GROUNDWATER CHEMISTRY

4.1 GENERAL

Groundwater is one of the important sources of water used for domestic and industrial purpose. In India, sedimentary aquifers are the important source of groundwater. Changes in groundwater quality are due to rock–water interaction and oxidation–reduction reactions during the percolation of water through the aquifers. In addition to these processes, water-borne pathogens, toxic and nontoxic pollutants are the major water quality degradation parameters which are transported from recharge area to discharge area through aquifers by groundwater motion. Undesirable and soluble constituents in the water cannot be controlled after entering the ground has explained that leaching of surficial salts, ion-exchange processes, and residential time of groundwater in the aquifer causes the hydro geochemical variations in the groundwater. In India and various parts of the world, numerous studies have been carried out to assess the geochemical characteristics of groundwater. Several comprehensive studies are also carried out in south India (Subba Rao et al. 2006; Elango et al. 2003; Krishnakumar et al. 2009; Jeevanandam et al. 2006).

Water pollution is the state of deviation from pure condition, whereby its normal functioning and properties are affected. Aggravated environment problems often reflect the misuse or misunderstanding of technology. Water intended for human consumption should be "safe and wholesome" i.e. free from

pathogenic agent and harmful chemicals, pleasant to taste and useable for domestic purpose. Water is the principal need of life on earth, the requirement of water in all lives, from micro-organism to man is a serious problem today because all water resource have been reached to a point of crises due to unplanned urbanization and industrialization. Moreover, over-exploitation, excessive agriculture pesticides, untreated effluents and wastes have caused deterioration in groundwater quality. Whereas paucity of clean drinking water can affect the general health and life expectancy of people, the use of poor quality water in irrigation can degrade the soils due to contamination. Thus, the issue of availability and sustainability of safe groundwater is of great importance and calls for a scientific action plan to ensure water security in the region.

Typical examples of GIS applications in groundwater studies are site suitability analyses, managing site inventory data, estimating vulnerability of groundwater to pollution potential from nonpoint sources of pollution, modeling groundwater movement, modeling solute transport and leaching, and integrating groundwater quality assessment models with spatial data to create spatial decision support systems have reported a number of studies about Texas groundwater quality. Vinten and Dunn (2001) studied the effects of land use on temporal changes in well water quality.

4.2. Major ground water problems and issues of the study area

The quality of formation water in the fractured aquifer varies from place to place. Ground water quality of phreatic aquifers in the study area, in general, is colourless, odourless and slightly alkaline in nature. Electrical Conductivity varies

from 487 (Kuruvarkulam) to 3620 µS/cm (Taruvai, Palayamkottai Union) at 250 C and Chloride content varies from 28 to 1049 mg/L. Electrical conductivity in major parts of the district is less than 2000 µS/cm at 250C. It is observed that the ground water is suitable for drinking and domestic uses in respect of all constituents except few places are having higher concentration of NO_3 than the BIS permissible limit. (Central Groundwater Board Chennai, May 2003).

4.3 METHODOLOGY

Altogether 36 groundwater samples were collected from the study area namely Alankulam, Manur and Palayamkottai unions (Figure 4.1). 36 samples (Table 4.1) were collected in pre-monsoon period. Most of the groundwater samples were collected from dug wells and shallow bore wells. The water samples were analyzed for various parameters (Table 4.2) like pH, Total Dissolved Solids and major ions like Chlorides, Calcium, Magnesium, Sodium and Potassium by adopting WHO (1993) (World Health Organisation) procedures (Table 4.3). The extensive agricultural industrial activities and urbanization played major role in the contamination of the aquifer.

Table 4.3 Groundwater permissible limits prescribed by WHO.

Sl.No	Parameters	WHO (1993)	
		Desirable	Permissible
1	pH (mg/l)	6.5 – 8.5	9.2
2	TDS (mg/l)	500	1500
3	Ca (mg/l)	75	200
4	Mg (mg/l)	50	150
5	K (mg/l)	-	12
6	Na (mg/l)	-	200
7	Cl (mg/l)	200	600
8	So$_4$ (mg/l)	200	400

4.4 GROUND WATER QUALITY ANALYSIS FOR DRINKING PURPOSE

4.4.1 pH

As per the (WHO, 1984) standards, the pH values are in the range of 7.1 to 8.5 indicating an alkaline nature. The pH of the water indicates the form in which CO_2 is present. The presence of carbonic acid is indicated when pH is less than 4.5, bicarbonate is present when the pH is between 4.5 and 8.2, and carbonate is associated with in pH of more than 8.2. The pH value depends on the CO_2–CO_3–HCO_3 equilibrium. As the equilibrium is significantly affected by temperature and pressure, it obviously changes the pH (Karanth 1989).

pH is the measure of the Hydrogen ion concentration in the water. Lower the pH values indicate that the sample is more acidic and the higher pH value indicates the sample is alkaline in nature. The lower pH of water makes more corrosive in nature and therefore more toxic with respect to the metals as compare to the basic water. However, the acceptable concentration of pH in drinking water given by WHO (1991) is 6.5 to 8.5.

pH values of the water samples in the study area ranges from a minimum of 7.1 to a maximum of 8.2. It indicates that the samples are alkaline in nature (Figure 4.2). pH value of all the samples is within the desirable (7.5 – 8.5 mg/l) (Table 4.4).

Table 4.4 pH concentration of the study area

pH	Classification	Sample numbers	% of samples
6.5 – 8.5	Desirable	All samples	100
8.5 – 9.2	Permissible	-	-
Above 9.2	Excessive	-	-

4.4.2 ELECTRICAL CONDUCTIVITY (EC)

Electrical conductivity is the ability of water solutions to conduct an electric current and is measured in [micro]mho/cm. Electrical conductivity (EC) of groundwater is a measure of degree of mineralization and is dependent on rock-water interaction and thereby residence time of water in rocks (Eaton 1954). However, improper water management and addition of salts to the soil by inorganic fertilizers may also increase its value.

However, suitability of groundwater for irrigation depends on the effects of the mineral constituents of water on the both the plant and the soil (Richards 1954; Wilcox 1955). With increase in EC, plant usable water in the soil solution is decreased because plants can transpire only pure water. As the yield is directly related to amount of water transpired through a crop, therefore, irrigation water with high EC reduces yield potential.

Pure water is not a good conductor of electricity. Ordinary distilled water in equilibrium with carbon dioxide of the air has a conductivity of about 10 x 10-6 W-1*m-1 (20 dS/m). Because the electrical current is transported by the ions in solution, the conductivity increases as the concentration of ions increases. Thus conductivity increases as water dissolved ionic species (Source: ENVI (Environmental information System) government of India, Vol.4 No.1, March 2007).

The areas in different EC zones are presented in the Study area (Figure 4.3). The distribution maps showed that in the desirable and good quality zones constituted 50 % (613 sq.km), 31 % (378 sq.km) of the area respectively,

Permissible limit and 19 % of the study area (238 sq.km) are above the permissible limit. in Sevalasamudram, Vadiyur, Kannadikulam, Pillaiyarkulam and Tidiyur (Table 4.5).

Table 4.5 EC concentration of the study area

EC	Classification	Total area	% of samples
< 1500	Desirable	613	50
1500 – 3000	Permissible	378	31
Above 3000	Excessive	239	19

4.4.3 TOTAL DISSOLVED SOLIDS (TDS)

Several hydrochemical processes, which may include movement of groundwater through rocks containing soluble mineral materials, Concentration of water by evaporation, and contamination of water due to industrial and municipal waste disposals may cause a huge increase in the dissolved solids and Major cations and anions usually comprised more than 90% of the TDS (Freeze and Cherry 1979). To ascertain the suitability of groundwater for any purposes, it is essential to classify the groundwater depending upon their hydrochemical properties based on their TDS values.

The groundwater falls in three categories, while most of the samples are brackish water with TDS ranging from 1,000 to 10,000 mg/l. The water, with TDS less than 500 mg/l are considered good for drinking purposes and water with more than 1,000 mg/l is considered unsafe (WHO 1984).

It is noted that the maximum permissible limit of portable water is <500 mg/l (WHO 1984). However, this much range of TDS is even objectionable for irrigation purposes.   The analyzed results show that 73 % (897 sq/km) of the area are permissible limit(TDS below 500 - 1500 mg/l) and 27 % (333sq/km) are presented in excessive limit (TDS above 1500) in Figure 4.4 & Table 4.6.

Table 4.6 TDS concentration of the study area

TDS	Classification	Total area	% of samples
< 500	Desirable	-	-
500 – 1500	Permissible	897	73
Above 1500	Excessive	333	27

4.4.4 SULPHATE (So$_4$)

Sources of sulphate include rainfall, fertilizers, and dissolution of sulfide minerals present in granite (Hem 1989). Sulphate (SO_4) can be found in almost all natural water. The origin of most sulfate compounds is the oxidation of sulfite ores, the presence of shales, or the industrial wastes. Sulfate is one of the major dissolved components of rain. Sulfates occur naturally in numerous minerals and are used commercially, principally in the chemical industry. They are discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. Sulfur is widely present in reduced forms in igneous, sedimentary, and metamorphic rocks as metallic sulfides. This Sulfur turns to Sulphate when weathered in contact with aerated water. Water in igneous or metamorphic rocks generally contains less than 100 mg/L Sulphate, but sedimentary rocks can contain much

higher levels. The presence of sulfate in drinking water can cause a noticeable taste, and very high levels might cause a laxative effect in unaccustomed consumers. Taste impairment varies with the nature of the associated cation; taste thresholds have been found to range from 250 mg/L for Sodium Sulphate to 1,000 mg/L for calcium sulphate WHO (World Health Organization 2004).

The Sulphate content is under the desirable limit 200 mg/l, 93 % (1145 sq/km) of the area are desirable limit and permissible limit 7 % (85 sq/km) Table 4.7 by WHO Drinking water specification 1993 (Figure 4.5).

Table 4.7 Sulphate concentration of the study area

So4	Classification	Total area	% of samples
< 200	Desirable	1145	93
200 – 400	Permissible	85	7
Above 400	Excessive	-	-

4.4.5 CALCIUM (Ca)

Calcium occurs in water naturally. Seawater contains approximately 400 ppm calcium. One of the main reasons for the abundance of calcium in water is its natural occurrence in the earth's crust. Calcium is also a constituent of coral. Rivers generally contain 1-2 ppm calcium, but in lime areas rivers may contains calcium concentrations as high as 100 ppm. Calcium cannot be found alone in nature. Calcium is found mostly as Limestone, Gypsum and Fluorite. Stalagmites and Stalactites contain calcium carbonate. The increase in ratio value may be due to lowering Calcium activity whereby high sodium activates the dissolution of fluoride bearing minerals at higher pH in groundwater system.

It may dissolve from rocks such as Limestone, Marble, Calcite, Dolomite, Gypsum, Fluorite and Apatite. Calcium is a determinant of water hardness, because it can be found in water as Ca^{2+} ions. Magnesium is the other hardness determinant. Calcium is present in various construction materials, such as cement, brick lime and concrete. It is present in batteries, and is applied in plaster as calcium sulphate. The metal is applies for zirconium and thorium production. In steel industries calcium is applied as a blotter, and is added to aluminium, copper and lead alloys. Calcium can extract sulphur dioxide from industrial exhaust, and neutralize sulphuric acids before discharge (Source: ENVI (Environmental information System) government of India, Vol.4 No.1, March 2007). The Calcium concentration is found to be in the range of 8 to 477 mg/lit (Figure 4.6). It is within the desirable limit 24 % (296 sq/km), permissible limit 68 % (837sq/km) and 8 % (96 sq/km) (Table 4.8).

Table 4.8 Ca concentration of the study area

Ca	Classification	Total area	% of samples
< 75	Desirable	296	24
200	Permissible	837	68
Above 200	Excessive	97	8

4.4.6 MAGNESIUM (Mg)

Calcium, magnesium and total hardness in the groundwater are inter-related (Gurugnanam et.al, 2009). Magnesium is the eighth most abundant element and constitutes about 2% of the Earth's crust by weight, and it is the third most plentiful element dissolved in seawater (WHO 1971). It's very

abundant in nature, and it's found in important quantities in many rocky minerals, like dolomite, magnetite, olivine and serpentine. It's also found in seawater, underground brines and salty layers. It's the third most abundant structural metal in the earth's crust, only exceeded by aluminum and iron (Domenico and Schwartz 1990).

A large number of minerals contains magnesium, for example dolomite (calcium magnesium carbonate; $CaMg(CO_3)_2$) and magnesite (magnesium carbonate; $MgCO_3$). Magnesium is washed from rocks and subsequently ends up in water. Magnesium has many different purposes and consequently may end up in water in many different ways. Chemical industries add magnesium to plastics and other materials as a fire protection measure or as filler. It also ends up in the environment from fertilizer application and from cattle feed.

The Magnesium concentration is found to be in the range of 12 to 347mg/lit (Figure 4.7). It is within the desirable limit 46 % (46 sq/km), Permissible limit 618 % (50 sq/km) and 4 %(48 sq/km) of the study area are above the permissible limit (Table 4.9).

Table 4.9 Mg concentration of the study area

Mg	Classification	Total area	% of samples
< 50	Desirable	564	46
50 – 150	Permissible	618	50
above 150	Excessive	48	4

4.4.7 CHLORIDE (CI)

Chlorides occur in all natural waters in widely varying concentrations. The chloride content normally increases as the mineral content increases (Sawyer and Mccarly 1967). The chloride ion occurs in natural waters in fairly low concentrations, usually less than 100 mg/L, unless the water is brackish or saline. No health-based guideline value is proposed for chloride in drinking water. High concentrations of chloride give a salty taste to water and beverages (WHO (World Health Organization) 2004). However, chloride concentrations in excess of about 250 mg/L can give rise to a detectable taste in water (WHO (World Health Organization) 2004; Sawyer and Mccarly 1967). Chloride in drinking water originates from natural sources, sewage and industrial effluents, urban runoff containing de-icing salt, and saline intrusion (WHO (World Health Organization) 2004). High chloride content has a deleterious effect on metallic pipes, structures, and agriculture crops. The natural process such as weathering, dissolution of salt deposits, and irrigation drainage return flow are responsible for chloride content in the groundwater, which is supported by Cl/HCO ratio of 0.4 to 3.0.

WHO prescribed desirable limit of Chloride is 200 mg/lit. The Sodium concentration is found to be in the range of 11 to 1489 mg/lit (Figure 4.8). It is Desirable limit 28 % (348 sq/km), Permissible limit 51 % (624 sq/km) and 21% (258 sq/km) of the study area are the excessive limit (Table 4.10).

Table 4.10 Chloride (Cl) concentration of the study area

Cl	Classification	Total area	% of samples
< 200	Desirable	348	28
200 – 600	Permissible	624	51
Above 600	Excessive	258	21

4.5 GROUND WATER QUALITY ANALYSIS FOR IRRIGATION PURPOSE

Understanding the quality of groundwater is as important as its quality because it is the main factor determining its suitability for drinking, domestic, agricultural and industrial purposes (Subramani 2005; Abdelkader Rouabhia et.al, 2009)). The table 4.2 clearly shows, the results of the SAR, RAC and TH understanding the spatial distribution of hydrogeochemical constituents of groundwater related to its suitability for agriculture use in the study area.

4.5.1 Sodium Adsorption Ratio (SAR)

The sodium concentration in ground water is important since increase of sodium concentration in waters effects deterioration of the soil properties reducing permeability (Tijani, 1994). Sodium concentration is important in classifying the water for irrigation purposes because sodium concentration can reduce the soil permeability and soil structure (Domenico and Schwartz 1990). The sodium or alkali hazard limit for irrigation is determined by the absolute and relative concentration of cations and is expressed in terms of sodium adsorption ratio (SAR). There is a significant relationship between SAR values of irrigation water and the extent to which sodium is absorbed by the soil. If groundwater

used for irrigation is high in sodium and low in calcium, the cation-exchange complex may become saturated with sodium.

This can destroy the soil structure owing to dispersion of the clay particles (Suresh and Gurugnanan 2010). Sodium adsorption ratio (SAR) is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops. Excess sodium in water produces undesirable effects of changing soil properties and reducing soil permeability. Sodium adsorption ratio (SAR) is an important parameter for determination of suitability of irrigation water (Todd 1980) and is expressed as below:

$$\text{Sodium adsorption ration (SAR)} = (Na + /\{[Ca^{2+} + Mg^{2+}/2]\}\,0.5)$$

The waters were classified in relation to irrigation based on the ranges of SAR values (Richards 1954). According to Richard's classification, all the samples of the study area have been classified as excellent for irrigation (SAR value <10). In the present study, the SAR values varied from 0.07 to 22 (Figure 4.9). The calculated SAR value was compared with the quality classification of groundwater in Table 4.11. It is excellent category 99 % (1220 sq/km) and good category 1 % (10 sq/km).

Table 4.11 Sodium absorbtion ratio(SAR) of the study area

SAR (meq/l)	Water class	Total area	%
< 20	Excellent	1220	99
20 – 40	Good	10	1

4.5.2 Residual Sodium Carbonate (RSC)

The residual sodium carbonate (RSC) was calculated to determine the hazard effects of carbonate and bicarbonate on the quality of groundwater for agricultural and irrigation purposes (Eaton 1954). The excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influences the unsuitability of groundwater for irrigation. This is denoted as residual sodium carbonate (RSC), which is calculated as follows (Ragunath 1987):

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+})$$

(Where the concentrations are reported in meq/l.)

The classification of irrigation water according to the RSC values is presented in Table 4.12. In the present study, the RSC values varied from 0.1 to 3.1 (Figure 4.10), where 17% of the groundwater samples fall in the categories of doubtful (RSC 1.25 – 2.5), and unsuitable 83 % (RSC >2.5) respectively for irrigation purpose.

Table 4.12 Irrigation quality of groundwater based on RSC

RSC (meq/l)	Water class	Total area	%
< 1.25	Good	-	-
1.25 – 2.5	Doubtful	207	17
>2.5	Unsuitable	1023	83

4.5.3 Total Hardness (TH)

The classification of groundwater (Table.4.13) based on total hardness (TH) shows that a majority of the ground water samples fall in the very hard water category. TH of the groundwater was calculated using the formula given below (Sawyer et al. 2003).

$$TH(as\ CaCO_3)mg/l = (Ca^{2+} + Mg^{2+})meq/l \times 50$$

Table 4.13 Irrigation quality of groundwater based on Total Hardness

TH (meq/l)	Water class	Total area	% Age
< 75	Soft	-	*
75 – 150	moderately high		
150 – 300	Hard	353	29
Above 300	Very hard	877	71

The hardness values range from 130 to 2616 mg/l with an average value of 567 mg/l. (Figure 4.11). The maximum allowable limit of TH for drinking purpose is 500 mg/l and the most desirable limit is 100 mg/l as per the WHO international standard. 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 McMcartly 1967). Where 29 percentage (353 sq/km) of the groundwater samples fall in the categories of hard type (150-300) and 71 percentage (877 sq/km) of samples in very hard type (above – 300).

4.6 ASSESSMENT OF WATER QUALITY INDEX FOR THE GROUNDWATER IN THE STUDY AREA.

The main objective of Water Quality Index is to turn complex water quality data into information that is understandable and useable by the public. Water Quality Index based on some very important parameters can provide a simple indicator of water quality. It gives the public a general idea of the possible problems with water in a particular region. The indices are among the most effective ways to communicate the information on water quality trends to the public or to the policy makers and water quality management. It is also defined as a rating reflecting the composite influence of different water quality parameters on the overall quality of water .the concept of indices to represent gradation in water quality.

Groundwater occurs almost everywhere beneath the earth surface not in a single widespread aquifer but in thousands of local aquifer systems and compartments that have similar characters. Knowledge of the occurrence, replenishment, and recovery of groundwater has special significance in arid and semi-arid regions due to discrepancy in monsoonal rainfall, insufficient surface waters and over drafting of groundwater resources. Groundwater quality depends on the quality of recharged water, atmospheric precipitation, inland surface water, and on sub-surface geochemical processes. Temporal changes in the origin and constitution of the recharged water, hydrologic and human factors, may cause periodic changes in groundwater quality.

Water pollution not only affects water quality but also threats human health, economic development, and social prosperity. River basins are highly vulnerable to pollution due to absorption and transportation of domestic, industrial, and agricultural waste water; therefore, it is significant to control water pollution and monitor water quality. Various geostatistical concepts are used for the interpretation of complex data sets which allows a better understanding of the water quality parameters. Assessing risk involves identifying the hazard associated with a particular occurrence, action, or circumstance and determining the probability of that hazard occurring. Hence, evaluation of groundwater quantity and quality is important for the development of further civilization and to establish database for planning future water resources development strategies.

4.6.1 GROUNDWATER QUALITY IN THE STUDY AREA

Groundwater chemistry has been utilized as a tool to outlook water quality for drinking and irrigation purposes (Subba Rao 2006). WQI is an important parameter for demarcating groundwater quality and its suitability for drinking purposes. WQI is defined as a technique of rating that provides the composite influence of individual water quality parameters on the overall quality of water for human consumption. The standards for drinking purposes as recommended by WHO (1993) and BIS 10500 (1991) have been considered for the calculation of WQI (Table.6.16). For computing WQI three steps are followed. In the first step, each of the 6 parameters (TDS, Cl, SO4, Ca, Mg, and pH) has been assigned a weight (Wi) according to its relative importance in the overall quality of water for drinking purposes (Table 4.14).

Table 4.14 Relative weight of chemical parameters

Chemical Parameters	Indian Standard (BIS 10500; 1991)	Weight (Wi)	Relative Weight $W_i = \dfrac{w_i}{\sum_{i=1}^{n} w_i},$
pH	7.5	4	0.160
Total Dissolved Solids (TDS)	500	5	0.200
Calcium (Ca)	75	3	0.120
Magnesium (Mg)	30	3	0.120
Chloride (Cl)	250	5	0.200
Sulphate (So$_4$)	200	5	0.200
	Sum	25	
Relative Weight = (Weight (Wi) / Sum)			

The maximum weight of 5 has been assigned to the parameters like nitrate, total dissolved solids, chloride, fluoride, and sulfate due to their major importance in water quality assessment (Srinivasamoorthy et al. 2008). Bicarbonate and phosphate is given the minimum weight of 1 as it plays an insignificant role in the water quality assessment. Other parameters like calcium, magnesium, sodium, and potassium were assigned weight between 1 and 5 depending on their importance in water quality determination. In the second step, the relative weight (Wi) is computed from the following equation:

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

Where

W_i is the relative weight

W_i is the weight of each parameter

n is the number of parameters.

Calculated relative weight (Wi) values of each parameter are given in Table 4.15. In the third step, a quality rating scale (qi) for each parameter is assigned by dividing its concentration in each water sample by its respective standard according to the guidelines laid down in the BIS 10500 (1991) and the result is multiplied by 100:

$$Q_i = (C_i/S_i) \times 100$$

Where, Q_i is the quality rating

C_i is the concentration of each chemical parameter in each water sample in milligrams per liter

S_i is the Indian drinking water standard for each chemical parameter in milligrams per liter according to the guidelines of the BIS 10500 (1991).

For computing the WQI, the SI is first determined for each chemical parameter, which is then used to determine the WQI as per the following equation.

$$SI_i = W_i \times q_i$$

$$WQI = \sum SI_i$$

Where, SI_i is the sub-index of ith parameter.

q_i is the rating based on concentration of ith parameter.

n is the number of parameters.

Water quality types, were determined on the basis of WQI. The computed WQI values ranges from 26 to 310. The WQI range and type of water can be classified in below.

Table 4.16 WQI range and type of water

Range	Type of Water
< 50	Excellent Water
50 – 100	Good Water
100 – 200	Poor Water
200 – 300	Very Poor Water
Above 300	Unsuitable for Drinking

Which indicates that majority of the sample exceeds the permissible limit set by ISI and WHO. Calculation of WQI for individual samples is represented in Table 4.15 and Water Quality Index map shows in Figure 4.12.