the groundwater quality will also be improved. Latest techniques need to be evolved to use dyes without using much water in dyeing units.

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