HYDROCHEMISTRY OF COASTAL AQUIFERS OF TUTICORIN, TAMIL NADU - AN INVESTIGATION BY STABLE ISOTOPE AND GEOSPATIAL TECHNIQUES

Thesis Submitted to the

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

for the award of the degree of

DOCTOR OF PHILOSOPHY

under the

Faculty of Environmental Studies

By

PRAGATH M

(Register No: 3571)

Geomatics Division
Centre for Water Resources Development and Management
Kunnamangalam, Kozhikode - 673571, Kerala, India

Cochin University of Science and Technology
Cochin - 682022, Kerala, India

January 2020

Hydrochemistry of Coastal Aquifers of Tuticorin, Tamil Nadu - An Investigation by Stable Isotope and Geospatial Techniques

Ph.D. Thesis under the Faculty of Environmental Studies

Cochin University of Science and Technology (CUSAT)

Submitted by

Pragath M
Research Scholar
Geomatics Division
Centre for Water Resources Development and Management
Kunnamangalam, Kozhikode - 673571

Supervising Guide

Dr. Girish Gopinath
Research Supervisor
Senior Scientist (On Lien)
Geomatics Division
Centre for Water Resources Development and Management (CWRDM)

Centre for Water Resources Development and Management
Kunnamangalam, Kozhikode, Kerala - 673571

January 2020

Certificate

This is to certify that the thesis entitled "**HYDROCHEMISTRY OF COASTAL AQUIFERS OF TUTICORIN, TAMIL NADU - AN INVESTIGATION BY STABLE ISOTOPE AND GEOSPATIAL TECHNIQUES"** submitted to Cochin University of Science and Technology in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Environmental Sciences is a record of original research work done by **Mr. Pragath M (Reg No. 3571)** under my supervision and guidance. The results presented in the thesis have not been submitted previously for any degree. All the relevant corrections and modifications suggested by the audience during the pre-synopsis seminar and recommended by the Doctoral Committee have been incorporated in the thesis.

Place: Kozhikode
Date : 18/01/2020

Dr. Girish Gopinath
Research Supervisor
Senior Scientist (On Lien)
Geomatics Division
Centre for Water Resources Development and Management
(CWRDM), Kunnamangalam, Kozhikode, Kerala-673571

DECLARATION

I hereby declare that the work presented in the thesis entitled "**HYDROCHEMISTRY OF COASTAL AQUIFERS OF TUTICORIN, TAMIL NADU - AN INVESTIGATION BY STABLE ISOTOPE AND GEOSPATIAL TECHNIQUES**" has been carried out by me under the supervision of Dr. Girish Gopinath, Senior Scientist (On Lien), Geomatics Division, Centre for Water Resources Development and Management and further declare that this has not been submitted earlier in part or in whole to any University or Institute for the award of any degree or diploma.

Pragath M

Place: Kozhikode
Date: 18/01/2020

Dedicated to My Beloved Father

Acknowledgments

First and foremost, I thank ALMIGHTY GOD for providing me patience, persistence and perspiration.

Working as a Ph.D student at Geomatics Division, Centre for Water Resources Development and Management, Calicut was a magnificent experience to me. In all these years, many people were instrumental directly/indirectly in shaping my academic career. It was hardly possible for me to thrive in my doctoral work without the precious support of these personalities. Here is a small tribute to all these people.

First of all, I am extremely thankful to my supervising guide Dr. Girish Gopinath, Research Guide, Senior Scientist(on lien), Geomatics Division, Centre for Water Resources Development and Management, for his patient guidance, critical insights, perceptive comments, prudent observations and painstaking efforts to improve the quality of my work from the initial motivation for the topic to the final write-up. His cheerful enthusiasm and ever friendly nature helped in completing this doctoral work in a respectable manner.

I wish to express my sincere and heartfelt gratitude to Dr. Anitha A. B, Executive Director, Centre for Water Resources Development and Management, for providing me the necessary facilities to carry out the research work.

I am also indebted to Dr. Dinesan V. P, Former Head, Geomatics Division, Centre for Water Resources Development and Management, for providing all the necessary facilities to complete the research work.

I am extremely grateful to Dr. Resmi T. R, Scientist & Head i/c, Isotope Hydrology Division, CWRDM for providing laboratory facilities to carry out the water quality analyses and immense help rendered in data interpretation.

I would like to thank Dr. R. D. Deshpande, Scientist-Sn G and Chairman, Geosciences Division, Physical Research Laboratory, Ahmedabad, for providing laboratory facilities to carry out the stable isotope analysis.

I wish to express sincere thanks to Dr. D. R. Prasada Raju, Scientist-G/Adviser & Head, Govt of India, Department of Science and Technology and Prof Dr. P. Rajendra Prasad, Department of Geophysics, Andra University, Visakhapatnam, for the help rendered to me during the course of my study.

I sincerely admire the contribution of Dr. Baiju K. R (M G University), Dr. P. S. Harikumar, Dr. Arun P. R, Dr. Surendran U, M R Venugopal and Dr. A. Shahul Hameed (CWRDM) for extending their unstinted support, timely motivation and unfailing help during the course of entire work.

I thank the Department of Science and Technology, Government of India for providing financial assistance to the project " Saline Water Intrusion Studies Along Tuticorin Coast Using Isotopic Systematics " under which my the thesis forms a part.

I also acknowledge my thanks to Dr Harindranathan Nair M V, Dr Suguna Yesodharan Amarnath A and Rani Varghese of School of Environmental Studies, Cochin University of Science and Technology for their immaculate support during the course of the Doctoral work.

I express my sincere thanks to Dr. K. Ch.V Naga Kumar, Vasanth K C, Ashitha Biju, Dr. Jesiya N. P, Mrs. Bineesha T. M, Ansad. A, Arjun p Sreerag A. S, Mrudulrag, Rajeesh Kumar, Pradeep P. K, Sherry Gregory and all the members in Geomatics Division, CWRDM for their invaluable co-operation in the time of need.

I also acknowledge with a deep sense of reverence, my gratitude towards my mother Lathika A M, Wife Sabitha A R and Son Arshu who sacrificed all their cheerful moments with me and provided with me continuous inspiration and endless support for the completion of this Doctoral work.

Pragath M

PREFACE

Groundwater forms the main source of domestic, irrigation and industrial purposes. The global dependency of groundwater is rapidly increasing. There is growing disquiet on deterioration of groundwater quality due to anthropogenic and geogenic activities. The over exploitation of groundwater resources has become very crucial in the last decades. The distinctive nature of coastal environments globally is overpopulation, over abstraction of groundwater, salinization problems, urbanization and industrialization. The intensive extraction of groundwater from coastal aquifers causing seawater to migrate inland and deteriorate the groundwater quality. Withdrawing rate of groundwater is more than recharging rate because of the variability in precipitation and climatic conditions. The present investigation is to analyse the impact of the groundwater resources of coastal and inland plains in Tuticorin, Tamil Nadu. Geomorphic settings of the study area include coastal/inland marine, fluvial marine, fluvial & Teri sands and inland crystalline consist of Hornblende Biotite Gneisse and Charnockite.

Evaluation of hydrochemical characteristics of the coastal and inland groundwater of Tuticorin coast portrayed a distinct spatial variations exist between the groundwater of coastal and inland aquifers. The water quality of groundwater in majority of the wells in the coastal region exceeded the permissible standard limits of BIS (2012) and WHO (2011) for drinkingwater purpose. Bacterial contamination was observed in some part of the study area and this is due to lack of proper sanitation facilities. Irrigation water quality was evaluated and found that ionic concentration of ground water in coastal zones affects the crop yield and soil structure. The hydrogeochemical facies obtained using Hill-Piper plots and Na-Cl water type is the predominant in all the wells. Inter-ionic relationships and multivariate statistical analysis of hydrogeochemical parameters revealed that coastal and inland aquifers geochemistry was controlled by evaporation, rock water interaction and ion-exchange process.

Stable isotopic ratios of waters of the study area were determined to identify the recharging mechanism and other hydrogeochemical processes of the coastal and inland aquifers. Local Meteoritic Water Lines (LMWL) for Tuticorin coast was established as part of the study, which helps in identifying the isotopic modifications of the waters in the area.

GIS based Multi Criteria Decision Making (MCDM) technique were employed to evaluate spatiotemporal variations of groundwater quality aspects and groundwater suitability zonation based on the BIS and WHO drinking water quality standards were derived for the study area. The DRASTIC model in a Geographical Information System environment was carried out to evaluate the vulnerability of the study area. The relative influence of DRASTIC parameters on vulnerability assessment was numerically derived using Analytical Hierarchy Process (AHP). Groundwater vulnerability zonation of coastal and inland aquifers pointed out that the coastal areas were most potential to groundwater contamination on the basis of hydrogeological conditions and human impacts.

Contents

List of Tables

List of Figures

List of Plates

Chapter 1

INTRODUCTION

1.1 Introduction

Groundwater systems is considered as a vital source of water supply in comparison with rest of the water resources, better protection from pollution like infection, less perennial and their larger uniform spread. The socio-economic and ecologic function of global coastal ecosystems is highly influenced by the groundwater resources (IPCC, 2007). This invisible source of water is the world's highly extracted raw material, estimated to be between 600 to 700 billion m^3/year (Zektser and Everett, 2004). The groundwater source caters to various needs such as drinking water supply, irrigation, livestock, industry and mining, the breakdown of percentage used per sector is drinking water (65%), irrigation and livestock (20%), industry and mining (15%) by Zektser and Everett, 2004. Groundwater is the primary and at sometimes the only source of water supply in most of the developing and developed countries. According to United Nations Environment Programme (UNEP) report, 60% of the world population dwells within 60 km of coastline and the primary source of water supply being groundwater. In the semiarid and arid regions around the world, groundwater caters to the supply of fresh water, in these regions the period of highest demand coincides with the lowest availability period (Post 2005; Unsal et al. 2014). Increasing demand and rapid urbanization leads to over extraction during the periods and in regions with high demand where the recharge is minimum (Post, 2005). Aquifer systems in comparison to surface water systems is least vulnerable to anthropogenic contaminants, if aquifers are contaminated the pollution is difficult to remediate because of reduced physical accessibility, longer residence time and extensive storage (Foster and Chilton, 2003).

Excessive draw down of groundwater will induce deterioration in its quality and salinization, which was reported across the globe by various researchers eg: Mediterranean region (Gimenez and Morell, 1997; Pulido Bosch et al. 1999), Croatia (Biondic et al. 2006), Mexico (Escolero et al. 2007), Israel (Kafri et al. 2007), and Greece (Panagopoulos, 2008). Salinization of groundwater is portrayed due to various processes like overexploitation adding to modern sea water intrusion (Custodio, 1997; Kim et al. 2003; Pulido Leboeuf, 2004; Andersen et al. 2005; Bianchini et al. 2005; Cary et al. 2013; Werner et al. 2013), Paleowater contributions (Vengosh et al. 1995,2003; Edmunds and Milne, 2001; Aquilina et al. 2002, 2013; Negrel and Casanova, 2001; Duriez et al. 2008; Han et al. 2011; Khaska et al. 2013; Armandine Les Landes et al. 2014; Sola et al. 2014) and dissolution of evaporates catalyzed or non-catalyzed by aquifer-rock interactions (Kloppmann et al. 2008 ; Cendon et al. 2008; Lucas et al. 2010; Mongelli et al. 2013; Merchan et al. 2015). Groundwater sources are prone to high vulnerability in coastal areas where the extent of saline water intrusion is controlled by aquifer lithology, topography, ratio of recharge and withdrawal and hydraulic gradient (Freeze and Cherry, 1979). Aquifers in the coastal region suffer intense damage facilitated by over-extraction leading to lowering of water table, land subsidence and intrusion of saline water into fresh water aquifers (Andreasen and Fleck, 1997; Capaccioni et al. 2005; Giambastiani et al. 2007). The extent of over extraction, anthropogenic activities, geolocation and regional geology are the key drivers in governing the quality of groundwater.

India is one of the largest consumers of groundwater; about 84% of irrigation in India is facilitated by groundwater. Domestic needs of 80% of the rural and 50% of the urban population of India are catered by the groundwater (CGWB, 2018). Nearly 25% of the total population in India resides in the eastern and western coastal stretch and the major cities of the country like Mumbai, Chennai, Kolkata, Vishakapatnam, Tuticorin, Cochin etc. falls in this coastal tract. The demand for freshwater resources to cater the needs of the human population is growing exponentially due to an increase in urbanization and industrialization and groundwater is the primary source of fresh water supply in coastal areas. Analysis of irrigation practices in India reveals that abstracting groundwater is showing an increased rate and since 1970, 60 % of the total irrigation in the country is catered by groundwater (Agriculture statistics, India, 2011). In the Indian subcontinent the groundwater behavior varies remarkably due to the occurrence of diversified geological formations, lithological and chronological variations, complex tectonic framework, climatological dissimilarities and various hydrochemical conditions (CGWB, 2018). The stage of groundwater development in majority of states in India is greater than 70% that envisages the fact that the rate of recharge is far below the rate of extraction of groundwater (Jat et al. 2009; CGWB, 2018). About 1186 administrative units out of 6881 are overexploited as per the CGWB report (2011). Climate change has induced many deleterious effects on the coastal aquifers of India. According to IPCC (2007) report, the sea level rise in the Bay of Bengal is higher when comparted to other Asian countries and this may result in inundation of approximately 60 km of coastal inland. The coastal aquifer in India is degraded by sea water intrusion driven by greater evaporation rate, low and erratic rainfall (Rajmohan et al. 2004). In the studies on the water quality of coastal aquifers along the country was carried out by many researchers, arrived on a consensus regarding the poor water quality and the potability levels beyond WHO limits (Amer 1995; Chidambaram et al. 2008; Dar et al. 2010). Poor groundwater quality in aquifers of western coastal region of India (Cochin) was reported by Laluraj et al. 2005.

Tamil Nadu is one of the states in India facing significant water scarcity. The state constitutes 7 % of the total population (62.11m.ha) and 4% (12.99 m.ha) of the total land area of the country, which is endowed with only 3% of water resources available in the country (ENVIS Centre). The state receives an average annual rainfall of 911.60 mm. There are 39202 tanks and 79 reservoirs which serve as the surface water resource for the state. Total water potential of the state is 1643 TMC attributed together from 853 TMC of surface water and 790 TMC of groundwater (DOLR,Tamil Nadu). It is estimated that 86 % of the total groundwater resources are already tapped and there is no scope for medium/major projects in tapping surface water (DOLR, Tamil Nadu). In the state out of 1166 administrative revenue blocks (firkas) 462 has been demarcated as overexploited and 35 categorized as saline (CGWB, 2019). Along the coastal tracts of Tamil Nadu location of fresh-saline groundwater has extended far inland due to the over exploitation, for example in the Minjur area of Chennai the fresh saline interface location was 3.5 km inland in 1972 which ingresses 15 km at present (CGWB, 2014).

Hydrochemical quality of groundwater in many areas of Tamil Nadu is in critical condition driven by anthropogenic and insitu salinity factors. Sea water intrusion was reported in Kuttam- Radhapuram area, Cuddalore Coast due to heavy pumping at SIPCOT, Tiruvanmiyur- Kovalam Tract, Southern part of Chennai City and insitu salinity was reported at Tuticorin district and Cuddalore Coast (CGWB, 2014). Some of the major cities of India, Chennai and Tuticorin port lies in Tamil Nadu where rapid urbanization leads to excessive draw down of these groundwater resource.

Groundwater has a significant role in sustaining socio-economic-environment values, sustainable use and proper management of this water resource is identified as critical globally. Water table observations, hydrochemical quality and recharge quality monitoring of aquifers is far from adequate in summarizing information for this resource management (Foster and Chilton, 2003). Analyzing the hydrochemistry of groundwater helps in categorizing water types, cataloguing water for various use, aquifer identification and in situ chemical process (Karanth, 1987; Sexena et al. 2003; Jalali, 2007; Sarwade et al. 2007). Hydrochemical quality along with isotopic signatures and spatial characteristics of aquifers facilitates in sustainable management of this resource.

The objective of the study is to decipher the hydrogeochemical characteristics of geologically and spatially separated coastal and inland aquifers using and their temporal variations. Stable isotopic signatures corroborated with the hydrogeochemical characteristics of the coastal and inland aquifer delineates the saline water ingress, being a sensitive indicator stable isotopic signature comprehends the source of salinity and helps in apprehending the complex hydrogeochemical process. Geospatial, multivariate and MCDM (multi criteria decision making) techniques assimilated substantiates in proffering the suitability and vulnerability characteristics of coastal and inland aquifers, an aquifer database of the study area is developed to perceptualize efficient sustainable management of this water resource by decision makers and planners.

1.2 Review of literature

Groundwater is one of the most valuable natural resources supporting human health and economic development (Abdul et al. 2017). Groundwater is important source of water supply throughout the world and its use in irrigation, industries, municipalities and rural homes continues to increase (Todd and Mays, 2005). Of the 37 million km3 of freshwater that is to be found on the planet, some 8 million km3 roughly 22 percent is stored underground in the form of groundwater and it constitutes some 97 percent of all the freshwater that is potentially available for human use on or beneath the Earth's surface (Foster, 1998). India is the largest groundwater user in the world, with an estimated usage of around 230 cubic kilometres per year, more than a quarter of the global total (World Bank report, 2010); with more than 60 percent of irrigated agriculture and 85 percent of drinking water supplies dependent on it, groundwater is a vital resource for rural areas in India.

The fact that coastal zones are the most densely populated areas in the world makes the need for freshwater even more acute (Gaaloul et al. 2012). The intrusion of seawater into coastal aquifers is a common problem in coastal zones of the world where increasing water requirements and arid climate have induced over exploitation of groundwater (Masciopinto, 2006). Protecting coastal aquifers requires a good understanding of their dynamics and a detailed knowledge of the variability of their parameters (Carrera et al. 2010). Saltwater intrusion is one of the most widespread and important processes that degrade water quality to levels exceeding acceptable drinking and irrigation water standards, and endanger future water exploitation in coastal aquifers (Nawal Alfarrah et al. 2018). In many parts of India wells located near the coastal areas intruded by seawater (Chidambaram et al. 2008; Sankaran et al. 2012). Periodic analysis of groundwater chemistry is one of the most common methods for assessing seawater intrusion into the wells or water sources near coastal areas (Todd, 1980; Sukhija et al. 1996; Sexana et al. 2003). The chemical composition of saline groundwaters in many locations in coastal aquifers deviates from simple conservative seawater–freshwater mixing (Apello and Geirnard, 1991; Chockalingam, 1993). An investigation on hydrogeochemistry and seawater intrusion in different coastal aquifers has been carried out by many researchers in various parts of the globe (Elango et al. 1992; Sathish et al. 2011; Rekha et al. 2013).

A knowledge on hydrogeochemical processes that control its chemical composition leads to improved understanding of hydrochemical systems and this can contribute to effective management and utilization of the groundwater resource by clarifying relations among many hydrogeological parameters (Manjusree et al. 2009). The hydrogeochemical characteristics depend on the chemistry of rock-forming minerals and on the physical process of erosion that creates favorable conditions for mineral dissolution (Tziritis et al. 2016). Zaporozec, 1972 stated that the knowledge of hydrochemistry is essential to determine the origin of chemical composition of groundwater. Increased knowledge of geochemical processes regulating the groundwater chemical composition will lead 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 evaluation and management of groundwater resources require an understanding of hydrogeological and hydrogeochemical properties of the aquifer (Umar et al. 2001). To ensure this irrigation benefit of groundwater, it is necessary to precisely identify its quality, which mainly depends upon the content of different ions (Tahmasebi et al. 2018). Agricultural irrigation has much higher demands on water quality than industrial and even household water (Li et al. 2018). Various important ions (such as Na+, Ca2+, Mg2+, and K+) in groundwater are indispensable for the maintenance of crop growth and development (Khalid, 2019). Vetrimurugan et al. 2015 were studied on the suitability of groundwater for irrigation using various parameters. Tziritis et al. 2016 stated that the hydrogeochemical characterization may be achieved by variable approaches, among which are the classic hydrogeochemical ratios and multivariate statistical techniques.

Application of isotopes to hydrology is demonstrated in several parts of the world. Various studies on hydrochemical isotopic investigation to a wide range of field applications like identification of sources of groundwater recharge (Navada et al. 1993; Mukherjee et al. 2007), study the effects of evaporation on groundwater systems (Krishnamurthy et al. 1991), elucidation of ground - surface water interaction (Navada et al. 1991; Richey et al. 1998), identification of the origin and possible mechanism of saline water intrusion (Saravana Kumar et al. 2009). Studies pertaining to synoptic view of the isotopic content of rainwater (Battacharya et al. 2003), river water (Pande et al. 2000; Dalai et al. 2002), groundwater (Deshpande et al. 2003; Shivanna et al. 2004; Gupta et al. 2005), lake water (Gupta, 2004) were done in India. Indu et al. 2015 studied the mechanism of sea water and groundwater mixing by using environmental isotopes. Parul Muraya et al. 2019 stated that the δD and δ^{18}O stable isotopes are known to be potential markers of the water origin. Among various isotopes used as tracers in hydrology, stable isotopes of oxygen ($^{18}0$) and hydrogen (^{2}H, also known as deuterium; D) are the most important (Deshpande, 2006) and referred as water isotopes. The stable isotopes of hydrogen (δD) and oxygen (δ18O) in precipitation have been used in studies of hydrological processes (Aggarwal et al. 2016; Sprenger et al. 2016; Fischer et al. 2017), and the relationship between these in precipitation underpins many studies (Wang et al. 2018).

To delineate groundwater prospects of an area, integration of conventional surveys along with satellite image data interpretation techniques, and geographical information systems (GIS) technology, are useful to increase the accuracy of results and to reduce the bias on any single theme(Gupta et al. 2010). Geospatial techniques provide efficient assistance in vulnerability assessment and there are various studies on the GIS based DRASTIC model for assessing groundwater vulnerability (Prasad et al. 2014; Prasad et al. 2011; Rahman, 2008; Jesiya et al. 2019b). The study using a combination of DRASTIC and GIS method was cited as an effective method for groundwater pollution risk assessment (Ghosh et al. 2015). Many approaches have been developed for assessing groundwater vulnerability such as statistical methods, process-based and index based methods (Sener and Sener, 2015; Ribeiro et al. 2017).

Analytic Hierarchy Process (AHP) and its extension, the Analytic Network Process (ANP) is a MCDM technique developed by Saaty, 1980. Jesiya and Gopinath 2019a, conducted a study on GIS based MCDM technique to evaluate groundwater suitability zonation and in this method the decision making occurs in such a way that the problem to be solved is broken down in to a hierarchy and solved through pairwise comparison. This pairwise comparisons determine the relative importance of parameters/themes and converting these comparisons to normalized weights (Swetha et al. 2017). The transparency thus obtained is the major reason behind the wide application of Multi-Criteria Decision Making (MCDM) in water resource management (Joubert, Stewart and Eberhard, 2003).

Kumar and Venugopal (2003) has done groundwater quality monitoring of Kancheepuram district, Tamilnadu. Vulnerability index equation was derived using GIS analysis, vulnerability index equation comprises of water level factors, soil characteristics, topography, hydrogeological factors and irrigation extend. The major finding of the study was acute pollutions resultant from effluent discharge from textile industry and distilleries, which has deletorius effect in water and soil characteristics. DRASTIC model was coupled with geospatial technique to delineate the vulnerability zone.

Multicriteria analysis (MCDM) intergrated with geospatial techniques was done by Sandeep Goyal et al (2009) for groundwater evaluation in Rawasen and Pile watershed, Uttar Pradesh, India. In the study various thematic maps, landuse/landcover, geopmorphology, geology, topography etc. were derived from satellite image products. Intergrating them along with groundwater data resulted in developing groundwater resource management plans for the area.

Remote sensing technology plays a pivotal role in detecting changes in the environment. Land Surface Temperature (LST) rapidly changes in both space and time, and knowledge of LST and its spatiotemporal variation is essential to understand the interactions between human activity and the environment (Phan et al. 2018). LST can provide information about the surface physical properties and climate which plays a role in many environmental processes (Weng et al. 2004). The changes in land use/cover include loss of agricultural lands, loss of forest lands, increase of barren area, increase of impermeable surface of the area because of the built up area (Kumar et al. 2012). SundaraKumari et al. 2012 stated that land surface temperature (LST) is increased by anthropogenic heat discharges due to energy consumption, increased land surface coverage by artificial materials having high heat capacities and conductivities, and the associated decrease in vegetation and water pervious surfaces which reduce the surface temperature through evapotranspiration. Remote sensing and geographical information system (GIS) techniques are used to detect the land use changes and its impact on the LST(Buyadi et al. 2013) and is very much useful to planners and policy makers.

1.3 Regional environmental settings

Coastal and inland area of Tuticorin district, Tamil Nadu located towards the north-eastern coast of India with north latitude of 8°31'00"N, 9°00'00"N and east longitude of 78°00'00"E, 78°16'00"E has been identified as the area of study (Fig.1.1). Study area has an areal extent of 980.80 Km^2, area extend from Bay of Bengal coast to 29.50 Km inland in the north and 13.50 Km inland towards the south. The aquifers in the study area is classified into three zones based on the hydrogeological factors as i) inland crystalline aquifers with an areal extent of 421.55 Km^2, comprising of Hornblende Biotite Gneiss/Charnockite ii) inland alluvium aquifer extending upto 164.79 Km^2 comprehended by fluvial and aeolin alluvium formations and iii) coastal alluvium aquifer with an area of 394.46 Km^2 which consist of coastal marine and fluvial marine formations. Majority of the bore wells in the study area is engulfed within the inland crystalline aquifer, whereas tube wells and dug wells were observed in the coastal/inland alluvium aquifer. The entire study area is bounded on the south by Tiruchendur and Sippikkulam in the north with a coastal stretch of 99.60 Km, out of the 12 major ports in India Tuticorin port is the second largest port in Tamil Nadu and this busy port is located in the study area. The name of the study area Thoothukudi is derived from local language where “Thoothu” means dig and “Kudi” means drink which demarcates the water scarcity prevalent in this area.

Tuticorin is one of the largest salt producing districts in Tamil Nadu (Plate.1.1) which accounts for 16.17 tonnes per annum and contributes a major share in the economic wellbeing of the district, the study area comprises of 52.90 Km^2 salt pans. The coastal and inland areas of the study area are classified accordingly by the underlying geological characteristics. As per 2011 census the total population of the district is 1,750,176 spread across the land area of 4,745 Km^2 and the density of population per sq km is 369 which portraits an increase of 11.32% since 2001. Agricultural activities are the predominant occupation and 70% of the population thrive on it, out of the 4,745 Km^2 total land area 1976.90 Km^2 of land is brought under cultivation which is estimated to be of 42% of the land area (District Statistical Hand Book, 2014-15). Numerous heavy industries like Sterlite, Southern Petrochemical Industries Corporation Ltd (SPIC), Tuticorin Alkali Chemicals and Fertilizers Limited (TFL), Heavy Water Plant (HWP), Thermal power plant etc. are also a part of the district. The primary source for irrigation, industrial activities and human needs are catered by the critical groundwater resource.

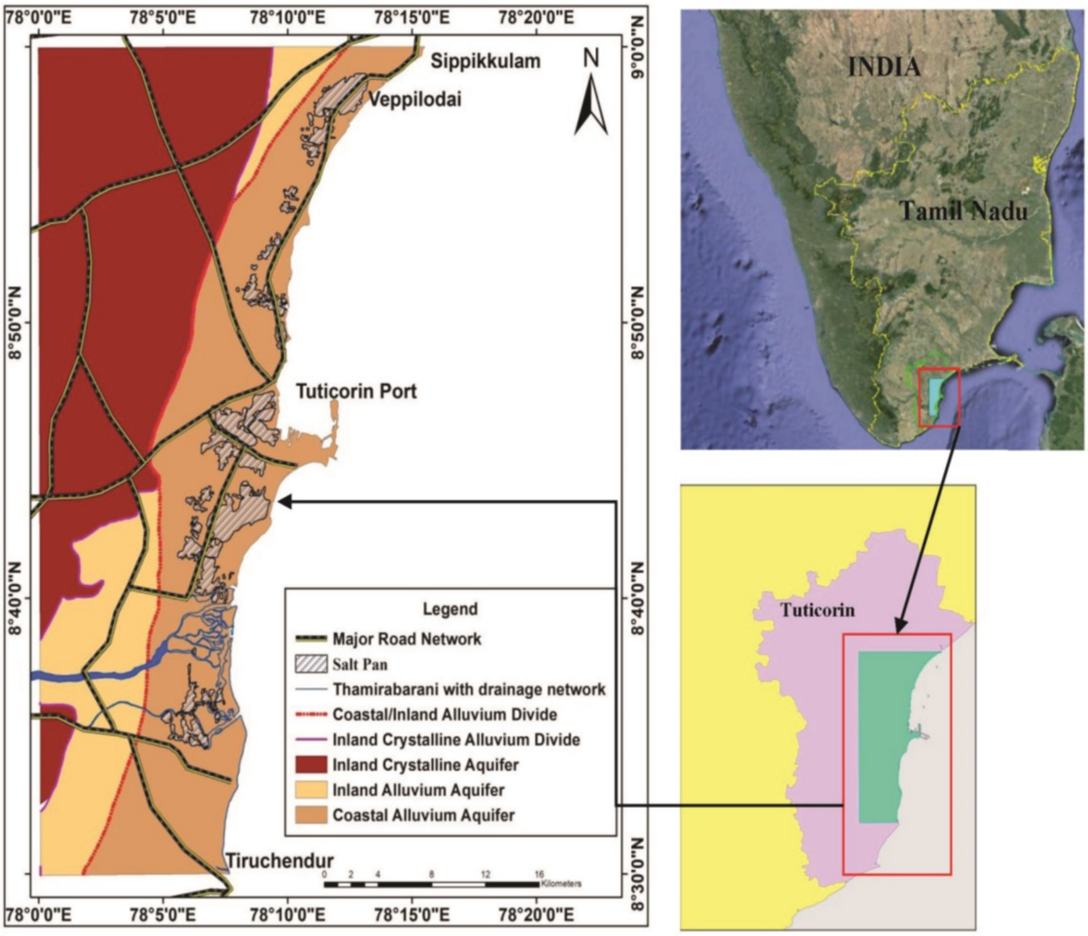


Fig 1.1. Base map of the study area showing coastal alluvium, inland alluvium and inland crystalline aquifer in the study area

The solitary drainage system is Thamirabarani river draining to Bay of Bengal towards the south of the study area forming a deltaic region, the river is ephemeral with run off only during rainy season. The area comprises of rain fed tanks and canals which is under stress to cater agricultural activities and human needs which increments the drawdown of aquifers. Varieties of crops are cultivated all across the Tuticorin district and their areal extent is given in Table.1.1, paddy. Extensive paddy (Plate.1.2), banana and beetlenut cultivations are perceived along Thamirabarani deltaic region.

Plate 1.1: Salt pan located in the northern part of the study area

Plate 1.2: Extensive paddy cultivation in the Thamirabarani deltaic region

Table 1.1: Nominal area of various crops in Tuticorin district (Source ENVIS Centre Tamil Nadu)

S.No	Name of the crops	Area in Ha
1	Paddy	14,400
2	Millet	61,800
3	Pulses	66,700
4	Cotton	4,500
5	Sugarcane	300
6	Oilseeds	3,500
7	Banana	10,300
8	Onion	1,400
9	Chillies	11,750
10	Vegetables	2,050
11	Coconut	4,500
Total		**1,81,200**

1.3.1 Hydrogeology and Lineament

The study area is in eastern coast of India with an undulating topography with general slope towards east. The study area represents a well-developed lithopackage of meta-sedimentary sequence inter banded with charnockite Group of rocks. The rock types exposed are of Charnockite, Calc-granulite, Limestone, Hornblende Biotite Gneiss belonging to Khondalite group of rock, Claystone, pink and grey Granite (Fig.1.2). Rich deposits of garnet and ilmenite sand occurs along the coastal part of Thiruchendur. Kayalpattinam and Vaippar areas show notable garnet and ilmenite sands occuurrences. The coastal stretch up to 9 km inland is of marine formations and it extends from north to south of the study area, fluvial-marine belt is observed from north to south with a maximum width of 5.50 Km towards the south. Hornblende biotite gneiss is the predominant geologic formations of inland with Charnockite formations in the North West inland area. An elongated strip of quartzite towards the NW and Calc granulite towards the SE of Charnockite formation is observed. Sandstone and Claystone formation are recorded towards the north of Thamirabarani river limited by Quartzite strips towards the the north.

The potentiality for groundwater occurrence in hard rock areas is influenced by the presence of lineaments. Presence of lineaments may act as a conduit for groundwater movement which results in increased secondary porosity and therefore, can serve as groundwater potential zone.

The occurrence of groundwater in hard rock areas are influenced by lineaments. Secondary porosity of groundwater is subjected to the lineaments which act as a duct for groundwater movement; they serve as a secondary aquifer in the regions of hard rocks. The prominent lineament type observed in the study area is structural - fractures, fractures are found in the northern inland region of the study area with hard rock formations. Lineaments parallel to ridges are observed in the inland area near to Charnockite geologic formation and with highest elevation (Fig.1.3).

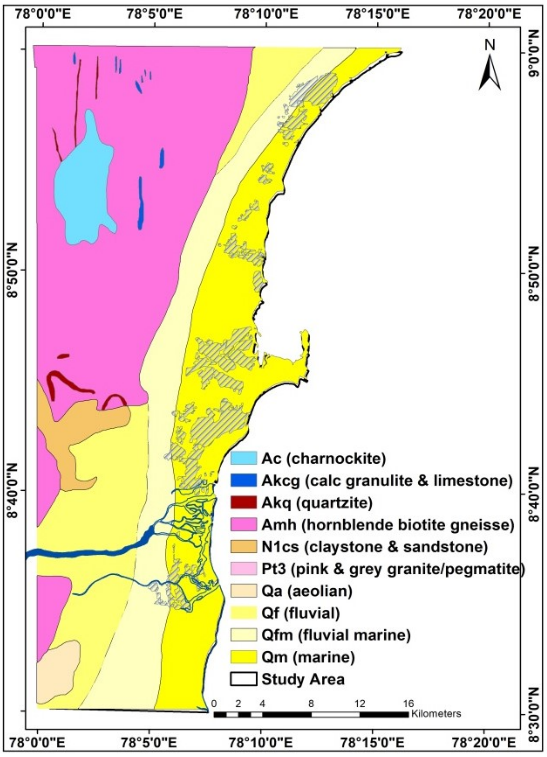


Fig 1.2: Geology map of the study area (*Source CGWB & Bhuvan*)

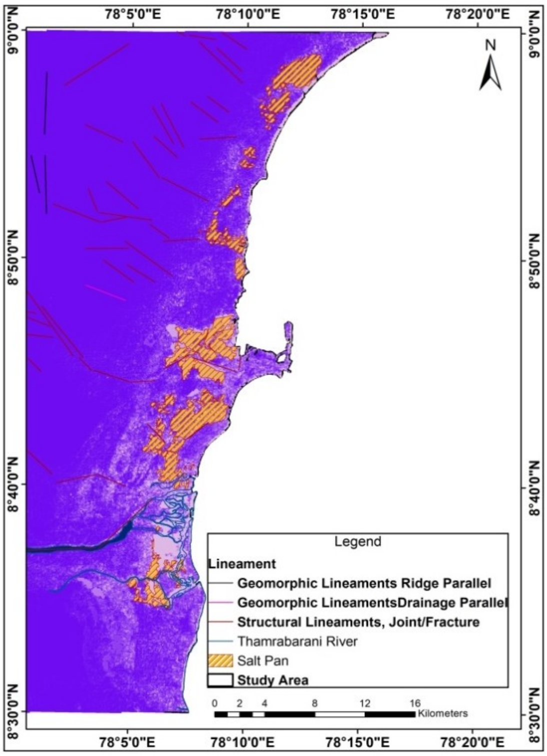


Fig 1.3: Lineament map of the study area (*Source CGWB & Bhuvan*)

1.3.2 Geomorphology and Litholog

The coastal study area is a cluster of dynamic landforms resultant from the actions of marine, estuarine, aeolian and fluvial processes (Fig 1.4). Investigation about these landforms provides us with the insight of their origin and process involved during their evolution. The drainage pattern observed in the area is co-linear. The prominent geomorphic units found along the coast are of younger coastal plain extending from north to south and parallel to this runs the older coastal plain, the inland areas are dominated by the pediment-pediplain complex. Anthropogenic units are identified in salt pan areas, Tuticorin port and the urbanized zones of Tuticorin. Active flood plain units form in inland area where Thamirabarani river enters the study area and eventually transforms into younger delta plains as the river drains into the Bay of Bengal. Aeolin plain with red teri sands in the Kudiramoli teri, south west inland area is another prominent geomorphic formation in the study area (Fig 1.4).

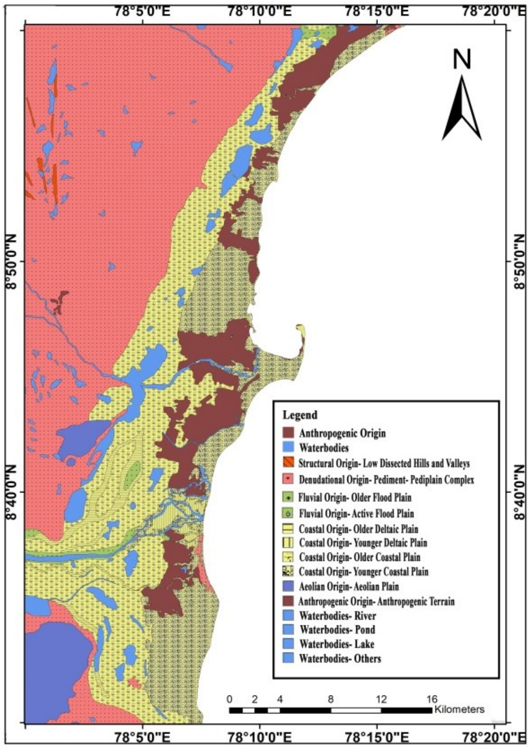


Fig 1.4: Geomorphology of the study area study area (*Source: CGWB, 2007-08)*

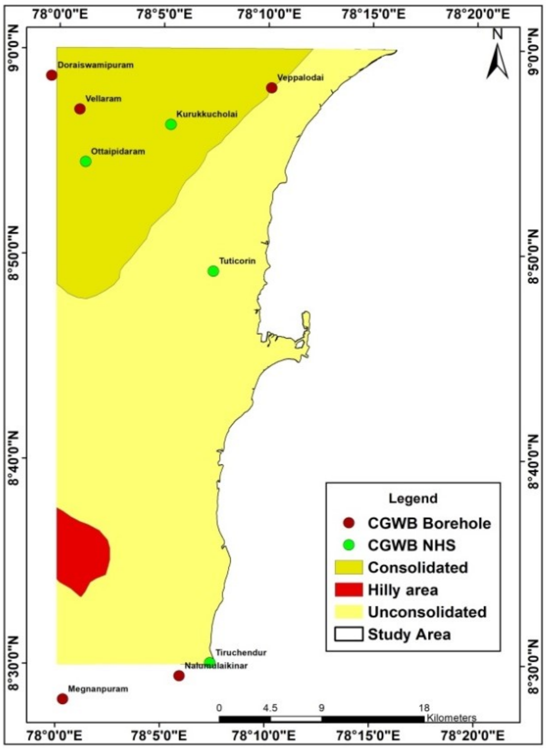


Fig 1.5: Litholog locations of the study area study area (*Source: CGWB, 2009)*

Subsurface hydrogeological units contribute to comprehensive capabilities to store and transmit groundwater and contaminants. The thickness and characteristics of subsurface geologic materials can be effectively determined by the borehole logging, which sustains in groundwater contamination remediation and placement of casing and screens in groundwater supply. Location map of the boreholes along the study area is shown in Fig 1.5. Borehole litholog of study area (Fig 1.6), Doraiswamipuram in the North Eastern inland region has weathered garnetiferous mica gneiss under the top soil followed by quartzite with pegmatite and quartzite veins. The subsurface geologic unit in Ottaipidaram under the top soil is weathered gneiss and weathered granite gneiss. Vellaram near to the north east inland area has weathered quartzite under the top soil, subsequent weathered mica gneiss, weathered granite gneiss, jointed granite are observed. The coastal borehole of Veppalodai in the northern part of the study area has sandstone and calcareous sandstone lithology, while the subsurface lithology of Naalumulaikinar in the southern tip of the study area are lateritic, kankar, dolomnitic limestone and lithomargic clay.

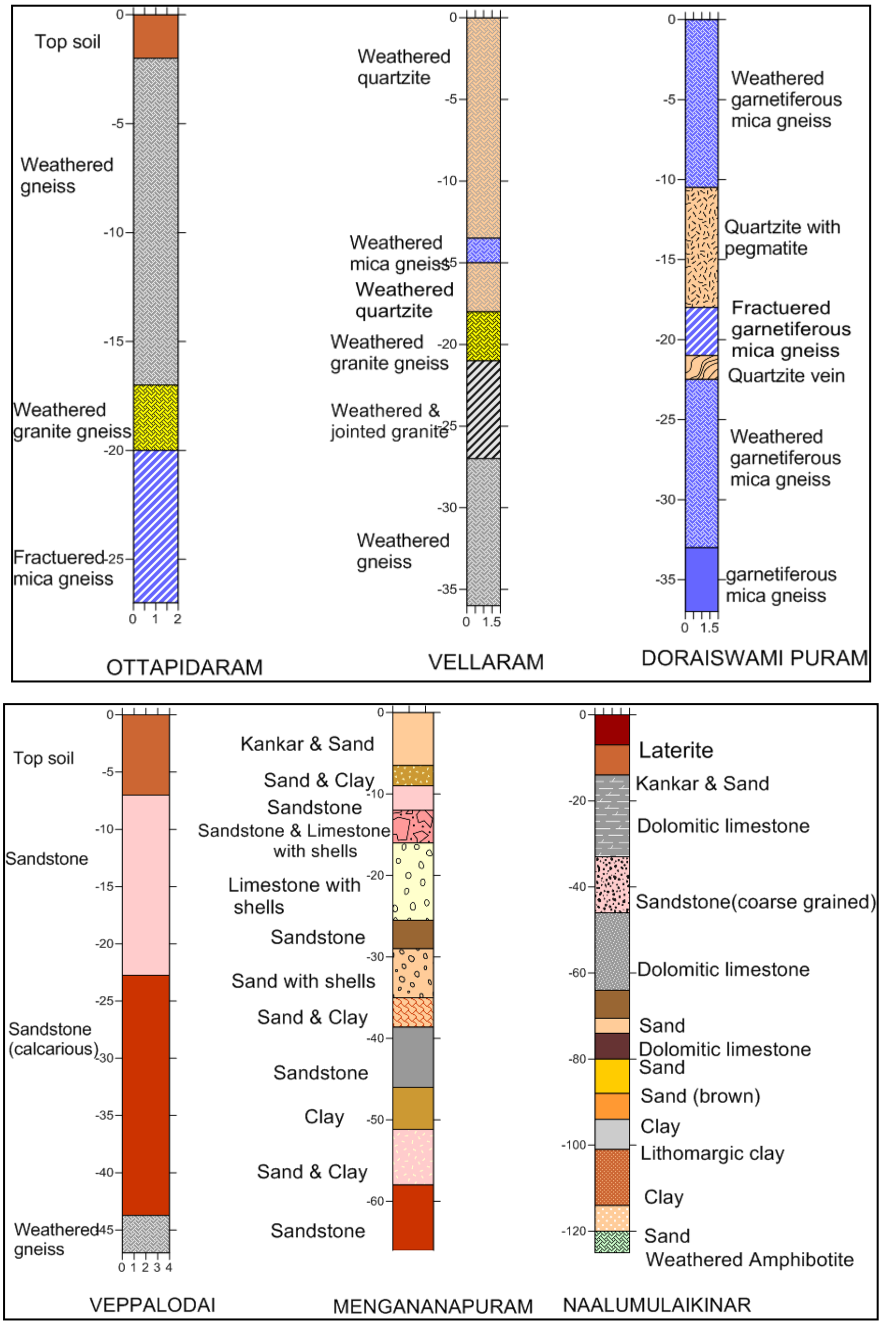


Fig 1.6: Selected litholog of the study area (*Source: CGWB, 2009*)

1.3.3 Soil texture

The prominent soil type spread across the study area are lateritic soil in Tiruchendur area, black soil in Vilathikkulam, Tuticorin and Ottaipidaram, sandy coastal alluvium in Tiruchendur, red sandy soil in Ottaipidaram. “Red Teri” is one of the indigenous soil type in Tuticorin, Kudraimoli Teri in the south eastern inland area of the study area comprises of this “Red Teri”. The soil texture for the region is procured from National Bureau of Soil Survey and Land Use Planning (NBSS & LUP, 1996).

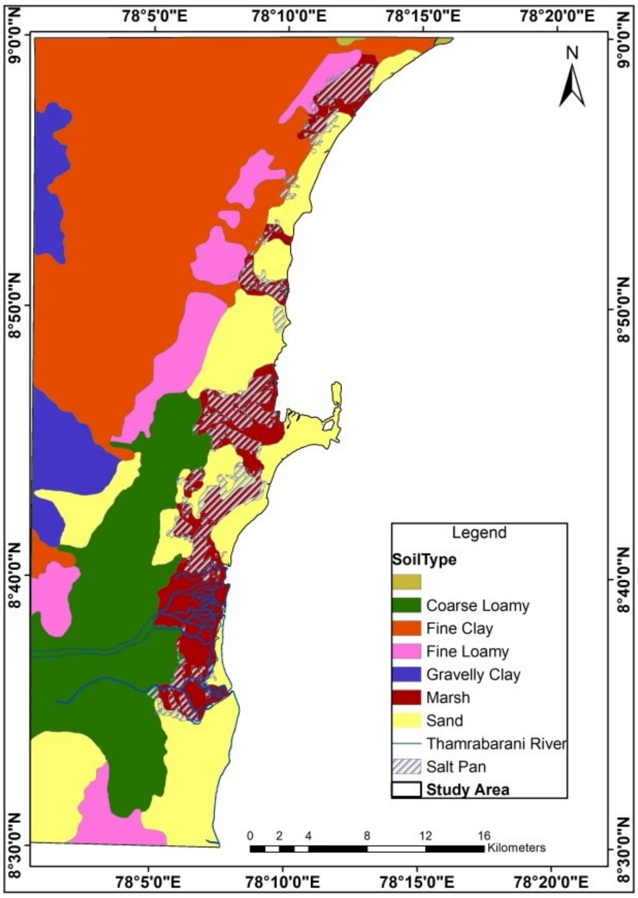


Fig 1.7: Soil texture of the study area (*Source: NBSS & LUP, 1996*)

Sandy soil texture is observed along the coast of Tuticorin from north to south with marsh texture in areas having salt pans and deltaic plain of Thamirabarani river where it drains into the Bay of Bengal (Fig 1.7). Coarse and fine loamy texture soil formations are observed in the mid region to southern inland area of the study area. The predominant soil texture observed along the north western inland area is fine clay along with patches of gravelly clay.

1.3.4 Rainfall and Climate

The study area receives the rain under the influence of both southwest and northeast monsoons; the northeast monsoon chiefly contributes to the rainfall in the district. The area is having a subtropical climate with hot and dry conditions from May to June and a pleasant climate from December to January. Various cyclonic storms due to depressions in Bay of Bengal also contribute to the Precipitation in the region.

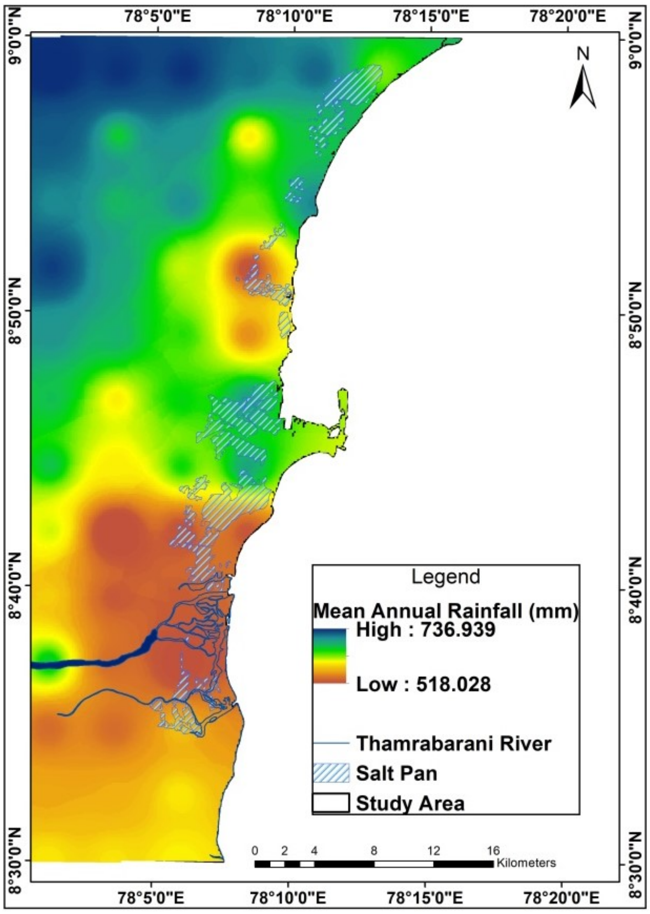


Fig 1.8: Interpolated mean annual rainfall pattern in the study area (*Source: CHRS, 2013*)

The southwest monsoon rainfall is highly erratic and summer rains are negligible. The normal annual rainfall over the district varies from about 570mm to 740mm (CGWB, 2009) (Table.1.2). Mean annual rainfall (Fig 1.8) of the study area was derived using geostatistical weighted interpolation technique from Centre for Hydrometeorology and Remote Sensing (CHRS) annual rainfall data.

Table 1.2: Range of variation in meteorological parameters in Tuticorin district (Source: CGWB, 2011)

Rainfall	570mm - 740mm
Temperature	22.9°C - 33.5°C
Humidity	68% -88%

1.3.5. Landuse/Landcover and Land Surface Temperature (LST)

LANDSAT 7 (30m, 2013) satellite data were subjected to image classification methods to delineate various landuse/landcover (LULC) pattern changes prevailing along the study area (Fig. 1.9). The classified data was iterated with ground truth to eliminate erroneous interventions, accuracy assessments for the classified images were iterated using Kappa statistics which resulted in a value of 0.89%. The landuse patterns for the study area show remarkable urbanization proliferation. Vegetated areas, water body, salt pan etc. are delineated from the classified image (Table 1.3).

Evapotranspiration, desertification and energy balance fluctuation arising in accordance with changes in land surface process is categorized through estimation of Land Surface Temperature (LST) (Peres et al. 2010). LST being sensitive to vegetation, soil moisture etc. helps in summarizing LU/LC changes like urbanization, desertification etc. LST is used globally in variety fields like climate change, hydrological cycle, vegetation monitoring, urban climate and environmental studies (Bastiaanssen et al. 1998; Kogan, 2001; Arnfield, 2003; Kalma et al. 2008; Hansen et al. 2010). Land surface temperature of the study area was summarized using the thermal band (Band 6) of LANDSAT 7 (60m) satellite (Fig 1.10).

Table 1.3: Areal extent of Landuse/Landcover of the study area

Landuse/Land Cover Class	Area in km^2-Year 2013
Settlement	55.19
Barren Land	373
Cultivated Land	15.9
Fallow Land	320
Mixed Vegetation	146
Water Body	40
Salt Pan	30
Total	**980.09**

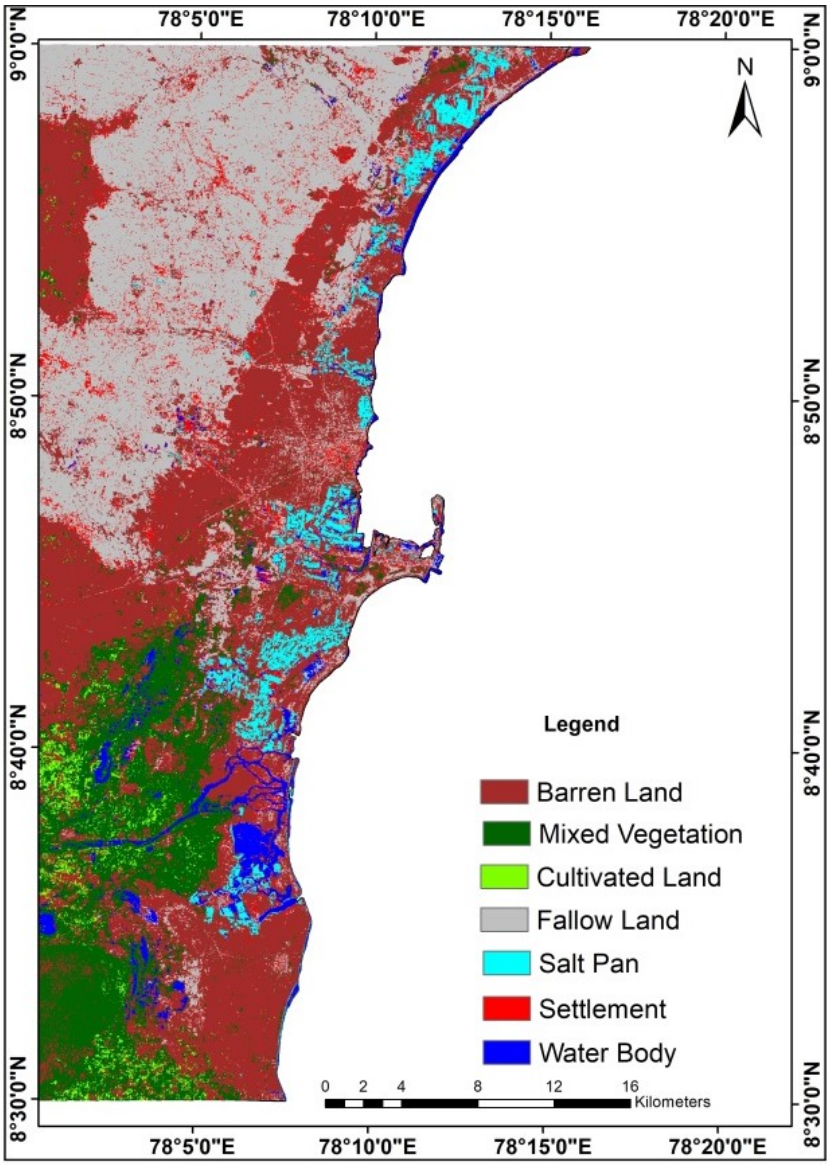


Fig 1.9: Landuse/Landcover of the study area during 2013

The Land Surface Temperature results elucidates the fact the area is receiving erratic rainfall, during the post monsoon season also many areas in the inland region is showing a temperature greater than 30^0C. The pre monsoon LST of inland areas, urbanized areas show an incremental rate atgreater than 35^0C elucidating the fact that the solitary source of water resource will be over extracted because evapotranspiration of other water resources like tanks and canals in these areas during this time scale leaves them dry.

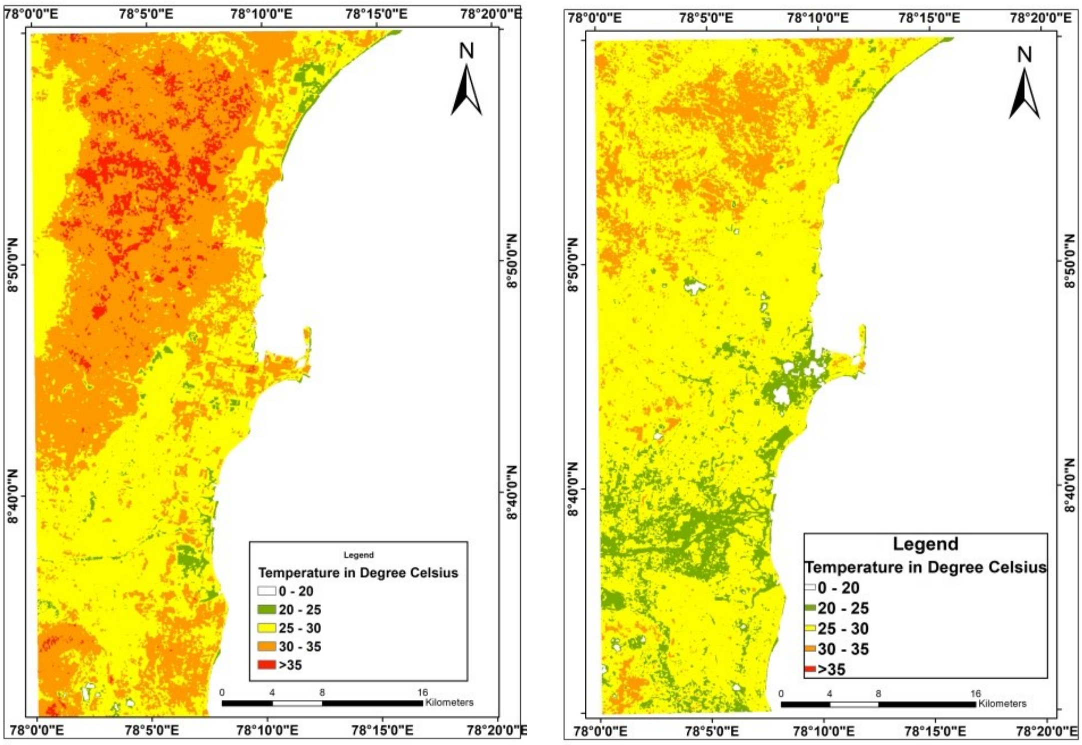


Fig 1.10: Land Surface Temperature (LST) of the study area during pre and post monsoon

1.4 Relevance of the study

The study area is characterized by salt pans along the coastal area, various industries like Sterlite, Southern Petrochemical Industries Corporation Ltd (SPIC), Tuticorin Alkali Chemicals and Fertilizers Limited (TFL), Heavy Water Plant (HWP), Thermal power plant etc. and extensive agricultural lands along Thamirabarani River. The area is facing acute shortage of drinking water supply throughout the year and is mainly depending on the groundwater to meet the daily deeds, besides; rainfall in the study area is erratic making the water scarcity much severe. Presently not much detail is available with regard to the Tuticorin coastal plain. The hydrogeochemical and isotope analysis of shallow (dug well and tube well) and deep (borewell) groundwater in the study area along with geospatial techniques will facilitate in characterization of the coastal and inland aquifers for sustainable management. The present investigation will facilitate in delineating the freshwater and saline water zones using hydrochemical and isotopic techniques. Further a detailed investigation has been carried out to appreciate the groundwater suitability and vulnerability of this region by integrating GIS and Multi Criteria Decision Making (MCDM) techniques. The present investigation will help in the sustainable management of this vital resource and suitable remedial measures to be adopted by the future planners

1.5 Objectives

A scientific evaluation of groundwater quality status using an integrated hydrogeochemical, isotopic and geospatial approach would facilitate an effective way for proper groundwater management in the study area to retard the deficit in water quality. In accordance with this, the present study envisages on the following objectives:

- To assess the hydrogeochemical characteristics of both inland and coastal aquifers of the study area through spatio-temporal analysis of the hydrogeochemical parameters.
- To investigate saline water ingress in the study area using stable isotope techniques.
- To decipher the groundwater suitability and vulnerability characteristics of the study area using Geographic Information System (GIS) based Multi Criteria Decision Making (MCDM) Technique.

******

Chapter 2

MATERIALS AND METHODS

This section of the study deals with the various methodologies and materials used for the study and is divided into four phases which comprises of (1) primary data collection (field exploration and data assortment), (2) water samplings and analytical techniques, (3) secondary data collection and geostatistical analysis and (4) intergration for a geospatial database repository creation.

2.1 Primary Data Collection

2.1.1 Field Investigation

Survey of India Toposheets (1:50000) scale was used as the base map for initial field investigation. Field reconnaissance was carried out to identify and ensure the sampling sites were true representations of the work addressed in the study. Surface geology of the study area was identified in the field (Plate 2.1.).

Plate 2.1: Kankar formation at Melthattapparai

2.1.1.1 Water sampling stations and study area

The study area was demarcated into coastal and inland areas based on the geologic characteristics (CGWB, Bhuvan) and the distance from the coast. Three major well types, Dug well, bore well and tube well was identified for the study and their locations were added to the repository using GPS aid. Samples were collected from coastal/inland alluvium and inland crystalline aquifer during pre monsoon and post monsoon season to identify the hydrochemical and isotopic temporal variations along the study area. Further, surface water, rain water and sea water samples were collected for isotopic characterization.

2.1.1.2 Water levels along coastal and inland aquifers

Water level measurements of sampling points (Plate 2.2) were recorded in-situ and a detailed inventory questionnaire was prepared to record hydrogeological scenario of the study area

Plate 2.2: Groundwater Level Monitoring

2.2 Sampling and analytical techniques

An inventory of 118 sampling sites was made and water samples were collected during pre and post monsoon season for hydrochemical investigation. Out of the 118 sampling sites identified, 40 were dug wells in the inland/coastal alluvium region, 27 tube wells in coastal/inland area, 8 dug wells 43 bore wells in the inland crystalline area. Out of the 118 groundwater samples, 71 samples were identified for isotopic investigation. The sampling procedure for hydrochemical analysis and isotopic analysis were done for pre and post monsoon season as per the American Public Health Association (APHA, 2012) standard methods for examination of water and waste water guidelines.

2.2.1 Groundwater sampling for hydrochemical investigation

Groundwater samples for hydrochemical analysis were collected from 43 bore wells, 48 dug wells and 27 tube wells in non-reactive plastic containers of two litres of capacity (Plate 2.3 and 2.4.). Insitu analysis of pH, electrical conductivity (EC) and total dissolved solids (TDS) were performed using the portable multi analyser kit. Individual sample was labelled with specific sample code, date & time. The samples were preserved under optimum condition for transportation to lab as prescribed by APHA (2012).

2.2.2 Groundwater Sampling for Bacteriological Investigation

Groundwater samples were collected for bacteriological analysis in 100 ml sterile plastic bottles according to the procedure described in APHA (MPN index) and were stored in the icebox.

2.2.3 Sampling for stable isotope investigation

Water samples for stable isotope analysis were collected in high density polyethylene bottle (HDPE) of 60 ml capacity. Samples from 25 dug wells, 29 bore well and 14 tube well, 2 surface water from Thamirabarani river and a sea water sample were collected for isotopic analysis. Temperature readings of the sample were recorded in the field. The samples are collected from the depth below the surface by using Standard Water Sampler (Ruttner 2L). Utmost care was given not to trap any air bubble inside as it may affect the isotopic signature of the sample (Plate 2.5.) by exchange of isotopic signature with air moisture**.** The samples were properly sealed and transported to isotopic facility for further investigation.

Plate 2.3: Collection of groundwater from dug well

Plate 2.4: Collection of groundwater from bore well

Plate 2.5: Groundwater samples for stable isotope analysis

Rainwater collection unit was developed and installed in the central region of the study area to harvest rainwater for stable isotope analysis. Rainwater sample is collected by using specially designed collectors. The rainwater collection unit developed and installed in the field is shown in Plate 2.6. To avoid evaporation, the collected precipitation should be transferred into a HDPE bottle and closed tightly.

Plate 2.6: Rainwater collection unit for stable isotope investigation

2.2.4 Hydrochemical analysis

All the groundwater quality parameters were analyzed as per the standard procedure proposed by American Public Health Association (APHA), 2012. Test method carried out is shown in table Table 2.1.

pH, electrical conductivity (EC) and total dissolved solids (TDS) were performed using the portable multi analyzer kit from the field itself. Total alkalinity as $CaCO_3$ is determined by using titration method. The method followed for total hardness as $CaCO_3$ is EDTA titrimetric method. Calcium is also measured by using EDTA titrimetric Method. Magnesium is obtained by calculation method that is from the difference between total and calcium hardness. Test method followed for the estimation of chloride is by Argentometric titration method. The sulphate is measured by spectrophotometer at 420 nm and the method adopted was turbidity method. The sodium and potassium is determined by using flame photometer. Ionic balance has been checked and the observed error computed on each set of complete analysis of water samples is within the range of acceptability (± 5%). The microbial analysis of water samples is by using multiple tube fermentation technique and the results are reported in the terms of the Most Probable Number (MPN) of organism present.

Table 2.1: Test method followed for various parameters

Parameters	Test Method
Total Alkalinity	APHA 2320
Total Hardness	APHA 2340
Chloride	APHA 4500 Cl
Calcium	APHA 3500 Ca
Magnesium	APHA 3500 Mg
Sulphate	APHA 4500 SO_4
Sodium	APHA 3500
Potassium	APHA 3500
Total Coliform	APHA 9221
Ecoli	APHA 9221

The statistical distribution of hydrochemical facies is analyzed by using Piper diagram, Chadhas plot and Gibbs diagram. Irrigation water quality is evaluated by using EC, TDS, soluble sodium percentage and USSL diagram. Wilcox (1955) classification on EC, TDS, soluble sodium percentage and boron is evaluated for irrigation water quality. US salinity laboratory (USSL) formulated a diagram for rating the irrigation water with reference to EC as an index for salinity hazard and Sodium Adsorbtion Ratio (SAR) as for sodium hazard. SAR is the ratio of concentration of sodium ion to that of calcium plus magnesium ions. Irrigation water quality can be determined by plotting the sodium hazard and salinity hazard value on a USSL diagram.

Multivariate statistical methods of environmental data are used to interpret the relationship among variables. Multivariate statistical analysis including factor analysis (FA), cluster analysis (CA), and correlation analysis is used to evaluate and to interpret the data. Correlation analysis and cluster analysis was carried out by using SYSTAT software and factor analysis by SPSS software. Correlation analysis was carried out by using bivariate correlation using Pearson correlation coefficient matrix. Using principal component analysis method in factor analysis (FA), varimax rotation with Kaiser-Mayer-Olkin test (KMO) was performed. In the present study Hierarchical Cluster analysis is carried out by using Ward's method applying Euclidean Distance as the similarity measure. Cluster analysis was used because a visual summary of intra-relationship amongst variations parameters can lead to a better understanding.

2.2.5 Stable Isotope Analysis

The oxygen ($\delta^{18}O$) and hydrogen (δ D) isotopes underwent equilibration using purified CO_2 and H_2 gases. This equilibrated gas of CO_2 (Epstein & Mayeda, 1953) and H_2 (Horita,1988) was analysed at the Isotope Ratio Mass Spectrometer facility at Physical Research Laboratory (PRL) to estimate the ratios of $^{18}O/^{16}O$ and D/H. Stable isotopes is represented as delta values and expressed in per mil (‰) units (mil =1000). Delta values are estimated by measuring the ratio of sample isotope against the international isotopic standard, the calibration is done by estimating the ratio between working (laboratory) standard against the international standard. The equations for calculating the δ values are cited below:

$$\delta\,(‰) = \frac{(R\ \text{sample} - R\ \text{standard})}{(R\ \text{standard})} \times 100$$

Where sample is the ratio of the heavy to the light isotope measured for the sample and R_{standard} is the equivalent for the standard.

Thus for ^{2}H,

$$\delta\,(‰) = \frac{(R\ \text{sample} - R\ \text{standard})}{(R\ \text{Standard})} \quad X100$$

$$\delta\,(‰) = \frac{[(^{2}H/H)_{\text{sample}} - (^{2}H/H)_{\text{standard}}]}{[(^{2}H/H)_{\text{standard}}]} X100$$

The stable isotopes of ($\delta^{18}O$) and hydrogen (δ D) are generally quoted to the international (Vienna Standard Mean Ocean Water) VSMOW standard. The analytical reproducibility of the results based on the repeated analyses of secondary standard is ± 0.08‰ for $\delta^{18}O$ and ± 1‰ for δ D.

2.3 Secondary Data Collection

Secondary data from various sources were procured for classification of study area based on its physiography and is listed in Table 2.2. Topographic data source for the study area was derived from SOI (Survey of India) Toposheet, physiographic data were derived from CGWB (Central Ground Water Year Book, 2007, 2008, 2009, 2011) along with ISRO geoportal (Bhuvan). Demographic and landuse pattern statistics for the study were used from Tamil Nadu Envis Centre and District Statistical Handbook.

To identify the vulnerability of groundwater resource in the study area using DRASTIC model was incorporated in the study and secondary data sources for this model is shown in Table 2.4.

Table 2.2: Secondary data source used for baseline investigation

Types of data	Layer captured	Data source
Topographic data	River/water bodies, Salt pans and roads	SOI (Survey of India) Toposheet, 1:50000, 58L/1, 58L/5 & 58L/2
Geographic data	Geology, Geomorphology Litholog and Soil	CGWB ISRO geoportal (Bhuvan)
Demographic data	Population density	Tamil Nadu Envis Centre District Statistical Handbook
Satellite data	LANDSAT 7 SRTM	USGS USGS
Aquifer Parameter Weather	Hydraulic Conductivity Rainfall	CGWB, INDIA-WRIS- http://www. indiawris. nrsc.gov.in/CHRS

2.3.1 Software used

The major software used for the study includes SPSS for statistical analysis, SYSTAT and Aquachem 12.1 for hydrochemical interpretation, ArcGIS 10.6/ open source GIS for geospatial analysis and models and Erdas Imagine 2013 for satellite image processing and classification. Superdecision software was used to derive priority scales through pairwise comparisons for suitability and vulnerability assessment.

2.4 Analysis based on geospatial techniques

Geospatial techniques adopted throughout the study were ArcGIS, Remote Sensing techniques (RS) and integration of GIS with AHP (Analytical Heirarchichal Process) and DRASTIC model. The 1:50000 scale SOI (Survey of India) Toposheets 58L/1, 58L/5 and 58L/2 were used to demarcate the base map of the study area and to extract features like road network, major drainage, salt pans etc. Satellite data from LANDSAT 7 (30 m) was used to derive the landuse/landcover pattern and thermal band to summarize the land surface temperature statistics.

2.4.1 Spatial interpolation Technique

The results from the hydrochemical and bacteriological analysis were attributed to the GPS measured geographic data collected from the field using open source mobile GIS software. Inverse Distance Weighted (IDW) technique of Geostatistical analyst extension in ArcGIS 100.6 software was further used for weighted interpolation of the attributed data for estimating the temporal ionic concentration variation and spatial distribution along the study area. The initial and resultant outputs are stored in a digital database repository for future planning and mitigation. The geospatial software used for the study comprises of ESRI's properatory GIS solution ArcGIS 10.6 and open source QGIS 1.8, Lisboa.

2.4.2. Multi criteria Decision Making (MCDM) and Aquifer Suitability

Groundwater suitability analysis for the study area (inland and coastal area) was done based on the BIS (Bureau of Indian Standards) and WHO (World Health Organization) drinking water quality standards Table 2.3. The flow chart diagram of suitability analysis is shown in Fig 2.1. The integrated application of GIS and MCDM technique is employed for groundwater in coastal and inland aquifers. The groundwater suitability was prioritized using the ANP model which was done using the super decision software developed by Thomas Saaty. The super decision software is well known for AHP and ANP analysis (Analytic Hierarchy Process and Analytic Network Process). The software does a pairwise comparison of groundwater quality parameters except bacteriological parameter within and between them to derive a normalized weight. The normalized weight obtained so is then used for reclassifying individual groundwater quality thematic layers using ArcGIS software, the reclassified images were then subjected to weighted sum overlay analysis with four classes namely good, moderate, poor and very poor. The resultant raster data for coastal and inland area of the study deciphers the groundwater suitability for sustainable management of this resource.

Table 2.3: Drinking water specification as per BIS (2012) and WHO (2011)

Parameters	BIS 2012	WHO 2011
Physical Parameters		
pH	6.5 - 8.5 No Relaxation	6.5 - 8.5
Electrical Conductivity, µs/cm	-	1500
Total Dissolved Solids, mg/l	500 (AL) 2000 (PL)	500
Chemical Parameters		
Sodium as Na^+, mg/l	-	200
Potassium as K^+, mg/l	-	12
Total Hardness as $CaCO_3$, mg/l	200 (AL) 600 (PL)	-
Calcium as Ca^{2+}, mg/l	75 (AL) 200 (PL)	75
Magnesium as Mg^{2+}, mg/l	30 (AL) 100 (PL)	50
Total alkalinity as $CaCO_3$, mg/l	200 (AL) 600 (PL)	500
Sulphate as SO_4^{2-}, mg/l	200 (AL) 400 (PL)	250
Chloride as Cl^-, mg/l	250 (AL) 1000 (PL)	250
Bacteriological Parameters		
Total Coliforms, MPN/100 ml	Shall not be detectable in any 100 ml sample(In case of large supplies, where sufficient)	-
Ecoli (Escherichia coli), MPN/100ml		

Note: As per BIS, Acceptable Limit – AL and Permissible Limit - PL in the absence of alternative source

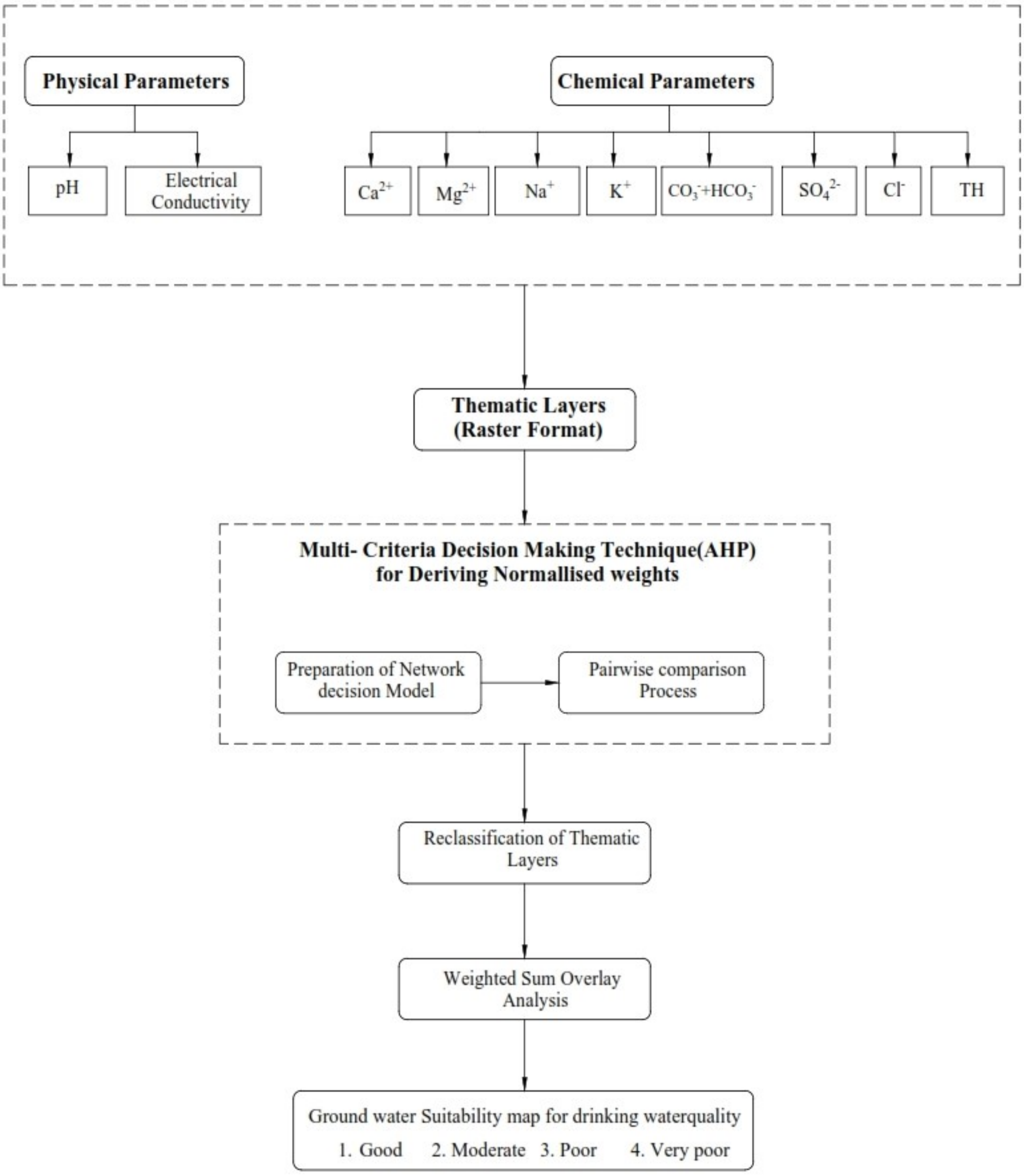


Fig 2.1: Flowchart diagram for suitability analysis

2.4.3 Vulnerability Analysis and DRASTIC

The groundwater vulnerability analysis for the study area was derived using the DRASTIC model. Various methods are available for vulnerability analysis and conceptualized mainly into three categories index, statistical and overlay method. DRASTIC is an overlay method as it covers a comprehensive region for vulnerability analysis and this method was implemented in the study. DRASTIC is the abbreviation of seven factors or layers used for the study which accounts for Depth to water table (D), Net recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of vadose zone (I), Hydraulic conductivity (C). The seven thematic layers was derived using GIS and weightage was given to these layers according to Aller et al. 1987; USEPA, 1992, these layers were subjected to weighted sum overlay analysis to derive the vulnerability map of the study area. The weights and ratings would be given to each of the seven parameters and classified in to classes on the scale of 1-10, in which 1 denotes least vulnerable while 10 is for the most vulnerable areas. This rating further scaled into weights based on the importance of the parameter in determining aquifer characteristics, these scaled on 1-5 where, 1 is least significant and 5 is most significant. The DRASTIC vulnerability index can be calculated by linear addition of the weights and rating. The equation for calculating the DI is

$$\textbf{DRASTIC Index} = \mathbf{DrDw + RrRw + ArAw + SrSw + TrTw + IrIw + CrCw}$$

where *r* is the rating value assigned to units of parameters and *w* is the weight assigned to each parameter. The data source of DRASTIC model preparation is in Table 2.4. and the flowchart of DRASTIC is shown in Figure 2.2.

The DRASTIC model was used to derive vulnerability zonation for the study area, weightage were assigned to the 7 layers by the MCDM technique using AHP. Pairwise comparison matrix was computed for the seven layers to derive the normalized weight, MCDM results were integrated with GIS using ArcMap 10.6 for deriving the vulnerability zonation of the study area. Groundwater vulnerability map developed by GIS identifies the region, most potent to groundwater contamination on the basis of hydrogeologic and anthropogenic factors. The reclassified images were subjected to weighted sum overlay analysis with four classes as very high, high medium and low vulnerable zone

Table 2.4: Data source for the preparation of DRASTIC model

Type of Layers	Data source	Data Format
Groundwater level	Field investigation	Vector
Slope	SRTM DEM	Raster
Geomorphology	CGWB, ISRO Portal	Raster
Soil texture	ICAR	Vector
Rainfall	CHRS	Raster
Litholog	CGWB	Vector
Hydraulic conductivity	CGWB, INDIA-WRIS- http://www. india wris. nrsc.gov.in/	Raster

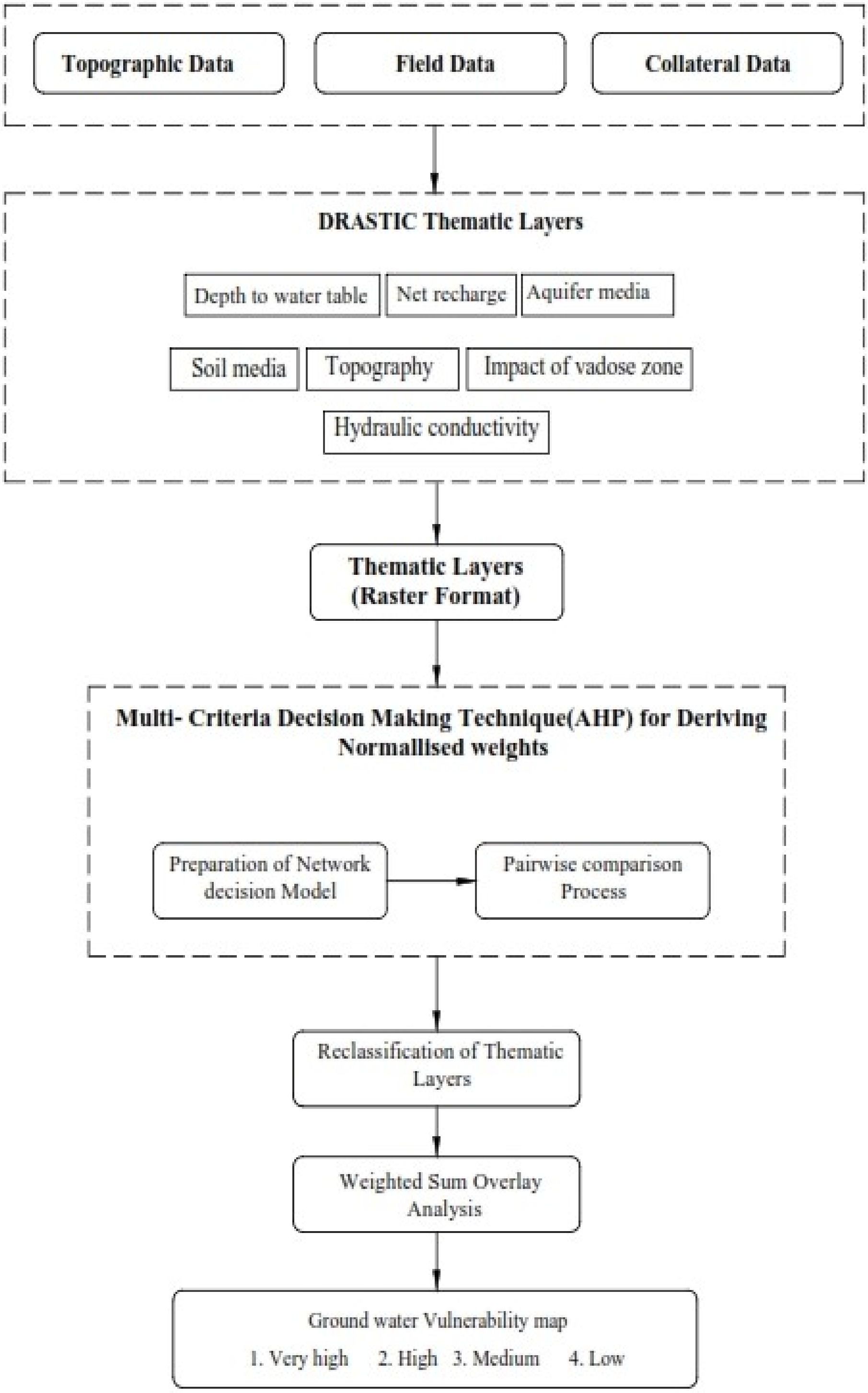


Fig 2.2: Flow chart diagram for drastic model

******

Chapter 3

HYDROGEOCHEMISTRY OF COASTAL AND INLAND AQUIFERS

3.1 Introduction

Water being an excellent solvent has the capability to dissolute various chemical constituents with it. Generally, high concentrations of dissolved constituents are found in groundwater than surface water because of its greater exposure to soluble minerals of the geological formations (Todd, 1980). Seven solutes make up nearly 95 percent of all water solutes in groundwater (Runnells, 1993; Herczeg and Edmunds, 1999). These solutes are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^{-}). Natural and anthropogenic effects including local climate, geology and irrigation practices (Ramesh & Elango, 2011) influence water quality. Groundwater formation gives a thrust in the variation of these chemical constituents in it as it moves through various rock materials and subsurface soil. The quality of groundwater is affected by both natural and anthropogenic activities, which differs its quality by varying geographic conditions. Anthropogenic activities escalates the ionic enrichment of groundwater leading to groundwater quality depletion. Acid-base reactions, oxidation-reduction reactions, temperature changes, influence of gaseous matter and the residual time in rock soluble aquifers are some of the natural factors that decide the providence of groundwater quality. World Health Organization and other standardisation agencies of various countries (BIS; WHO) have formulated the water quality standards for potability, agriculture and industrial uses. Water in our nearby well is not safe enough to drink without evaluation the quality of water.

Water quality analysis ascertains the spatial variations in water quality and helps in classifying the suitability of water for various uses. In hydrology water, analysis results are widely used in creating spatial distribution maps. These maps serves in the initial assessment for the relationship between aquifer mineralogy and groundwater composition. Geochemical characteristics of groundwater helps hydrogeologists in determining the physical properties of flow system. Frequent hydrogeochemical work is carried out round the globe as groundwater is of higher quality, less subject to seasonal and perennial fluctuations and much more uniformly spread over large regions than surface water.

India is one of the highest groundwater abstractors in the world and Tuticorin is one among the highest groundwater abstractors in India. Coastal areas of Tuticorin mainly rely on groundwater for meeting their domestic, agricultural and industrial water needs. Hence, a detailed study on physico chemical quality of the study area has been taken up in estimating groundwater quality and its evolution.

3.2 Spatio-temporal variations of physicochemical parameters

The quality of groundwater is depended on both spatial and temporal variations. Studies from the past supplements the fact that regional changes may impart their effects on major physicochemical parameters like pH, conductivity, total dissolved solids and major ions. Geographical location and anthropogenic activities such as landuse change, intensive irrigated agriculture, urbanization, disposal of untreated sewage in river, lack of rational management, etc. influences the quality of underlying groundwater (Voudouris, 2009). Studies on groundwater quality over various agro-climatic regions in India depicts the influence of climate on ion enrichment in these water sources (Lawrence et al. 2000; Umar and Sami Ahmed, 2000; Ahmed et al. 2002; Rajesh and Murthy, 2004). Insitu physical parameters such as pH, conductivity and total dissolved solids supplemented with the major ion analyses acts as a guide in understanding the importance of sampling the specified source of groundwater. Physical parameters and ionic concentration range is shown in Table 3.1 and 3.2.

The study area lies in the south eastern coast of India comprising of one of the major port Tuticorin District. The area is subdivided into two as inland and coastal aquifers depending on the type of underlying geologic formation and distance from the coast. Physico chemical parameters for 118 wells were analysed for pre monsoon and post monsoon season, out of which 40 dug wells and 27 tube wells were in coastal/inland alluvial region, 8 dug wells and 43 bore wells in the inland crystalline region. This classification of wells and sampling helped in elucidating the spatio-temporal behaviour of groundwater quality in the study area. The spatial distribution of sampling sites across the aquifers are shown in the figure 3.1. Hydrochemical data of groundwater for pre monsoon and post monsoon seasons are shown in the Table 3.3. and Table 3.4 respectively.

Table 3.1: Statistics of physico chemical parameters in groundwater during pre monsoon season

Well Type	pH	EC	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	$HCO_3^-+CO_3^-$	SO_4^{2-}	Cl^-
		µs/cm	mg/l							
Coastal/inland alluvial dug well										
Average	7.80	2681.87	1971.61	352.88	52.31	69.56	61.27	336.63	400.38	521.10
Max	8.60	11480.00	8150.80	2213.00	296.00	609.00	281.88	927.20	2011.23	3748.84
Min	7.09	294.41	293.00	29.00	4.00	12.00	7.29	158.60	23.13	24.99
Coastal/inland alluvial tube well										
Average	7.73	4039.51	2868.88	866.82	285.10	88.63	91.73	403.05	418.06	644.98
Max	8.60	45619.20	32400.00	14520.00	6480.00	840.00	1336.50	902.80	4316.11	4798.51
Min	7.03	543.49	386.00	53.00	3.00	12.00	4.86	97.60	17.18	29.99
Inland bore well										
Average	7.58	2712.99	1929.03	302.75	23.14	113.08	63.36	269.39	647.04	299.25
Max	8.75	9623.68	6835.00	1337.00	106.00	480.00	252.72	585.60	4363.73	1309.59
Min	6.83	421.00	298.91	46.00	2.00	12.00	2.43	73.20	25.12	19.99
Inland dug well										
Average	7.99	1985.10	1503.46	276.25	19.88	68.00	50.73	265.35	456.67	315.53
Max	8.56	5670.00	4025.70	870.00	39.00	200.00	184.68	707.60	2417.98	1599.50
Min	7.58	1.41	293.00	30.00	2.00	12.00	2.43	146.40	35.04	19.99

Table 3.2: Statistics of physico chemical parameters in groundwater during post monsoon season

Well Type	pH	EC	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	$HCO_3^-+CO_3^-$	SO_4^{2-}	Cl^-
		µs/cm	mg/l							
Coastal/inland alluvial dug well										
Average	7.49	1871.03	1197.46	283.16	46.61	65.66	42.97	232.18	160.16	356.51
Max	8.43	7922.29	5070.26	1567.50	288.00	330.00	191.36	1006.50	1364.66	2399.26
Min	6.93	295.24	188.96	10.50	3.75	1.50	3.65	54.90	9.36	15.00
Coastal/inland alluvial tube well										
Average	7.31	2174.46	1391.66	291.90	39.97	81.56	71.50	290.72	258.40	352.64
Max	8.00	12602.19	8065.40	1161.00	232.50	780.00	965.25	640.50	2898.89	2211.81
Min	6.80	323.48	207.02	20.63	0.75	6.00	1.82	82.35	13.09	15.00
Inland bore well										
Average	7.19	1473.50	943.04	224.03	15.98	68.02	31.95	188.86	159.12	230.23
Max	8.05	6212.28	3975.86	1698.00	96.25	315.00	145.80	549.00	1038.77	1724.47
Min	6.75	298.41	190.98	18.75	0.75	3.00	1.82	36.60	0.08	7.50
Inland dug well										
Average	7.41	1451.13	928.72	219.15	13.59	84.00	56.19	157.33	91.02	302.81
Max	7.71	5585.07	3574.44	1204.50	33.00	255.00	191.36	384.30	294.72	1649.49
Min	7.12	267.43	171.16	13.50	0.75	3.00	0.91	54.90	18.71	7.50

Table 3.3: Hydrochemical analytical results of groundwater samples of Tuticorin area (pre monsoon)

Coastal/inland alluvial dug well										
Well No.	EC	pH	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	$HCO_3^-+CO_3^-$	SO_4^{2-}	Cl^-
	(µs/cm)		(mg/l)							
DW1	2710.00	7.62	1924.10	42.00	10.00	40.00	9.72	195.20	74.72	59.98
DW2	2650.00	7.45	1881.50	236.00	27.00	160.00	63.18	170.80	189.80	599.81
DW4	1098.24	7.49	780.00	94.00	20.00	16.00	38.88	390.40	82.66	129.96
DW5	1630.00	7.71	1157.30	262.00	14.00	12.00	24.30	427.00	94.56	289.91
DW6	2097.92	7.94	1490.00	281.00	26.00	56.00	19.44	585.60	94.56	409.87
DW7	1892.00	7.62	1343.32	199.00	15.00	20.00	72.90	524.60	169.96	249.92
DW8	2230.00	7.68	1583.30	174.00	58.00	16.00	38.88	292.80	132.26	409.87
DW9	816.64	8.39	580.00	73.00	32.00	20.00	24.30	219.60	102.50	94.97
DW10	2280.96	7.69	1620.00	377.00	170.00	72.00	63.18	244.00	162.02	529.84
DW11	3027.20	8.60	2150.00	370.00	234.00	32.00	58.32	927.20	275.12	249.92
DW12	723.71	7.89	514.00	56.00	14.00	24.00	14.58	170.80	58.85	64.98
DW13	2154.24	7.69	1530.00	285.00	15.00	16.00	26.73	634.40	150.12	209.93
DW14	1915.00	7.94	1359.65	270.00	41.00	20.00	46.17	427.00	187.82	349.89

DW15	2749.82	7.80	1953.00	377.00	65.00	88.00	97.20	244.00	574.72	479.85
DW16	643.46	7.70	457.00	62.00	15.00	24.00	14.58	183.00	42.98	64.98
DW17	1360.13	8.16	966.00	139.00	44.00	32.00	48.60	463.60	94.97	64.98
DW18	795.52	7.57	565.00	61.00	25.00	44.00	21.87	219.60	74.72	104.97
DW19	680.06	7.52	483.00	63.00	11.00	32.00	26.73	158.60	72.74	109.97
DW20	689.92	8.22	490.00	78.00	4.00	20.00	17.01	195.20	64.80	104.97
DW21	858.88	7.09	610.00	84.00	12.00	36.00	14.58	256.20	62.82	134.96
DW22	822.27	7.51	584.00	87.00	11.00	16.00	26.73	317.20	23.13	84.97
DW23	872.96	8.09	620.00	66.00	36.00	28.00	38.88	207.40	146.15	89.97
DW24	2518.91	7.83	1789.00	454.30	17.30	128.26	53.46	596.65	190.00	650.00
DW25	2550.00	7.32	1810.50	357.00	12.00	64.00	72.90	195.20	566.79	539.83
DW26	1154.00	7.56	819.34	77.00	30.00	36.00	24.30	256.20	90.60	94.97
DW28	11480.00	8.34	8150.80	2213.00	93.00	120.00	170.10	292.80	709.64	3748.84
DW29	670.21	8.24	476.00	46.00	10.00	40.00	12.15	244.00	62.82	24.99
DW30	946.18	8.13	672.00	29.00	14.00	104.21	17.01	234.31	169.24	98.00
DW31	765.95	7.63	544.00	76.00	21.00	24.00	7.29	195.20	132.26	84.97
DW32	5617.92	7.80	3990.00	276.00	130.00	609.00	150.00	487.95	2000.00	422.00
DW33	9820.00	8.01	6972.20	905.00	296.00	160.00	243.00	683.20	1856.47	1799.44
DW34	1563.00	7.71	1109.73	103.00	4.00	120.00	77.76	219.60	419.96	164.95
DW42	5275.78	7.56	3747.00	449.00	122.00	104.00	218.70	219.60	1503.29	539.83
DW43	5424.41	7.85	5423.00	1419.00	73.00	16.00	63.18	707.60	2011.23	999.69
DW44	294.41	7.67	293.00	52.00	25.00	20.00	7.29	195.00	56.87	49.98
DW45	3564.41	7.58	3563.00	785.00	52.00	160.00	145.80	512.40	412.02	1299.60
DW46	7580.00	7.71	5381.80	1010.00	76.00	192.00	281.88	219.60	1368.37	1799.44
DW47	9567.36	7.55	6795.00	1792.00	179.00	12.80	11.66	195.20	987.42	3248.99
DW48	2555.52	7.63	1815.00	222.00	27.00	12.00	46.17	366.00	255.28	239.93
DW49	1227.78	8.43	872.00	114.00	12.00	36.00	41.31	190.32	290.99	149.95
Coastal/inland alluvial tube well										
Well No.	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**$HCO_3^-+CO_3^-$**	**SO_4^{2-}**	**Cl^-**
	(µs/cm)		**(mg/l)**							
TT 1	2107.78	7.30	1497.00	269.00	34.00	88.00	43.74	219.60	342.58	499.85
TT 2	1178.00	8.32	836.38	136.00	3.00	40.00	36.45	302.56	108.45	159.95
TT 3	3935.36	7.20	2795.00	829.00	103.00	24.00	4.86	902.80	511.23	409.87
TT 4	9502.59	7.37	6749.00	1540.00	39.00	200.00	194.40	146.40	1757.26	2749.15
TT 5	2328.83	8.46	1654.00	461.00	105.00	40.00	14.58	463.60	237.42	289.91
TT 6	823.68	7.68	585.00	101.00	14.00	12.00	9.72	341.60	52.90	44.99
TT 7	4153.35	7.54	2949.82	848.25	12.75	250.00	200.47	109.20	130.61	1599.01
TT 8	10700.80	7.03	7600.00	857.00	18.00	840.00	243.00	341.60	1967.58	3049.05
TT 9	2837.12	7.12	2015.00	373.00	48.00	175.00	26.00	448.00	311.00	710.00
TT 10	858.88	8.04	610.00	126.00	16.00	20.00	7.29	329.40	54.88	49.98
TT 11	1112.00	7.98	789.52	109.00	9.00	64.00	17.01	97.60	52.90	184.94

TT 12	543.49	7.38	386.00	78.00	8.00	20.00	12.15	209.84	17.18	39.99
TT 13	2640.00	7.70	1874.40	351.00	149.00	24.00	19.44	780.80	114.40	349.89
TT 14	971.52	7.61	690.00	163.00	11.00	20.00	19.44	292.80	76.71	99.97
TT 15	2069.76	7.76	1470.00	320.00	19.00	12.00	4.86	878.40	138.21	94.97
TT 16	1365.76	7.35	970.00	109.00	47.00	68.00	26.73	512.40	94.56	109.97
TT 17	2013.44	7.81	1430.00	334.00	18.00	12.00	17.01	805.20	112.42	129.96
TT18	3013.12	7.89	2140.00	496.00	299.00	40.00	14.58	732.00	88.61	459.86
TT 19	2380.00	7.61	1689.80	319.00	101.00	40.00	58.32	97.60	234.00	449.86
TT 20	815.23	7.76	579.00	57.00	7.00	44.00	29.16	199.20	175.91	114.96
TT 21	2656.90	7.67	1887.00	166.00	61.00	16.00	41.31	463.60	80.67	399.88
TT 22	2110.00	7.62	1498.10	421.00	30.00	24.00	38.88	463.60	118.37	269.92
TT 23	929.28	7.95	660.00	138.00	11.00	16.00	19.44	329.40	86.63	109.97
TT 24	1051.78	7.95	747.00	158.00	11.00	12.00	7.29	378.20	27.10	114.96
TT 25	668.80	8.33	475.00	72.00	24.00	24.00	9.72	244.00	19.17	29.99
TT 26	680.00	7.79	482.80	53.00	20.00	28.00	24.30	183.00	60.83	94.97
TT27	45619.20	8.60	32400.00	14520.00	6480.00	848.00	1336.50	610.00	4316.11	4798.51
Inland bore well										
Well No.	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-+CO_3^-**	**SO_4^{2-}**	**Cl^-**
	(µs/cm)		**(mg/l)**							
TB 1	1807.87	8.30	1284.00	253.00	95.00	12.00	7.29	402.60	380.28	104.97
TB 2	663.17	7.87	471.00	46.00	9.00	20.00	31.59	207.40	74.72	39.99
TB 3	1405.18	7.75	998.00	199.00	11.00	20.00	19.44	500.20	142.18	79.98
TB 4	1584.00	7.78	1124.64	209.00	10.00	36.00	31.59	353.80	247.34	169.95
TB 5	1299.58	7.93	923.00	186.00	2.00	12.00	9.72	488.00	164.01	54.98
TB 6	1716.35	7.79	1219.00	180.00	19.00	92.00	51.03	366.00	330.67	179.94
TB 7	653.31	7.34	464.00	75.00	2.00	16.00	9.72	207.40	102.50	24.99
TB 8	1137.00	7.65	807.27	169.00	13.00	12.00	36.45	268.40	199.72	19.99
TB 9	577.28	7.68	410.00	47.00	6.00	20.00	21.87	183.00	74.72	49.98
TB 10	2140.00	6.83	1519.40	73.00	34.00	232.00	48.60	268.40	98.53	409.87
TB 11	619.52	7.34	440.00	88.00	13.00	16.00	9.72	122.00	130.28	29.99
TB 12	1154.00	6.90	819.34	62.00	58.00	24.00	65.61	122.00	68.77	164.95
TB 13	3490.00	7.36	2477.90	255.00	9.00	360.00	58.32	122.00	356.47	1029.68
TB 14	1140.48	7.46	810.00	138.00	66.00	16.00	4.86	317.20	183.85	74.98
TB 16	9623.68	7.07	6835.00	1337.00	20.00	480.00	252.72	170.80	3264.52	1309.59
TB 18	1196.80	7.66	850.00	187.00	4.00	20.00	2.43	439.20	126.31	44.99
TB 19	9292.80	7.09	6600.00	1120.00	13.00	256.00	184.68	195.20	4133.57	649.80
TB 20	1163.00	7.54	825.73	127.00	4.00	40.00	36.45	126.88	352.50	104.97
TB 21	985.60	7.27	700.00	150.00	11.00	12.00	9.72	451.40	25.12	39.99

TB 22	9335.04	7.67	6630.00	805.00	24.00	432.00	238.14	244.00	4363.73	519.84
TB 23	5068.80	7.90	3600.00	652.00	11.00	64.00	106.92	341.60	2116.39	299.91
TB 24	3322.88	8.75	2360.00	530.00	106.00	48.00	38.88	585.60	459.64	499.85
TB 25	1840.00	8.37	1306.40	258.00	11.00	44.00	43.74	402.60	237.42	59.98
TB 26	1265.79	7.80	899.00	190.00	4.00	16.00	21.87	424.56	54.88	184.94
TB 27	4576.00	8.24	3250.00	618.00	33.00	120.00	72.90	195.20	1691.79	499.85
TB 28	5380.00	7.30	3819.80	714.00	72.00	280.00	170.10	366.00	546.94	129.96
TB 29	2490.00	7.44	1767.90	337.00	59.00	72.00	48.60	170.80	138.21	339.89
TB 30	2230.00	7.31	1583.30	162.00	14.00	232.00	111.78	170.80	535.04	169.95
TB 31	1177.09	7.34	836.00	72.00	11.00	96.00	48.60	280.60	243.37	79.98
TB 32	3124.35	7.42	2219.00	280.00	33.00	168.00	24.30	170.80	231.47	1299.60
TB 33	1184.00	7.50	840.64	161.00	14.00	20.00	17.01	370.88	80.67	79.98
TB 34	1350.00	7.25	958.50	60.00	5.00	164.00	60.75	85.40	62.82	49.98
TB 35	1676.93	7.26	1191.00	163.00	12.00	84.00	51.03	122.00	616.39	79.98
TB 36	3717.12	7.36	2640.00	426.00	22.00	136.00	92.34	146.40	1479.48	309.90
TB 37	3370.00	7.64	2392.70	359.00	13.00	184.00	131.22	170.80	660.04	519.84
TB 39	3160.00	8.00	2243.60	538.00	12.00	40.00	72.90	439.20	552.90	449.86
TB 40	680.06	7.42	483.00	46.00	22.00	24.00	21.87	195.20	64.80	79.98
TB 41	4720.00	7.46	3351.20	201.00	24.00	456.00	194.40	170.80	773.13	1269.61
TB 42	2175.00	7.71	1566.00	337.00	30.00	73.74	38.39	157.00	138.00	580.00
TB 43	796.93	7.07	566.00	71.00	12.00	52.00	17.01	268.40	74.72	64.98
TB 44	3567.87	7.81	2534.00	462.00	11.00	64.00	97.20	366.00	1239.40	289.91
TB 45	421.00	8.05	298.91	49.00	11.00	28.00	7.29	73.20	29.09	79.98
TB 46	8380.00	7.23	6033.00	626.45	30.00	268.70	105.24	354.16	976.45	346.36
Inland dug well										
Well No.	**EC**	**pH**	**TDS**	**Na$^+$**	**K$^+$**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-+CO_3^-**	**SO_4^{2-}**	**Cl$^-$**
	(µs/cm)		**(mg/l)**							
DW3	2846.98	7.79	2022.00	491.00	39.00	80.00	48.60	707.60	209.64	439.86
DW27	5670.00	7.92	4025.70	870.00	23.00	200.00	121.50	170.80	721.55	1599.50
DW35	1.41	7.89	459.00	51.00	27.00	24.00	17.01	195.20	50.91	74.98
DW36	1.41	8.56	293.00	30.00	2.00	16.00	2.43	146.40	70.75	24.99
DW37	523.78	8.24	372.00	48.00	9.00	12.00	4.86	183.00	84.64	19.99
DW38	695.55	8.33	494.00	39.00	23.00	48.00	12.15	280.60	35.04	54.98
DW40	791.30	7.58	562.00	51.00	18.00	36.00	14.58	292.80	62.82	49.98
DW41	5350.40	7.61	3800.00	630.00	18.00	128.00	184.68	146.40	2417.98	259.92

Table 3.4: Hydrochemical analytical results of groundwater samples of Tuticorin area (post monsoon)

Coastal/inland alluvial dug well										
Well No.	EC	pH	TDS	Na^+	K^+	Ca^{2+}	Mg^{2+}	$HCO_3^-+CO_3^-$	SO_4^{2-}	Cl^-
	(µs/cm)		(mg/l)							
DW1	404.67	7.35	258.99	77.25	9.00	27.00	4.56	73.20	29.25	33.74
DW2	2446.94	7.35	1566.04	340.50	33.00	165.00	45.56	109.80	81.92	787.26
DW4	662.22	7.25	423.82	50.25	3.75	10.50	30.07	219.60	30.67	74.98
DW5	1226.25	7.40	784.80	207.75	12.75	10.50	18.23	274.50	48.89	206.19
DW6	1195.67	7.84	765.23	183.00	19.50	15.00	21.87	237.90	37.28	243.67
DW7	2240.76	7.52	1434.09	297.00	22.50	15.00	54.68	512.40	156.63	374.88
DW8	3013.23	7.59	1928.47	361.50	288.00	30.00	18.23	311.10	162.88	749.77
DW9	596.59	7.83	381.82	63.75	31.50	18.00	19.14	155.55	22.40	67.48
DW10	2242.87	7.64	1435.44	231.00	114.00	270.00	91.13	292.80	56.63	374.88
DW11	4272.31	8.43	2734.28	542.25	91.50	105.00	45.56	1006.50	440.56	284.91
DW12	299.56	7.64	191.72	28.50	8.25	1.50	7.29	100.65	10.29	26.24
DW13	1410.95	7.21	903.01	265.50	18.00	15.00	7.29	366.00	102.76	127.46
DW14	2374.56	7.81	1519.72	276.00	31.50	30.00	54.68	457.50	250.67	412.37
DW15	1691.67	7.52	1082.67	195.00	73.50	45.00	45.56	183.00	274.19	262.42
DW16	579.58	7.32	370.93	66.00	12.75	22.50	9.11	82.35	59.01	116.21
DW17	1182.57	7.91	756.85	43.50	51.00	18.00	11.85	521.55	29.72	71.23
DW18	523.95	7.31	335.33	31.50	21.75	37.50	4.56	183.00	22.28	33.74
DW19	578.14	7.43	370.01	60.75	6.00	12.00	13.67	128.10	45.02	97.47
DW20	1461.54	7.63	935.39	240.75	7.50	13.50	6.38	448.35	46.21	168.70
DW21	599.36	6.93	383.59	87.75	17.25	10.50	11.85	118.95	31.33	104.97
DW22	521.50	7.50	333.76	64.50	9.00	13.50	3.65	173.85	9.78	52.48
DW23	699.87	7.30	447.92	53.25	37.50	31.50	13.67	118.95	132.82	56.23
DW24	1880.59	7.70	1203.58	298.50	4.50	45.00	36.45	237.90	124.36	449.86
DW25	1971.76	7.09	1261.92	300.00	9.75	60.00	82.01	146.40	209.90	449.86
DW26	566.16	7.05	362.34	51.00	12.00	49.50	16.40	82.35	58.11	89.97
DW28	7922.29	7.99	5070.26	1567.50	59.25	330.00	109.35	329.40	271.51	2399.26
DW29	295.24	8.06	188.96	10.50	9.00	16.50	3.65	118.95	9.36	15.00
DW30	384.70	7.43	246.21	18.75	8.25	21.00	11.85	128.10	17.52	33.74
DW31	739.34	7.55	473.18	67.50	15.00	21.00	11.85	173.85	63.77	116.21

DW32	3436.30	7.07	2199.23	190.50	66.00	195.00	100.24	54.90	1364.66	224.93
DW33	3692.65	7.21	2363.30	360.00	285.00	90.00	118.46	292.80	373.29	839.74
DW34	644.74	7.62	412.63	66.00	9.00	33.00	17.31	82.35	71.51	127.46
DW42	2825.33	7.11	1808.21	340.50	109.50	105.00	173.14	219.60	291.15	562.33
DW43	3822.79	7.45	2446.58	847.50	39.00	30.00	63.79	256.20	534.31	674.79
DW44	635.41	7.48	406.67	73.50	21.75	19.50	7.29	118.95	46.21	112.47
DW45	3817.89	7.55	2443.45	646.50	46.50	180.00	164.02	219.60	245.61	937.21
DW46	2775.42	7.32	1776.27	1057.50	81.00	210.00	191.36	164.70	46.21	22.49
DW47	6687.95	7.45	4280.29	1254.00	126.00	240.00	36.45	201.30	350.67	2061.86
DW48	1290.99	7.44	826.23	244.50	30.00	25.50	28.25	173.85	110.20	209.93
DW49	1227.06	7.43	785.32	165.00	13.50	39.00	8.20	210.45	136.98	206.19
Coastal/inland alluvial tube well										
Well No.	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**$HCO_3^-+CO_3^-$**	**SO_4^{2-}**	**Cl^-**
	(µs/cm)		**(mg/l)**							
TT 1	462.96	7.25	296.29	50.25	9.00	18.00	11.85	146.40	34.31	22.49
TT 2	783.13	7.01	501.20	123.00	8.25	22.50	7.29	201.30	55.14	78.73
TT 3	7356.55	7.15	4708.19	395.25	42.00	13.50	3.00	492.75	282.00	216.75
TT 4	1784.47	7.07	1142.06	1161.00	40.50	150.00	173.14	274.50	1056.63	1844.43
TT 5	1346.65	7.35	861.85	432.75	9.75	45.00	45.56	292.80	232.22	74.98
TT 6	4168.39	7.48	2667.77	246.00	11.25	13.50	12.76	256.20	114.96	206.19
TT 7	7536.47	7.01	4823.34	708.00	19.50	390.00	218.70	164.70	110.20	1049.67
TT 8	2367.00	6.80	1514.88	1027.50	28.50	270.00	173.14	109.80	998.59	2211.81
TT 9	510.80	7.10	326.91	269.25	34.50	120.00	9.11	329.40	224.78	524.84
TT 10	481.39	7.12	308.09	66.00	14.25	21.00	1.82	155.55	35.79	22.49
TT 11	323.48	7.37	207.02	54.75	2.25	30.00	2.73	109.80	25.08	82.47
TT 12	688.50	7.20	440.64	20.63	0.75	18.00	12.76	100.65	17.25	29.99
TT 13	1260.01	7.57	806.41	344.25	120.75	12.00	25.52	585.60	137.82	262.42
TT 14	751.93	6.96	481.24	74.25	16.50	36.00	2.73	118.95	105.73	82.47
TT 15	1497.91	7.68	958.66	188.25	26.25	6.00	10.94	484.95	32.79	56.23
TT 16	1939.35	7.30	1241.18	72.75	30.00	24.00	16.40	219.60	40.26	71.23
TT 17	1982.99	7.80	1269.12	284.25	12.00	7.50	5.47	503.25	44.72	97.47
TT 18	524.43	7.18	335.64	324.00	214.50	60.00	36.45	457.50	104.25	37.49
TT 19	1091.89	7.41	698.81	282.00	77.25	30.00	54.68	384.30	136.98	299.91
TT 20	1892.57	7.38	1211.24	45.75	11.25	19.50	22.78	118.95	50.67	63.73

TT 21	1048.81	7.36	671.24	143.25	47.25	12.00	35.54	256.20	58.11	142.46
TT 22	902.79	7.59	577.79	199.50	21.75	15.00	45.56	640.50	73.00	209.93
TT 23	417.46	7.33	267.18	117.75	20.25	12.00	8.20	411.75	34.31	59.98
TT 24	384.28	7.40	245.94	123.75	9.75	13.50	10.02	265.35	35.20	116.21
TT 25	12602.19	7.08	8065.40	35.25	10.50	33.00	9.11	137.25	24.07	15.00
TT26	2330.24	7.46	1491.35	30.75	8.25	30.00	10.02	82.35	13.09	67.48
TT27	2273.83	8.00	1455.25	1061.25	232.50	780.00	965.25	549.00	2898.89	1574.51
Inland bore well										
Well No.	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**$HCO_3^-+CO_3^-$**	**$SO4^{2-}$**	**Cl^-**
	(µs/cm)		**(mg/l)**							
TB1	1470.56	8.05	941.16	93.00	4.50	75.00	36.45	549.00	66.75	112.47
TB2	919.74	7.19	588.63	96.75	12.00	28.50	13.67	164.70	173.29	93.72
TB3	803.35	7.39	514.14	99.75	8.25	18.00	3.65	301.95	53.06	22.49
TB4	828.42	7.07	530.19	154.50	2.25	7.50	12.76	210.45	104.25	37.49
TB5	1346.85	7.35	861.98	180.00	4.50	39.00	3.65	192.15	293.23	142.46
TB6	359.97	7.52	230.38	18.75	10.50	16.50	13.67	137.25	7.22	22.49
TB7	485.60	7.11	310.78	46.50	10.50	16.50	6.38	164.70	46.21	15.00
TB8	1371.78	7.40	877.94	228.75	20.25	3.00	20.96	292.80	292.94	11.25
TB9	441.33	7.44	282.45	28.50	7.50	18.00	18.23	164.70	10.29	26.24
TB 10	1578.54	6.76	1010.26	60.00	36.00	90.00	118.46	128.10	51.86	524.84
TB 11	344.37	7.28	220.39	18.75	9.75	10.50	11.85	146.40	8.65	7.50
TB 12	598.19	6.83	382.84	54.75	52.50	27.00	20.05	82.35	44.72	97.47
TB 13	2101.98	7.04	1345.27	177.00	18.00	225.00	91.13	183.00	160.79	487.35
TB 14	1140.58	7.27	729.97	120.00	2.25	60.00	36.45	183.00	59.60	258.67
TB 16	6212.28	6.83	3975.86	1698.00	27.00	45.00	145.80	292.80	35.79	1724.47
TB 18	762.41	6.75	487.94	120.75	8.25	12.00	6.38	247.05	70.02	22.49
TB 19	4209.17	6.92	2693.87	1029.00	7.50	225.00	72.90	292.80	309.90	749.77
TB 20	577.69	7.12	369.72	49.50	9.75	34.50	8.20	155.55	74.48	33.74
TB 21	752.37	7.17	481.52	123.00	8.25	6.00	5.47	256.20	26.86	48.73
TB 22	814.96	7.00	521.57	139.50	8.25	3.00	12.76	256.20	56.63	41.24
TB 23	3377.64	7.26	2161.69	490.50	16.50	60.00	127.57	237.90	1038.77	187.44
TB 24	712.41	7.65	455.94	89.63	3.00	12.00	6.38	292.80	33.14	15.00
TB 25	1122.98	7.70	718.71	216.00	18.00	27.00	5.47	183.00	98.29	164.95
TB 26	736.22	7.25	471.18	114.75	9.00	10.50	13.67	256.20	0.08	59.98

TB 27	1639.48	7.01	1049.26	268.50	21.00	15.00	9.11	274.50	232.22	224.93
TB 28	3750.13	7.28	2400.08	903.00	70.50	315.00	72.90	128.10	157.82	749.77
TB 29	2199.83	7.10	1407.89	438.75	96.25	60.00	18.23	201.30	74.48	374.88
TB 30	1985.01	7.24	1270.40	166.50	0.75	255.00	100.24	109.80	294.72	337.40
TB 31	906.45	7.22	580.13	51.75	6.00	61.50	36.45	109.80	273.89	33.74
TB 32	4458.40	7.13	2853.38	612.00	27.00	300.00	45.56	128.10	562.58	1177.13
TB 33	1031.25	7.20	660.00	208.50	15.00	15.00	10.02	137.25	165.26	104.97
TB 34	562.27	7.18	359.85	41.25	3.75	87.00	12.76	109.80	65.56	33.74
TB 35	1110.73	6.98	710.87	99.00	9.00	78.00	20.05	118.95	311.39	67.48
TB 36	1752.74	6.98	1121.75	258.00	19.50	60.00	63.79	201.30	293.23	224.93
TB 37	1088.14	7.08	696.41	190.50	12.75	30.00	2.73	155.55	177.16	123.71
TB 39	628.90	7.91	402.50	82.50	10.50	22.50	11.85	164.70	77.46	29.99
TB 40	518.63	7.37	331.92	48.75	8.25	21.00	1.82	164.70	45.91	37.49
TB 41	2635.98	6.95	1687.02	142.50	27.00	300.00	63.79	73.20	287.28	787.26
TB 42	1119.01	6.97	716.17	135.00	12.00	36.00	3.65	91.50	22.40	408.62
TB 43	426.85	6.85	273.18	32.25	6.75	21.00	14.58	91.50	58.11	44.99
TB 44	588.53	7.02	376.66	66.00	3.75	16.50	7.29	237.90	27.22	15.00
TB45	298.41	7.12	190.98	36.00	6.75	22.50	1.82	36.60	25.08	56.23
TB46	3590.25	7.12	2297.76	405.00	16.50	139.50	65.25	215.25	573.75	160.50
Inland dug well										
Well No.	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**$HCO_3^-+CO_3^-$**	**SO_4^{2-}**	**Cl^-**
	(µs/cm)		**(mg/l)**							
DW3	2472.37	7.71	1582.32	382.50	31.50	120.00	54.68	384.30	227.46	374.88
DW27	5585.07	7.66	3574.44	1204.50	33.00	255.00	191.36	201.30	35.79	1649.49
DW35	353.77	7.66	226.41	34.50	19.50	19.50	0.91	109.80	18.71	22.49
DW36	267.43	7.31	171.16	21.00	3.00	3.00	13.67	54.90	61.09	7.50
DW37	498.29	7.40	318.91	27.00	4.50	7.50	3.00	105.75	39.75	12.00
DW38	382.32	7.23	244.69	23.25	12.00	39.00	25.52	155.55	25.85	33.74
DW40	1733.35	7.12	1109.35	13.50	4.50	33.00	5.47	118.95	24.78	37.49
DW41	316.41	7.19	202.50	46.95	0.75	195.00	154.91	128.10	294.72	284.91

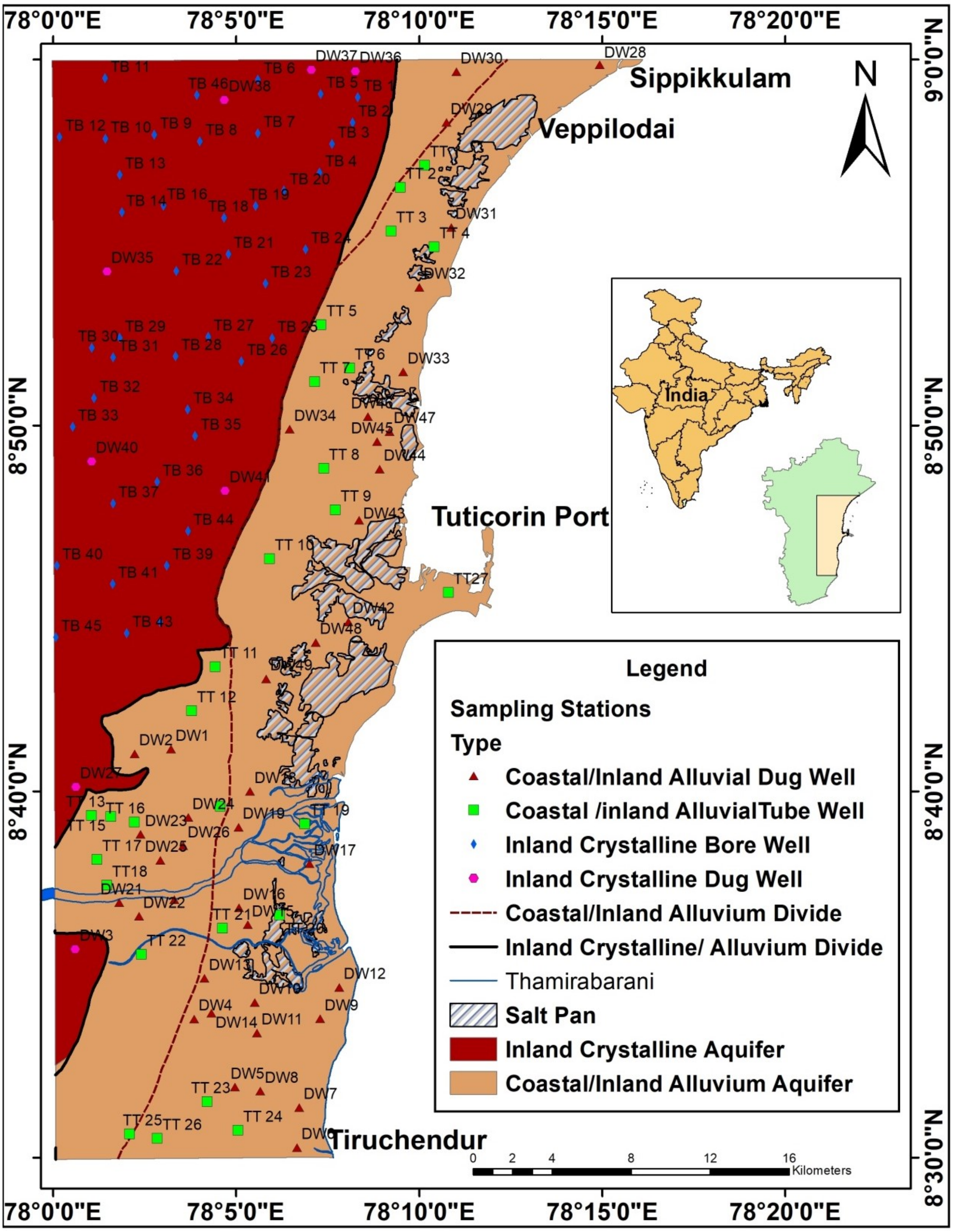


Fig 3.1: Location map of coastal/inland alluvial and inland crystalline groundwater sampling sites

3.2.1 Hydrogen ion concentration (pH)

It is defined as the negative logarithm to the base 10 of hydrogen ion concentration. The pH of water is a measure of acid base equilibrium in natural environment. The pH value will be lowered due to the presence of carbon dioxide and the absence of carbon dioxide increases the pH value. Hydrogen ion concentration in combination with temperature, pressure and oxidation-reduction potential elucidates the solubility of mineral, precipitation of compounds and the residence period of an ion. The desirable range of pH for drinking water as per BIS (2012) and WHO standards is 6.5-8.5 while that of EEC (Lloyd and Heathcote, 1985) is 6.5 – 9.0. The relationship between human health and pH cannot be ascertained as the acids and alkalis in water will be dilute. pH in association with gases, colloidal material electrolytes and non-electrolytes present in natural water determines the extent of corrosion in a system, lower levels of pH boosts the corrosion level (Langelier, 1946; McClanahan & Mancy, 1974; Nordberg et al. 1985; Murrel, 1987; Stone et al. 1987; Webber et al. 1989). pH should be controlled at all stages of water treatment for effective disinfection and water having corrosive level of pH on reaching the distribution mains may upset the drinking water quality aesthetics. The measured pH is a very important piece of information in many types of geochemical equilibrium or solubility calculations (Gibbs, 1970).

The average pH levels for coastal and inland aquifers for pre and post monsoon season demarcates the prevalence of alkaline nature in the area. Distribution of pH in coastal/inland alluvial and inland aquifers for pre and post monsoon season is depicted in Table 3.3 and 3.4 respectively. The pH distribution for coastal/inland alluvial dug wells varies between 7.09 to 8.60 in pre monsoon and 6.93 to 8.43 in post monsoon, in coastal/inland alluvial tube well the pH ranges between 7.03 to 8.60 during pre monsoon and 6.80 to 8.00 during the post monsoon season. The pH value for the inland bore well recorded is 6.83 to 8.75 in the pre monsoon and 6.75 to 8.05 in the post monsoon season, for inland aquifers 7.58 to 8.56 and 7.12 to 7.71 is the extent of pH distribution for pre and post monsoon season (Table 3.3 and 3.4). The pH values are spatially plotted for coastal/inland alluvial and inland aquifers for both the season as shown in figure 3.2a, 3.2b and 3.2c.

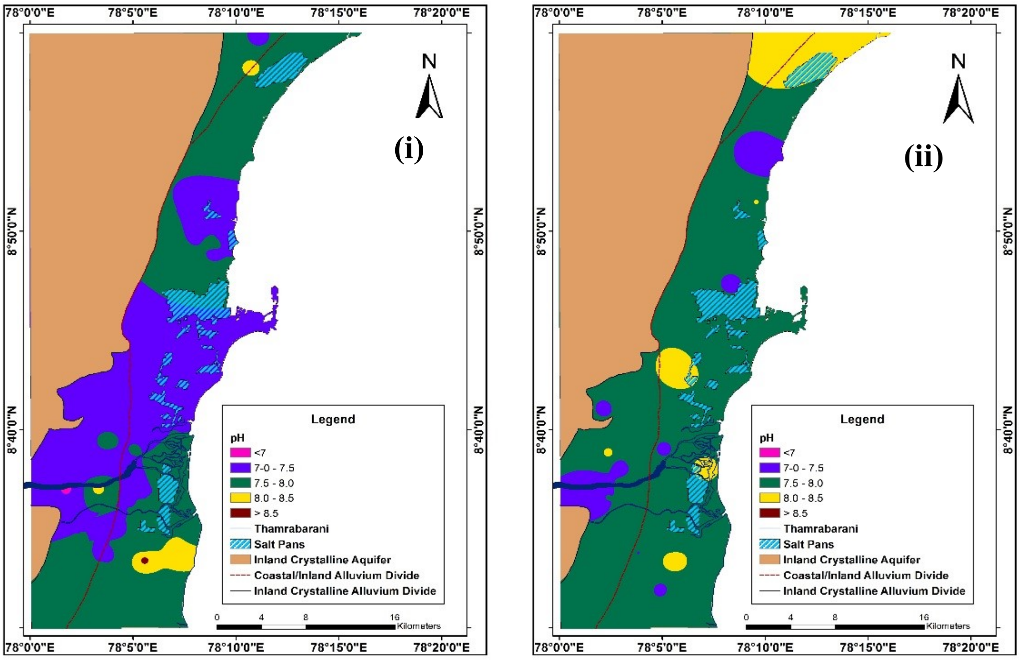


Fig 3.2a: Spatial distribution of pH in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

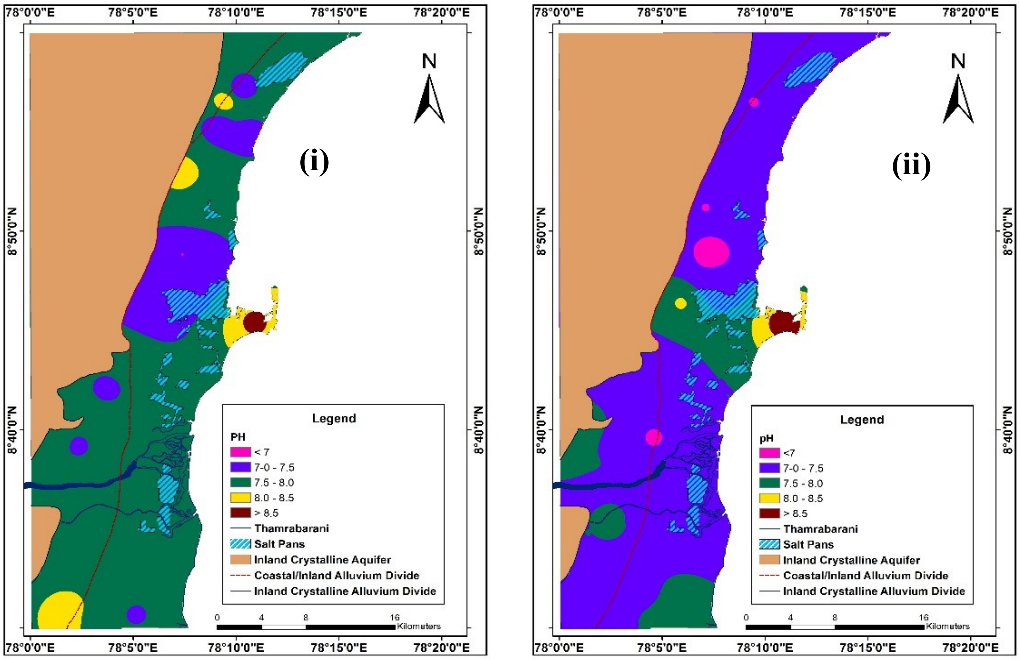


Fig 3.2b: Spatial distribution of pH in tube wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

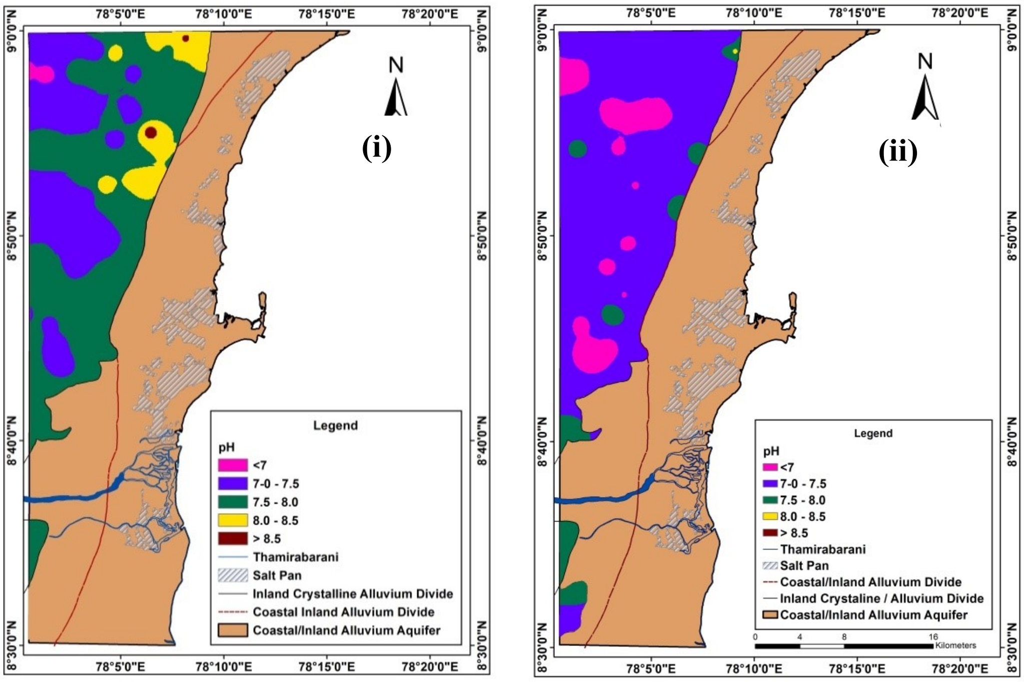


Fig 3.2c: Spatial distribution of pH in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

The coastal/inland alluvial aquifers during the pre monsoon season show more alkaline nature and a narrow drop in the pH value is shown in the post monsoon season (Fig 3.2a.i & 3.2b.i). Higher pH values is recorded in TT27 and DW11, where TT27 is located near to Tuticorin port and DW11 is located near the Thamirabarini delta. Alkaline nature of TT 27 may be imparted by the saline water interaction from the sea. North east inland dug well DW 37 and TB 24 near to Sindalakottai is more alkaline in nature during the pre monsoon season, while lower pH value is observed in the north west and central inland wells during the post monsoon season (Fig 3.2c). Inland bore wells TB 10, TB 12, TB 16, TB 18, TB 19, TB 36, TB 42, and TB 43 are all adjacent to agricultural lands, which can cause for lowering the pH. Therefore, one of the main reasons for the observed low pH could be related to the use of acid producing fertilizers like ammonium sulphate and super phosphate of lime as manure for agriculture purpose (Rajesh et al. 2001). Inland bore wells TB35 and TB41 are spatially located within a radius of 2 km near to copper producing industry where the by products are phosphoric acid and sulphuric acid which will supplement for lower pH value. BIS standards (2001) for potable water ranges within 6.5 to 8.5. The majority of the water satisfy the required pH value. Increased alkaline nature in the area is due to the proximity of coastal aquifers towards sea and the reduced precipitation in the area.

3.2.2 Electrical Conductivity (EC)

Electrical conductivity is the measurement of dissolved substances in a solution, which allows the substance to conduct electricity through it. It is usually represented as micro/milli Siemens per unit area (ms/cm or µs/cm). Electrical conductivity is the measure of concentration of electrolyte in water in the form of ions (Karanth, 1987). Electrical conductivity is widely used for monitoring the mixing of fresh and saline water, for separating stream hydrographs and for geophysical mapping of contaminated groundwater (Hayashi, 2004). Electrical conductivity is a crude indicator of water quality as it is the sum of all ionized solutes or dissolved solids. Groundwater being an excellent liquid solvent it dissolute many metals and minerals during its formation leading to an increase in the electrical conductivity. Electrical conductivity in the coastal/inland alluvial dug well of the study area extends from 294.41 µs/cm to11480.00 µs/cm and 295.24 µs/cm to 7922.29 µs/cm during the pre and post monsoon season. Conductivity recorded for coastal/inland alluvial tube well ranges between 543.49 µs/cm to 45619.20 µs/cm (Table 3.1. and 3.2.)during pre monsoon season.

The inland bore well conductivity varies from 421.00 µs/cm to 9623.68 µs/cm and 298.41µs/cm to 6212.28 µs/cm (Table 3.1. and 3.2.) for pre and monsoon season whereas for inland dug well conductivity recorded is in between 1.41 µs/cm to 5670.00 µs/cm and 267.43 µs/cm to5585.07 µs/cm. Spatiotemporal distribution of electrical conductivity is plotted as isochrones map in figure 3.4 and 3.5 for coastal and inland aquifer for both pre and post monsoon season. Coastal aquifers along north east coast and north eastern tip show an increased conductivity value during the pre monsoon season (Fig 3.3a.i & 3.3b.i) with aquifer at Tuticorin port recording the maximum value.

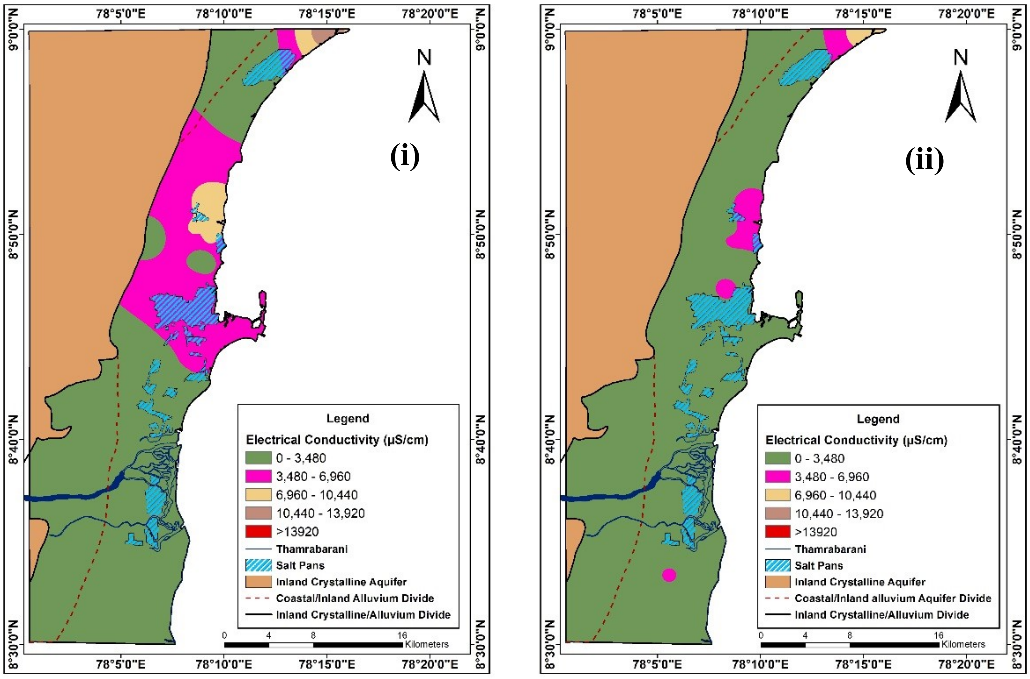


Fig 3.3a: Spatial distribution of electrical conductivity in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

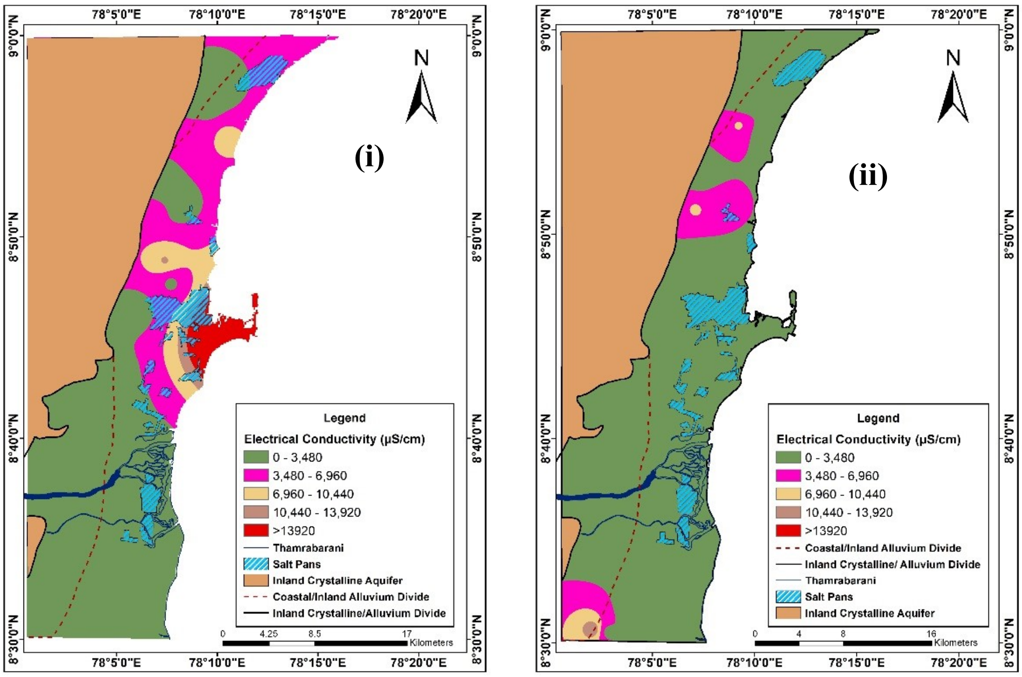


Fig 3.3b: Spatial distribution of electrical conductivity in tube wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

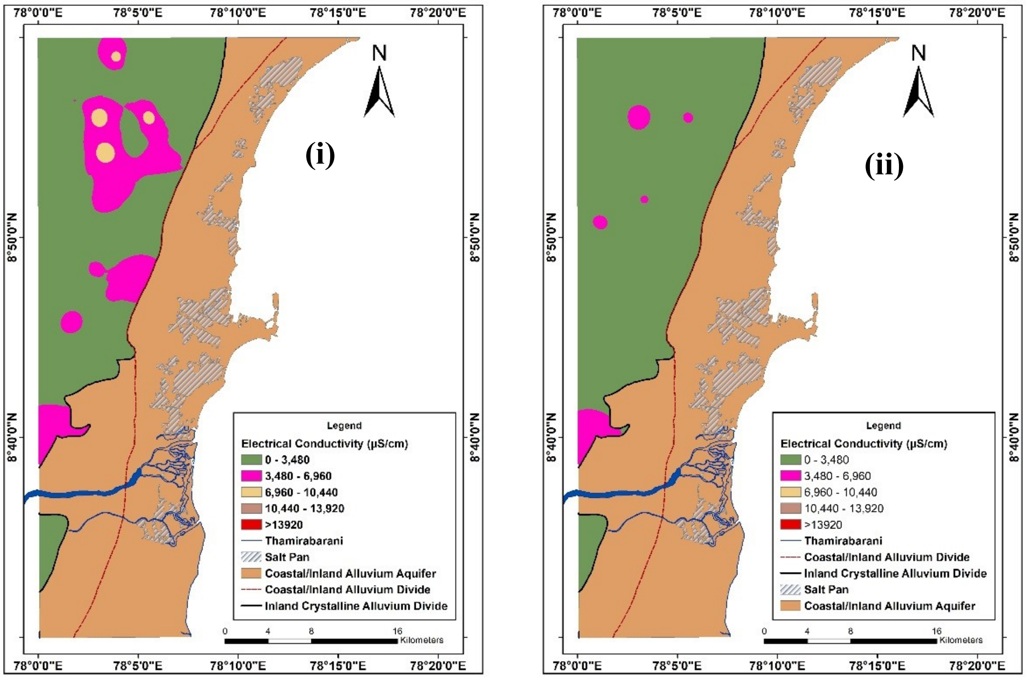


Fig 3.3c: Spatial distribution of electrical conductivity in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

During post monsoon aquifer at Sippikulam lying in the north east tip and Therikudiyirippu towards south west recorded the maximum value. In inland aquifers high conductivity values were observed in patches at the north central part of the basin (Fig 3.3c) and the value was low during the post monsoon. Higher conductivity value at Tuticorin port might be its spatial adjacency with the seawater and fertilizer application near to the Sippikulam might have facilitated the aquifer with higher conductivity value. The lower values of conductivity during post monsoon will be the resultant dissolution of soluble salts by rainwater.

3.2.3 Total Dissolved Solids (TDS)

Minerals dissolved in water are expressed in the form of Total Dissolved Solids. The concentration of TDS in water will depend on resident time of groundwater in aquifers, local geological conditions, climate and waste discharges. TDS concentration in water is influenced by many factors, which includes movement of groundwater through rocks containing soluble minerals, salt concentration by evaporation and contamination due to waste water disposal (Karanth 1987). Palatability of water is strongly influenced by the TDS value and water having TDS more than the permissible limit may lead to many gastrointestinal disorders. High TDS values imparted by salts like chlorides, sulfates, magnesium, calcium, and carbonates will lead to corrosion and scale formation in distribution pipes of industries and household. As per WHO (1984) classification of groundwater (Table 3.5) having a TDS value of less than < 300 mg/l is considered excellent for drinking and water with a TDS value > 1200 mg/l is the unacceptable level for drinking. TDS value has a higher concentration in the coastal aquifers during the pre monsoon. The northern part above the Tamiraibharani delta has the highest TDS value for the pre monsoon season. A reduction in TDS value of coastal/inland alluvial aquifer is seen during the post monsoon. The TDS value of Tuticorin port has the highest value of 32400.00 mg/l for both the season. The inland aquifers also has a higher TDS value of >1200 mg/l during the pre monsoon season (Fig 3.4) and the value is decreasing in the post monsoon season. The deep aquifer located towards the north east part of the study area at Akilandapuram (TB 16) has the TDS value of 6835.00 mg/l and 3975.86 mg/l for both the seasons respectively. According to Venugopal (1998) and Aravindan (1999) the TDS values are higher during pre monsoon than the post monsoon. The spatial interpolation map for TDS value for coastal/inland alluvial and inland aquifers for both the season substantiates the poor palatability of groundwater resources in the area. Dissolved solids will be high in areas having less groundwater flow velocities and the higher values of TDS can be attributed to the distribution of sparse rainfall.

Table 3.5: Groundwater palatability based on TDS by WHO (1984)

Water Class	TDS (mg/l)
Excellent	<300
Good	300-600
Fair	600-900
Poor	900-1200
Unacceptable	>1200

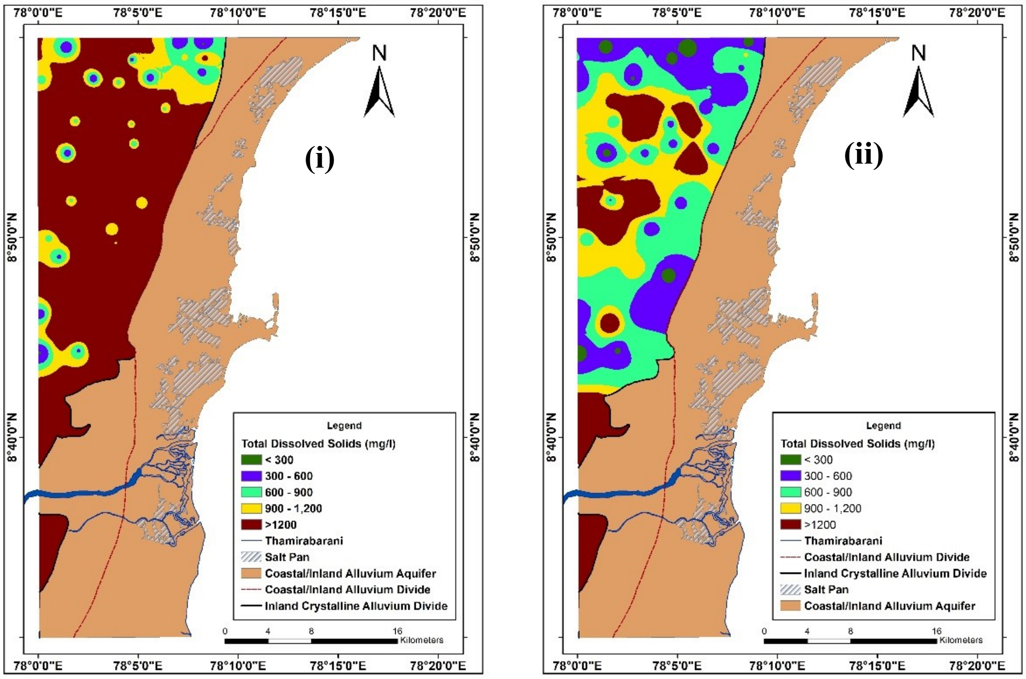


Fig 3.4: Spatial distribution of total dissolved solids in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.2.4 Total Hardness (TH)

The groundwater hardness is defined as the sum of divalent cations in solution but depends largely upon the concentrations of aqueous calcium and magnesium (Taylor and Howard, 1994). Bicarbonates of Ca and Mg cause temporary hardness while chlorides, sulphates and carbonates of calcium and magnesium contribute for permanent hardness. Hardness contribute to the formation of scales and scum in water distribution system of industrial and domestic consumers. Hard water when used in industries or heaters for domestic purpose results in the formation of scales which are the resultant calcium carbonate ($CaCO_3$) residuals formed. Hardness of water increases the soap consumption to form lather and makes it aesthetically bad for potability. The hardness of water has been classified as soft, moderately hard, hard and very hard (Table 3.6.) by Sawyer and McCarty (1967). Aquifer water is formed after progressive movement through various rock and soil movement through various rock and soil formation. Being excellent solvent water will dissolve calcium and magnesium leaving it hard. Thus, the geologic formation along the source of groundwater plays an inevitable role in making it hard. The dominant water type in the area is hard and very hard.

Table 3.6: Classification of the degree of hardness in water (Sawyer and McCarty, 1967)

Water class	Hardness, mg/l as Ca CO_3
Soft	0-75
Moderately hard	75-150
Hard	150-300
Very hard	> 300

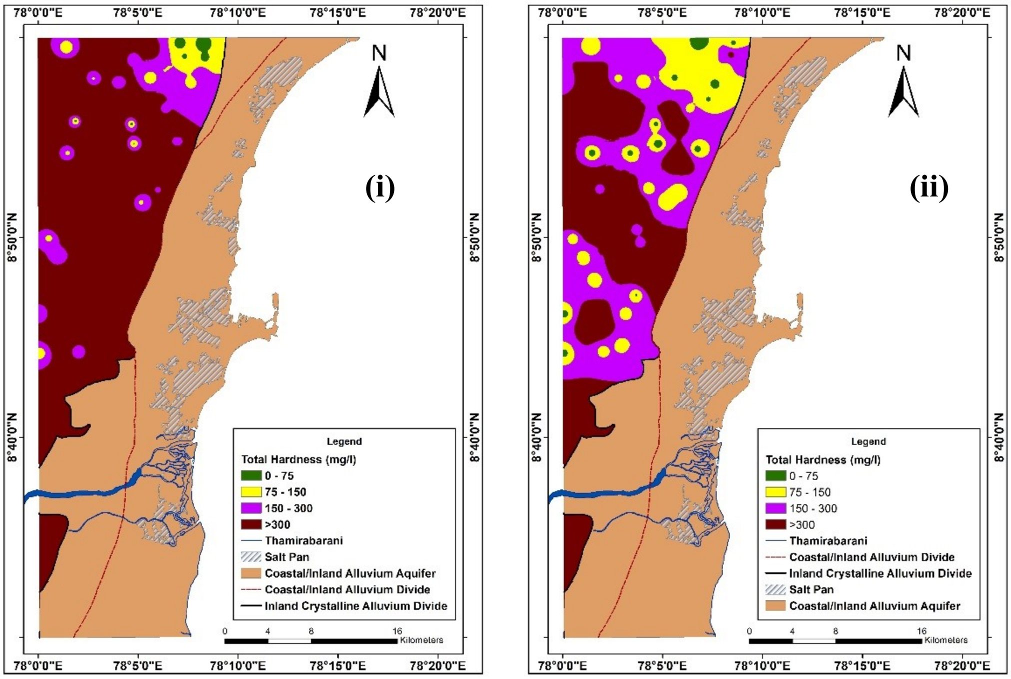


Fig 3.5: Spatial distribution of total hardness in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

The coastal aquifers show higher hardness value towards the northern region of the study area ranging between 49.92 mg/l as $CaCO_3$ to 6079.70 mg/l as $CaCO_3$ with Tuticorin port recording the highest value. Higher hardness values for coastal/inland alluvial aquifers is seen in the central region and extreme northern region during the post monsoon season. The value ranges between 33.64 mg/l as $CaCO_3$ to 5907.5 2mg/l as $CaCO_3$. During pre monsoon and post monsoon inland aquifers retains higher hardness value and this is seen all across the study area (Fig 3.5), the value ranges between 49.93 mg/l as $CaCO_3$ to 2236.15 mg/l as $CaCO_3$ for pre monsoon and 31.05 mg/l as $CaCO_3$ to 1422.08 mg/l as $CaCO_3$. Decrease in hardness is observed in all aquifers during post monsoon as compared to the pre monsoon.

3.3 Major ion chemistry of inland and coastal aquifers of the study area

3.3.1 Sodium

Sodium is one of the highly soluble and naturally occurring element in groundwater. Sodium is deposited into aquifer water during the chemical weathering of minerals like plagioclase feldspar, nephiline, sodalite, glaucophine, clay minerals and soda bearing pyroxene and amphibolites (Hem, 1985). The permissible limit of sodium as per WHO (1984) is 200 mg/l. Increase in sodium concentration above ambient level indicates point and non-point source of pollution or salt water ingress.

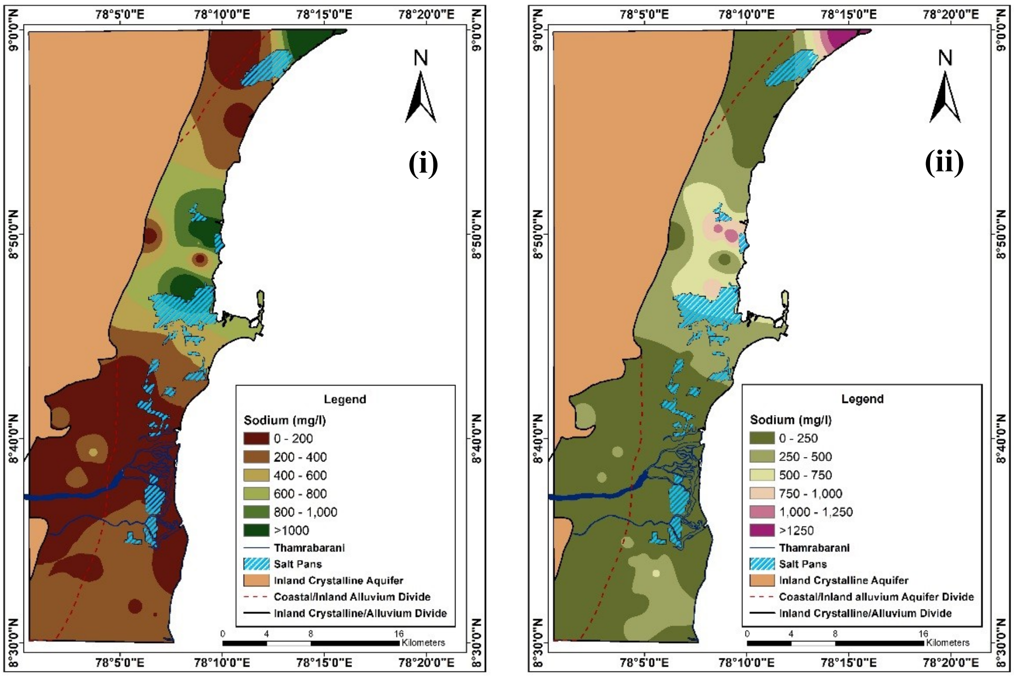


Fig 3.6a. Spatial distribution of sodium in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

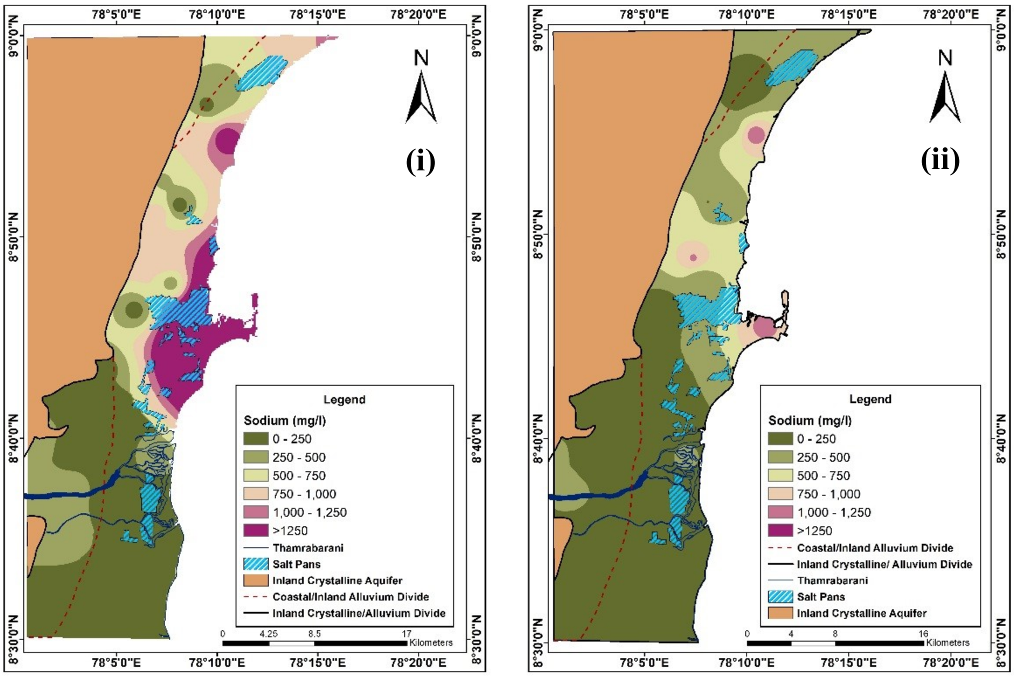


Fig 3.6c: Spatial distribution of sodium in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

Coastal/inland alluvial aquifers of the central eastern part and north east tip has the highest sodium ion concentration for the pre monsoon season (Fig 3.6a.i) and the value ranges between 29.0 mg/l to 14520.00 mg/l, where the aquifer at Tuticorin port recorded the highest value. During post monsoon coastal/inland alluvial tube well has the sodium ion concentration in the range 10.50 mg/l to 1567.50 mg/l with the north eastern tip showing the highest concentration (Table 3.4.and Fig 3.6b.ii). The central eastern part has a deteriorated ionic concentration for the post monsoon in comparison with the pre monsoon. Highest ionic concentration is seen in the north central part of inland aquifer for both pre and post monsoon season (Fig 3.6c.i & ii). Aquifers lying near coast is having the highest sodium ion concentration that may be due to saline water ingress.

3.3.2 Potassium

Potassium is one of the most abundant alkali earth metal present in water. Potassium is a major component of fertilizer and is present in majority of rocks. Most of these rocks are soluble and dissolution of these rocks may result in increased potassium level in groundwater. Potassium in groundwater is formed by weathering of rocks rich in orthoclase, microcline, leucite and biotite (Hem, 1992). Potassium nitrate is one of the major compounds in fertilizers thereby high concentration of potassium is seen in water below agricultural lands.

Aquifers of central north east coast extending all across Tuticorin port and above the port recorded the highest potassium distribution for pre monsoon. Patches of high concentration is recorded at the southern part and south west part near to the inland area during the pre monsoon season. Similar distribution of potassium was observed for the post monsoon season but the values are lesser as compared to the pre monsoon season. Highest potassium value is recorded at Tuticorin port for both the season. Isoconic distribution of potassium of inland aquifer for both the season is plotted in Fig 3.7.i & ii respectively.

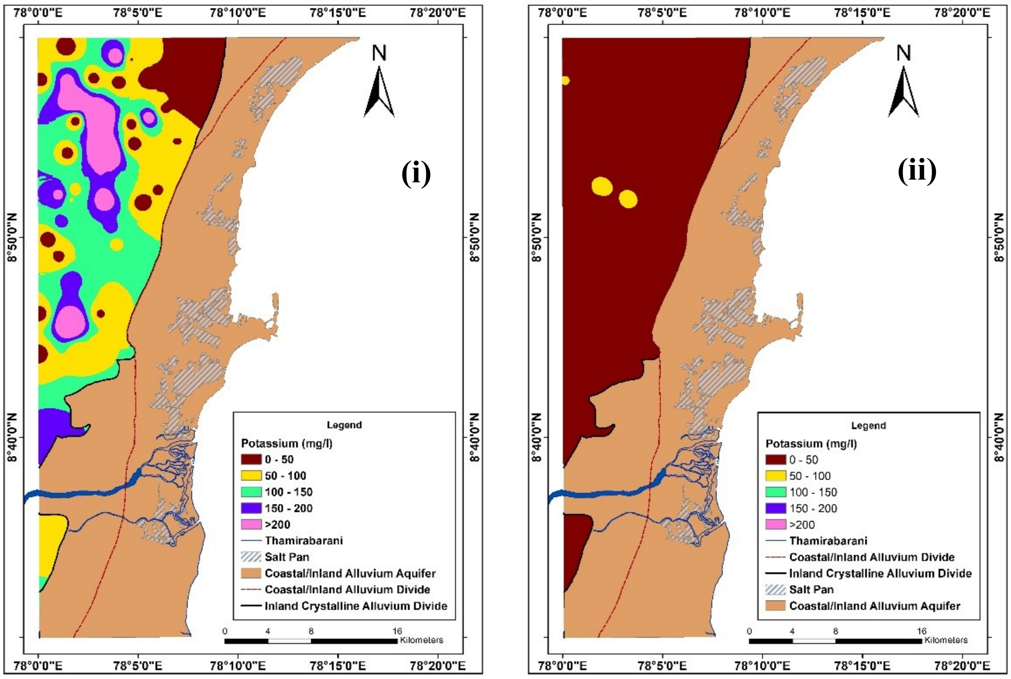


Fig 3.7: Spatial distribution of potassium in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.3.3 Calcium

Calcium is the fifth most abundant element and is found in natural waters. Calcium is dissipated and leached into groundwater from limestone, marble, calcite, dolomite, gypsum, fluorite and apatite. Solubility of calcium is stimulated by the presence of sodium and potassium in water. Calcium in association with carbonates, bicarbonates and sulfates imparts hardness to the water, this may lead to scale formation. According to BIS standards the desirable limit of calcium is 75 mg/l and permissible limit is 200 mg/l.

During pre monsoon season coastal/inland alluvial aquifers records highest concentration of calcium in the northern region. North east region at Tuticorin port, Tharuvaikulam and Sankaraperi located near to the Sterlite industries has the highest calcium concentration for the pre monsoon. Post monsoon season also has a similar calcium distribution but less as compared to the pre monsoon season. Inland aquifers for pre monsoon has a higher calcium concentration distribution in the northern region with highest concentration recorded at Akhilandapuram and Allikulam at the central region (Fig 3.8.i). Post monsoon season has a depleting level of calcium concentration (Fig 3.8.ii).

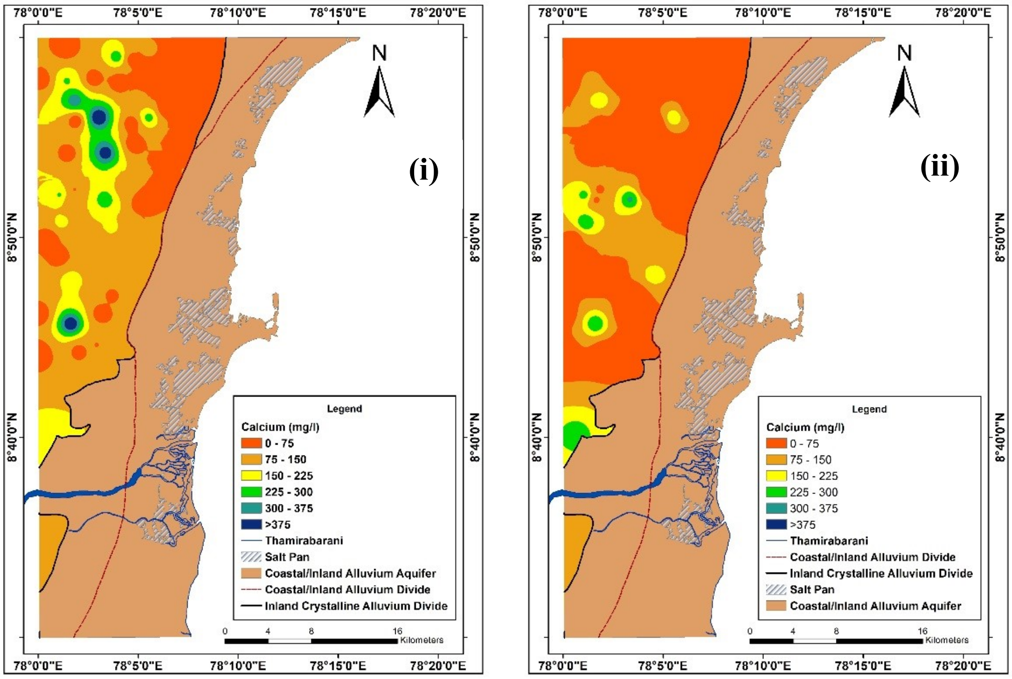


Fig 3.8: Spatial distribution of calcium in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.3.4 Magnesium

Magnesium is the second most abundant cation in oceans after sodium. Magnesium and other alkali metals imparts hardness for the water. Magnesium carbonate minerals are more soluble than the calcium carbonate minerals. The ratio of Mg:Ca is much higher in sea water (Ca 5.0) than a typical fresh water (Wedepohl 1978). Majority of the magnesium present in rain water is of marine origin and the remaining from soil dusts. Fertilizers and liming are the anthropogenic source of magnesium. The desirable limit of magnesium is 30 mg/l and permissible limit is 100 mg/l as per the BIS standards.

High magnesium concentration distribution is observed for the coastal aquifers in the north eastern region and Tutiocrin port during the pre monsoon season (Fig 3.9a & 3.9b). Highest concentration for coastal aquifers is recorded at the Tuticorin port for both the season. The inland aquifers has the higher concentration in the north and central region. Inland bore well at Akhilandapuram and dug well near Sterlite industries limited is having the highest magnesium value for the pre monsoon season (Fig 3.9c.i). Post monsoon season dug well at Nallathy is recorded with the highest value for magnesium (Fig 3.9c.ii).

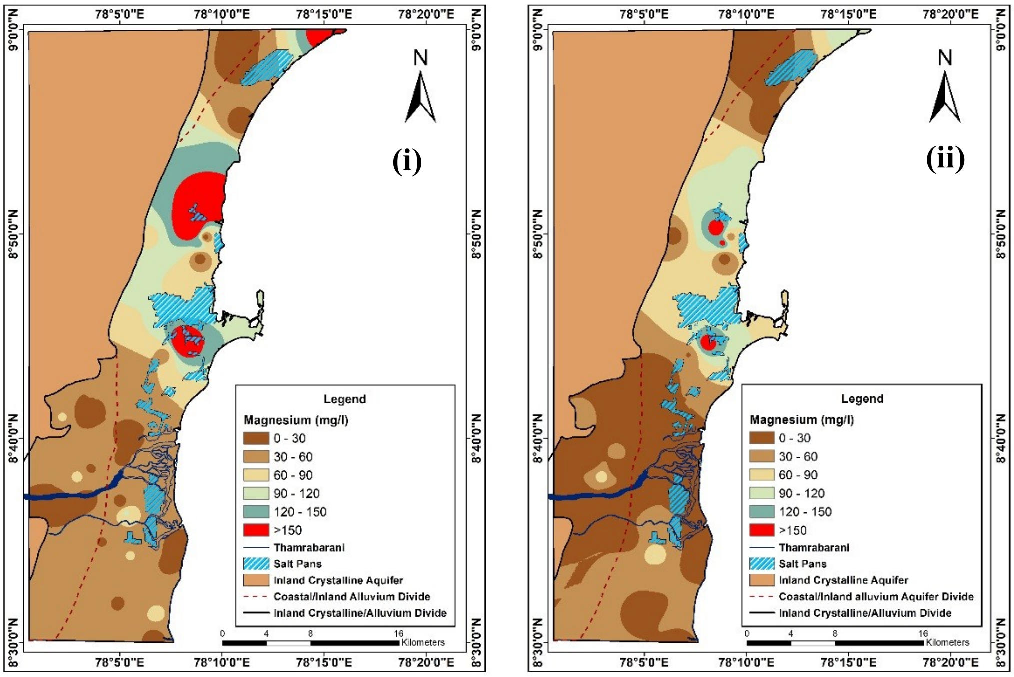


Fig 3.9a. Spatial distribution of magnesium in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

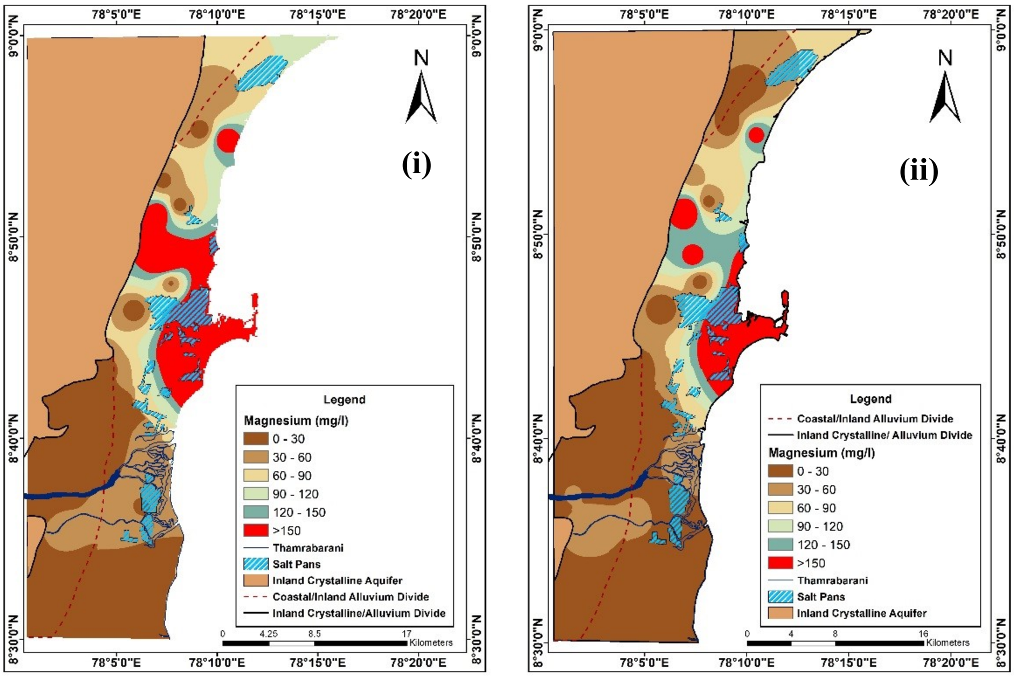


Fig 3.9b: Spatial distribution of magnesium in tube wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

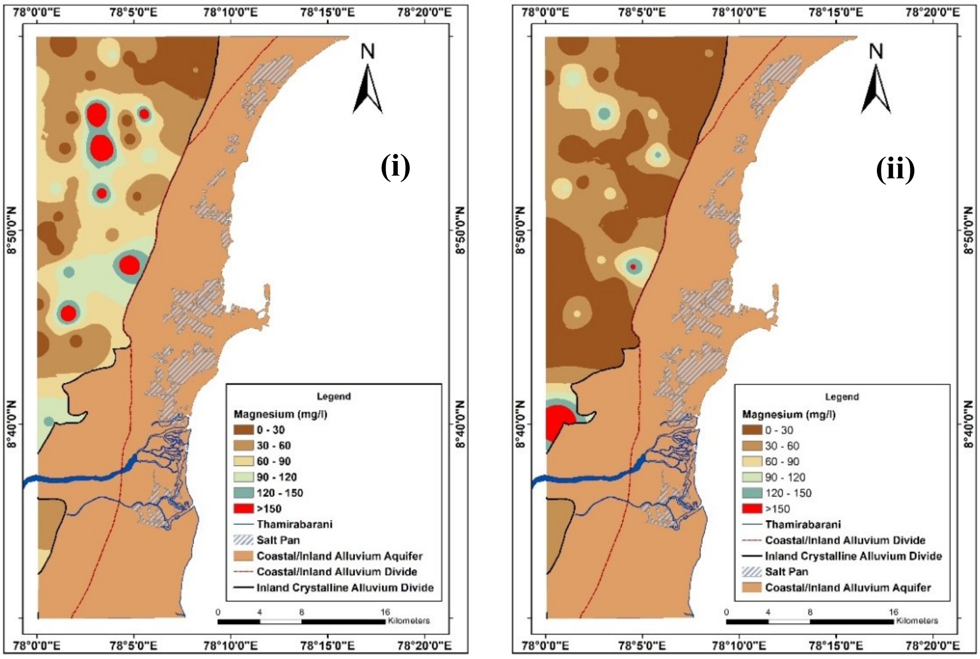


Fig 3.9c: Spatial distribution of magnesium in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.3.5 Carbonates and bicarbonates

Carbonates and bicarbonates are the predominant base anions which contributes for the alkalinity of water. Carbonate rich sedimentary rocks principally formed from deposition of biogenic marine materials (Wedepohl, 1978), are by far the most common geogenic source of alkalinity in water. Fertilizers, water and waste water from industries and cleaning reagents used in house hold are the anthropogenic sources of bicarbonates in water. Carbon dioxide present in the soil and atmosphere on hydration forms carbonic acid which further dissociates into two stages forming HCO_3^- and then CO_3^{2-}. Carbonic acid during percolation dissolves calcite and carbonate minerals from rock and soil resulting in elevated HCO_3^- level in water.

A higher concentration of bicarbonates in coastal aquifers is observed in the Tuticorin port and adjacent region above during the pre monsoon season. Elevated bicarbonate distribution of coastal/inland alluvial aquifers is observed in the south east coast and southern region during the pre monsoon season. Coastal aquifers during the post monsoon recorded highest value at Tuticorin port, south east region and southern region adjacent to inland area. Highest concentration for coastal aquifers is recorded at Kandaswamipuram.in the south for both the season.

The inland aquifer in the southern region and north east region shows a higher concentration during the pre monsoon season, while in the post monsoon season the concentration is dissoluted (Fig 3.10).

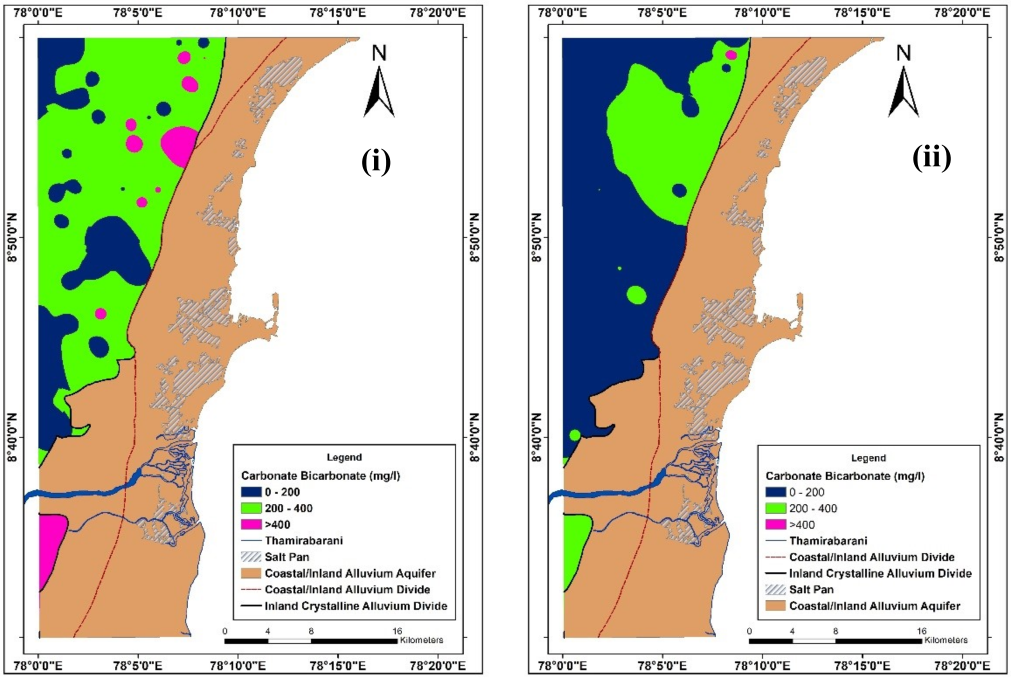


Fig 3.10: Spatial distribution of $CO_3^{2-} + HCO_3^{-}$ in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.3.6 Sulphate

Sulphate occurs naturally in various minerals like barite ($BaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) (Greenwood & Earnshaw, 1984). Sulphate being a major component in naturally occurring minerals gets dissoluted into groundwater easily. Depending on the pH conditions Sulphur can occur as three separate ions: sulphate ($[SO_4]^{2-}$), bisulfide ($[HS]^{1-}$) and hydrogen sulfide (H_2S). Sulphur reducing bacteria reduces the naturally occurring sulphates in water to hydrogen sulphide and these bacteria thrive in oxygen deficient environment imparting a rotten egg like smell to water. Increased sulphate ion in water may lead to scale formation in pipes, blackening and slime formation of water. The desirable value of sulphate in drinking water as per BIS standards is less than 200 mg/l and between 200 mg/l to 400 mg/l is the permissible limit.

Coastal aquifers at Tuticorin port and the north east coast is having the highest sulphate concentration during the pre monsoon season. During the post monsoon season the coastal/inland alluvial aquifers of the north eastern coastal region show a reduction in sulphate value but is still above the permissible limit as per the BIS standards. Inland wells in the northern region and wells adjacent to the coastal region is having a higher sulphate concentration during the pre monsoon season and during the post monsoon season the concentration is reduced (Fig 3.11c). Maximum sulphate ion concentration is recorded at the Tuticorin port among the coastal/inland alluvial aquifers and Lakshmipuram among the inland aquifers.

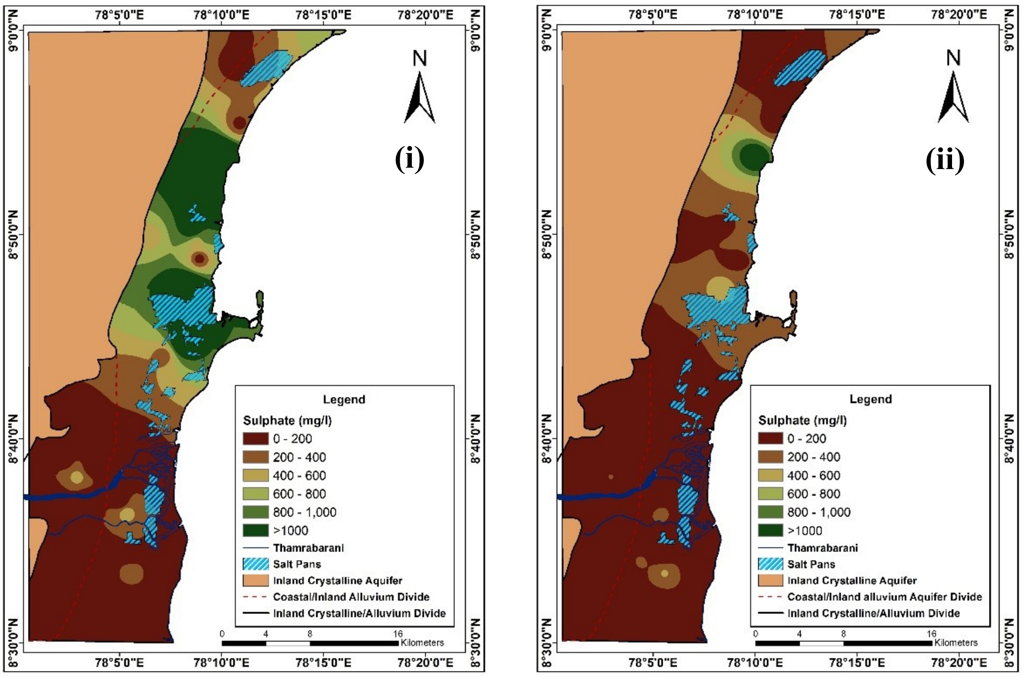


Fig 3.11a: Spatial distribution of sulphate in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

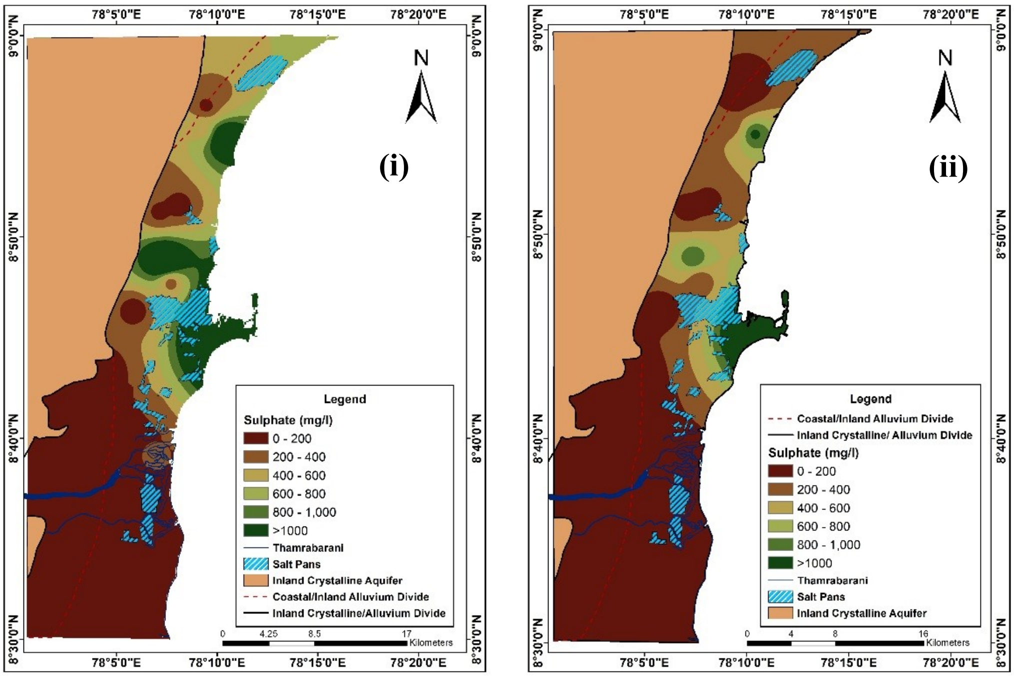


Fig 3.11b: Spatial distribution of sulphate in tube wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

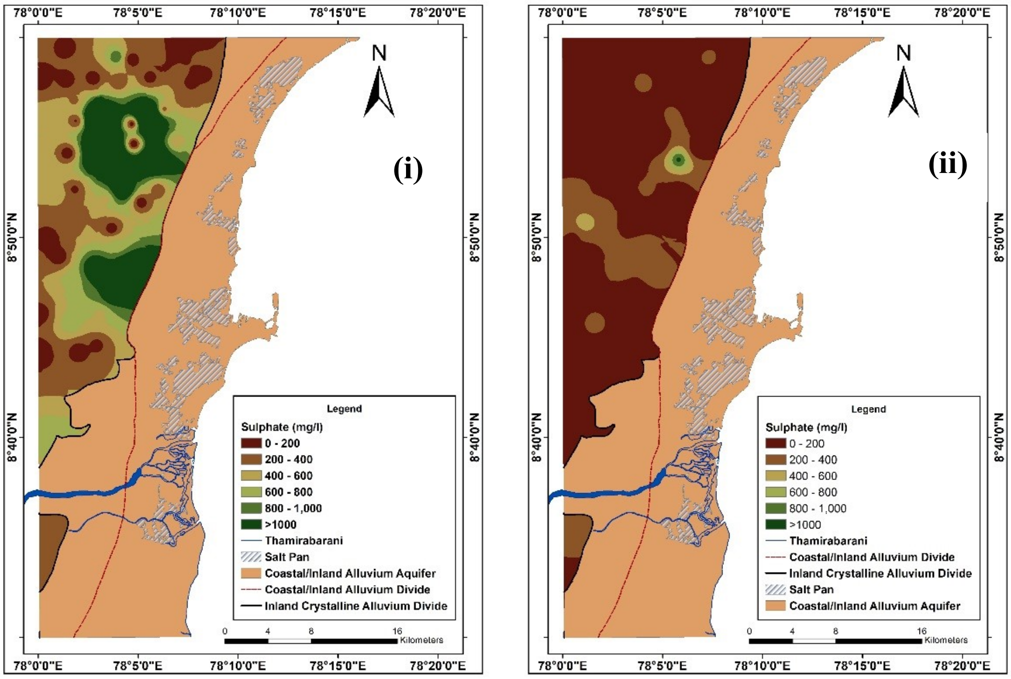


Fig 3.11c. Spatial distribution of sulphate in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

3.3.7 Chloride

Chloride is the omnipresent anion in natural water. The movement of chloride is not retarded by interaction of water with sediments, soil and rocks hence it is known as a conservative ion. Chloride being a conservative ion, is used as tracers in various studies. Chloride is present in the nature as salts of sodium (NaCl), pottassium (KCl) and calcium ($CaCl_2$). Sodium chloride is the primary source of chloride in groundwater and the major contributor of chloride in groundwater is from the sea through the hydrologic cycle. Chloride in excess may reduce the potability of water imparting it with a salty taste. Anthropogenic activities like application of inorganic fertilizers, landfill leachates, septic tank effluents and industrial effluents contribute to the elevated chloride levels in water. The desirable limit of chloride as per BIS standards is 250 mg/l and the permissible limit is 1000 mg/l.

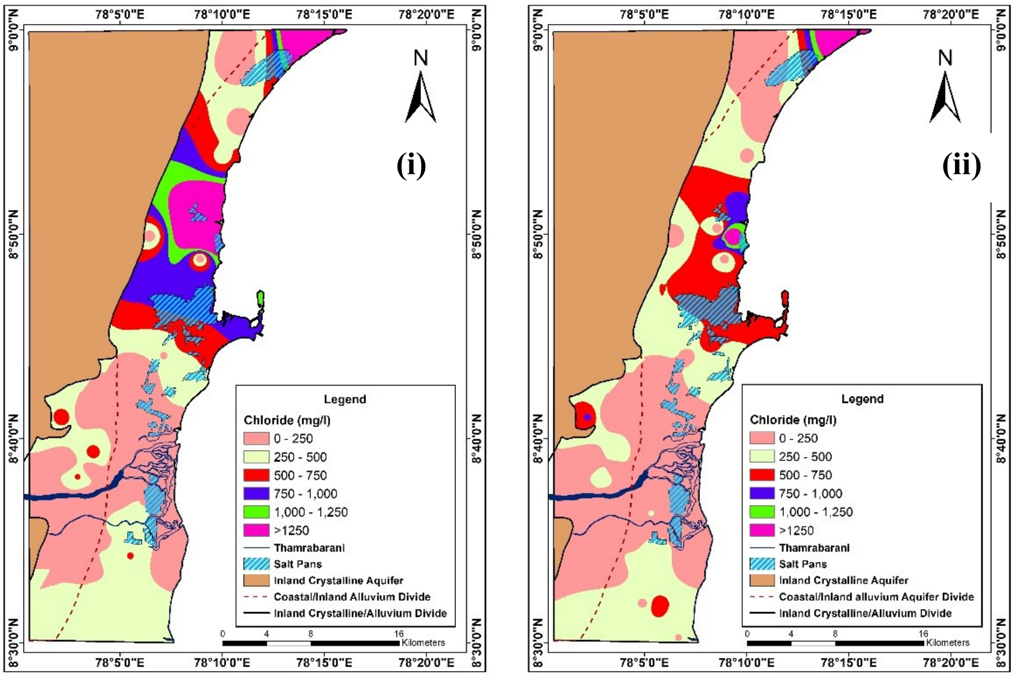


Fig 3.12a: Spatial distribution of chloride in dug wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

The isochrones of coastal/inland alluvial aquifers during pre monsoon shows chloride concentration at higher levels at Tuticorin port and extending towards the north eastern coast of Tuticorin (Fig 3.12a.i & 12b.ii). The chloride values are higher than the permissible limit on the coastal aquifers of north eastern region and Tuticorin port. The highest chloride value for coastal/inland alluvial aquifers for pre monsoon is recorded at Tuticorin port. During the post monsoon season coastal/inland alluvial aquifers is showing a decrease in the chloride concentration (Fig 3.12b.ii). The inland aquifers during the pre monsoon season is having higher chloride concentration in the central region (Fig 3.12c). The highest chloride concentration in the inland aquifers is observed at Subhramanyapuram for both the season (Fig 3.12c.i & ii).

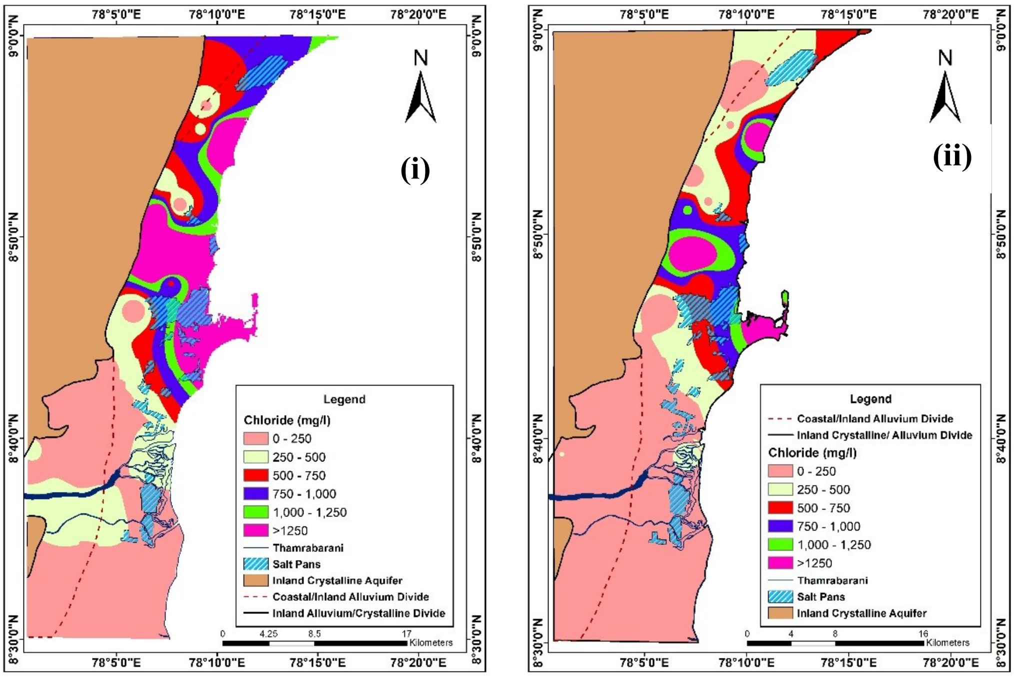


Fig 3.12b: Spatial distribution of chloride in tube wells of coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

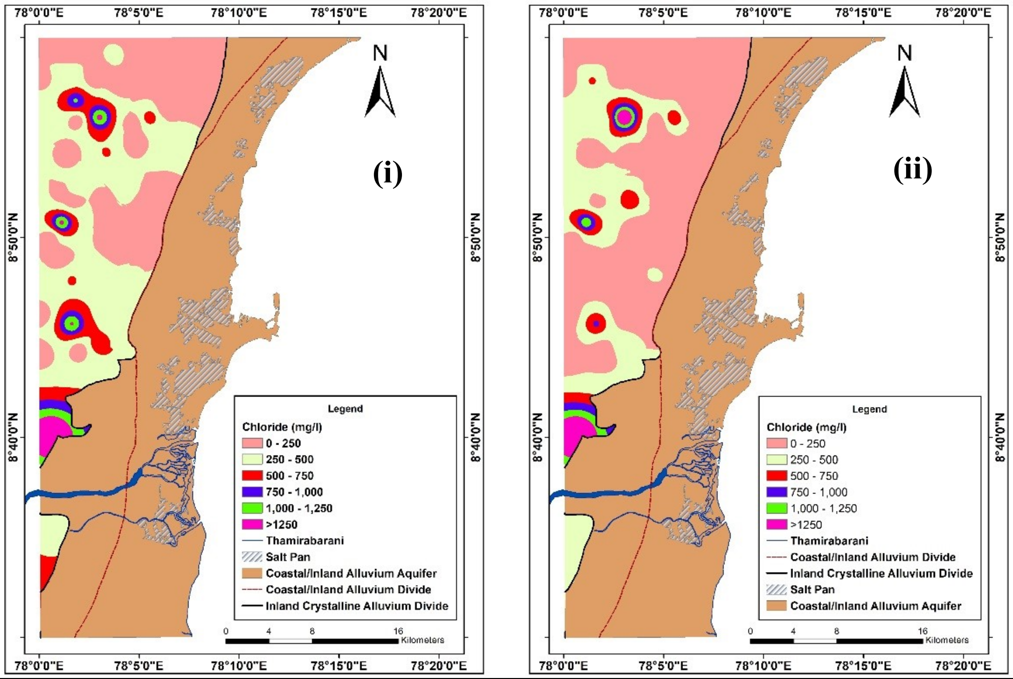


Fig 3.12c. Spatial distribution of chloride in bore wells of inland aquifers during (i) pre monsoon (ii) post monsoon

Higher ionic concentration are observed in north eastern coastal region during two seasons. Among the anions, chloride and bicarbonate showed high concentration in regions adjacent to the Thamirabarni River also, apart from the coastal regions. In contrast to these ions, sulphate was found to have higher concentration further inland regions. In the case of cations, higher concentration of calcium, sodium and magnesium was observed towards the northern parts, whereas, potassium showed more distribution towards southern side also.

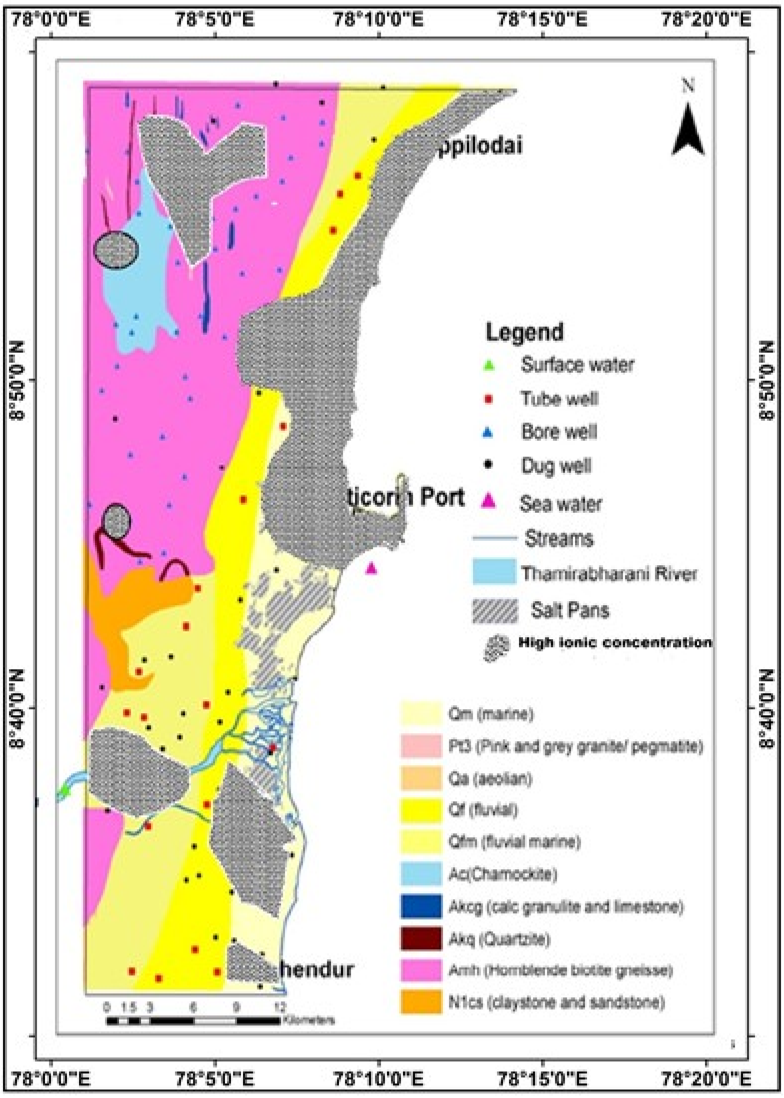


Fig 3.13: Spatial distribution of high ionic concentration in coastal/inland alluvial and inland aquifers

3.3.8 Bacteriological parameters

Transient bacteria can also populate the natural waters. Through fecal contamination the human pathogens that gain entry to water. *Eshcerichia coli* used as the indicator of human fecal contamination of water and food. The spatial distribution of Total coli form and *E.Coli* along the study area is shown in the Fig 3.14.

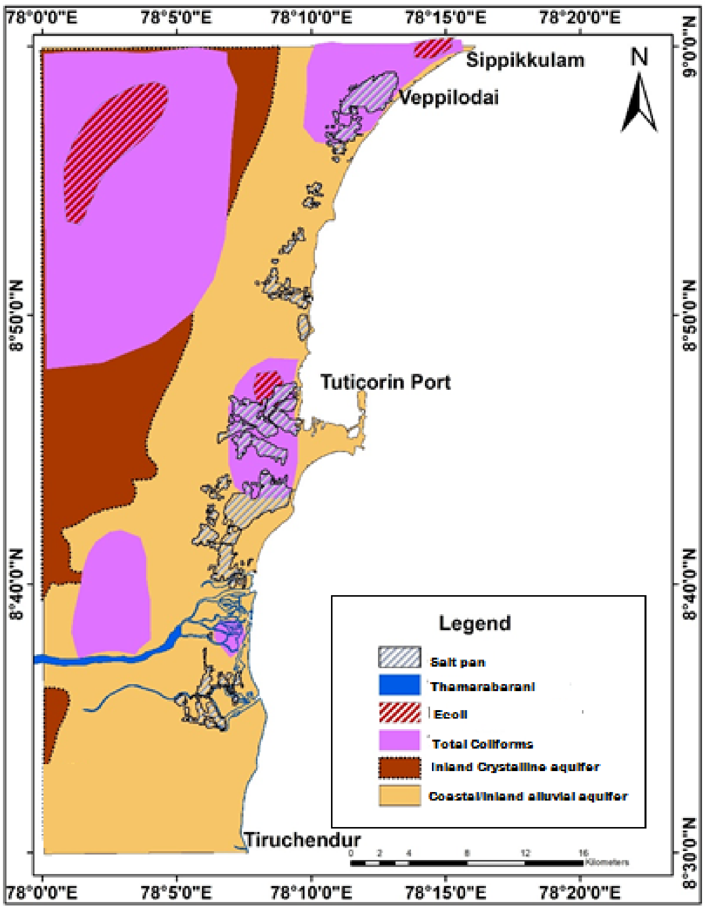


Fig 3.14: Spatial distribution of Total coliforms and E.Coli

E.coli presence was observed in areas near to Tuticorin port, mostly due to high demographic pattern in the area. North-west part of inland areas also show *E.coli* contamination, as rural areas lacking in sanitation facilities.

3.4 Irrigation water quality based on EC, TDS and percentage sodium

The ionic and salt concentration of groundwater ascertains the quality of irrigation water for agriculture. Higher concentration of alkali and alkaline earths will affect directly the texture, structure, permeability and aeration of soils and indirectly plant growth (Lloyd and Heathcote, 1985). Soluble salt concentration in water will elevate the osmotic pressure reducing the ability of plants to absorb water. Increased sodium level concentration and low calcium concentration reduces the infiltration capability of soil. High concentration of boron, selenium, cadmium etc. is toxic to the growth of plants (Todd, 1980).

Water for irrigation moves through various rocks or soils dissolving numerous chemical substances in solution and their concentration determines the quality of water for irrigation. Wilcox (1955) classified the groundwater based on EC, TDS, soluble sodium percentage and boron. The increased concentration of EC makes the soil saline and sodium makes it alkaline. Sodium concentration is very important in classifying the irrigation waters because sodium reacts with soil easily resulting in the reduction of permeability (Houk, 1951). Sodium in combination with carbonate form alkaline while with chloride form saline soils. Soluble sodium percentage (SSP) also referred to, as percentage sodium is the sodium content present in the irrigation water and is calculated using the formula below where all the concentrations are expressed in meq/l.

$$SSP = \frac{(\mathrm{Na} + \mathrm{K})\ \mathrm{x}\ 100}{\mathrm{Ca} + \mathrm{Mg} + \mathrm{Na} + \mathrm{K}}$$

Table 3.7: Classification of groundwater quality Wilcox (1955)

Class of Water	EC at 25°C (µS/cm)	TDS (mg/l)	Sodium %	Boron (mg/l)
Excellent	< 250	< 175	< 20	< 1
Good	250 -750	175 - 525	20 - 40	1- 2
Permissible	750 - 2000	525 - 1400	40 - 60	2 -3
Doubtful	2000 - 3000	1400 - 2100	60 - 80	3 - 3.75
Unsuitable	> 3000	> 2100	> 80	> 3.75

The soluble sodium percentage indicates that majority of the area falls in the class doubtful and unsuitable (Fig 3.15a & b). Transformation from permissible zone to doubtful zone is observed during the post monsoon in the Thamirabharini deltaic region (Fig 3.15a & b). This may be due to the dissolution of sodium by rainwater to the groundwater. Thamirabharini deltaic region comprises of agricultural lands and application of fertilizers in these agricultural lands will enhance the soluble sodium percentage. In the inland area majority of the area falls under the doubtful zone and certain zones come under the class unsuitable. Predominant TDS value is greater than 1200 mg/l and electrical conductivity is greater than 3000 µS/cm resulting in the conclusion that groundwater in the area comes under the class doubtful.

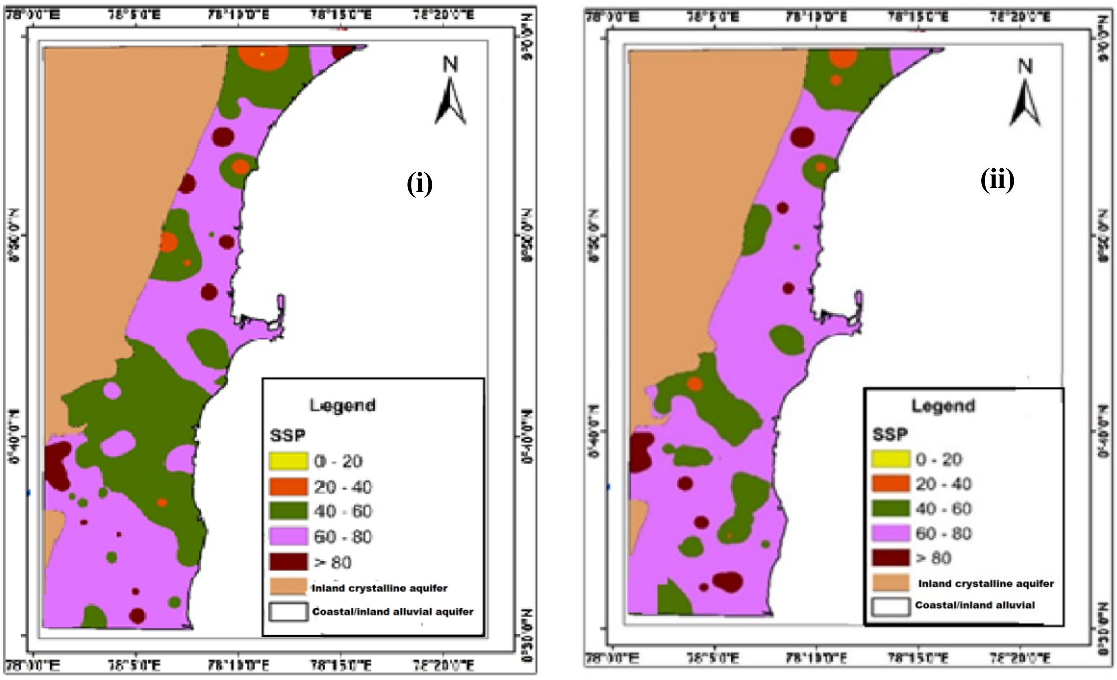


Fig 3.15a. Spatial distribution of soluble sodium percentage in coastal/inland alluvial aquifers during (i) pre monsoon (ii) post monsoon

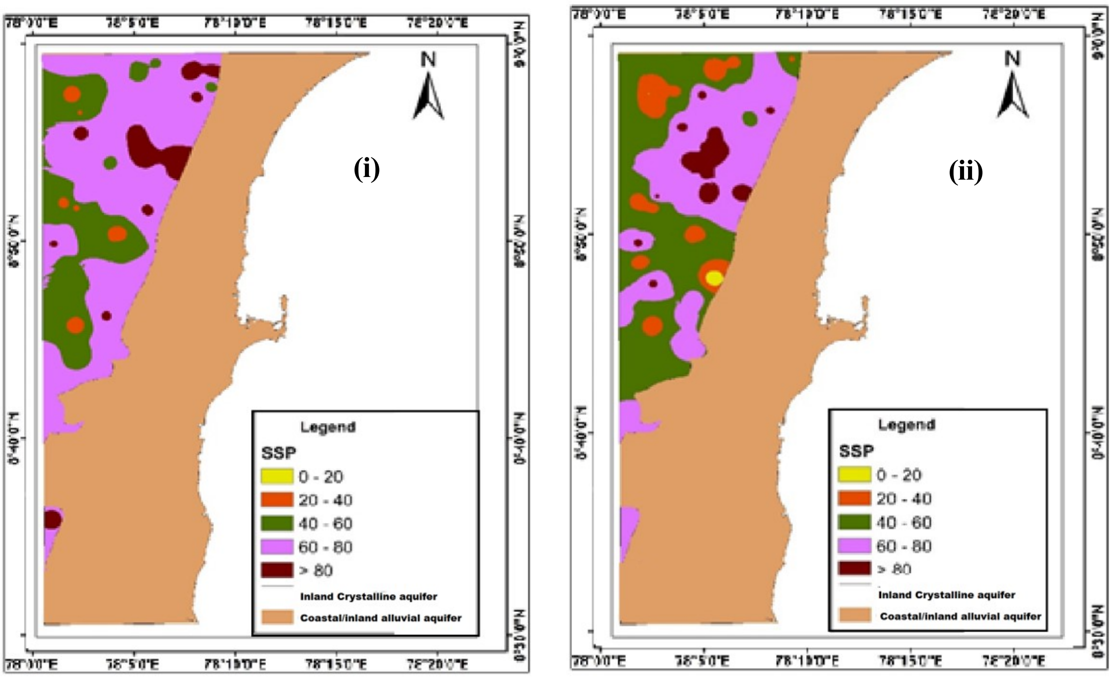


Fig 3.15b. Spatial distribution of soluble sodium percentage in inland aquifers during (i) pre monsoon (ii) post monsoon

3.5 Irrigation water quality assessment using USSL diagram

Irrigation water quality depends primarily on the chemical constituents in water used for irrigation. The predominant water quality concern for irrigation is salinity as it affects crop yield and soil structure. Dissolved salts in water influence the osmotic pressure, which has a direct impact on the ability of plants to absorb water. Higher concentration of dissolved salts increases the osmotic pressure reducing the ability of plants to absorb water. Higher concentration of alkali and alkaline earth will affect directly the texture, structure, permeability and aeration of soils and indirectly plant growth (Lloyd and Heathcote, 1985). Increased concentration of trace elements like boron, selenium, cadmium etc intercepts the plant growth (Todd, 1980).

The US salinity laboratory department of agriculture in 1954 classified the quality of irrigation water using SAR and salinity hazard. US salinity laboratory formulated a diagram for rating the irrigation water with reference to SAR as an index for sodium hazard and EC as an index for salinity hazard. Presence of excessive sodium in the irrigation water will lead to permeability problems and is evaluated using the sodium adsorption parameter, which is the ratio of concentration of sodium ion to that of calcium plus magnesium ions and is expressed as

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

where all the ionic concentrations are expressed as meq/l.

Irrigation water quality can be determined by plotting the SAR and specific conductance value on a USSL diagram. According to the USSL classification based on salinity hazard water is classified into C1, C2, C3, C4 and based on sodium hazard is classified into S1, S2, S3, S4.

Salinity Hazard

Electrical conductivity is the measure of salinity hazard of water used for irrigation purpose. In average conditions conductivity of irrigation water and conductivity of the saturation extract of soil is closely related. Plant growth is inhibited by the prevalence of higher saturation extract concentration. Based on the conductivity irrigation water is classified into four groups low salinity(C1), medium salinity(C2), high salinity (C3)and very high salinity (C4). Low salinity (C1) group of water can be used for irrigation on most of the crops and soil with chances of developing salinity with time. Some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability. Medium salinity (C2) water can be used when moderate amount of leaching occurs. Moderately tolerant crops can be cultivated without much salinity control practices. High salinity (C3) waters cannot be used on soils with restricted drainage and plants with very high salt tolerance can be irrigated using this water. Salinity management and adequate drainage is required for using this water for irrigation. Very high salinity (C4) water can be used only in special circumstances, the soils must be permeable drainage should be adequate, irrigation water must be applied in excess to provide considerable leaching and very high salt tolerant crops should be selected. In the present study, coastal and inland aquifers show a temporal transformation from very high saline in the pre monsoon to the next less saline water type in the post monsoon season. C3 water type was predominant in the pre monsoon season for coastal/inland alluvial dug well and tube well, while C2 water type is predominant during the post monsoon season (Fig 3.16a & Fig 3.16b). In the inland bore well during the pre monsoon season, the predominant water type is C3 and C4 while in the post monsoon season the water type is C3 and C2. C4 is the predominant water type for inland dug well during the pre monsoon season (Fig 3.16c & Fig 3.16d).

Sodium Adsorption Ratio (SAR)

Classification of irrigation water with respect to SAR is based on the effect of exchangeable sodium on the physical condition of the soil. Plants sensitive to sodium may face serious injury because of high sodium accumulation. Based on SAR classification irrigation water is classified into four groups such as low sodium water (S1), Medium sodium water (S2), high sodium water (S3) and very high sodium water (S4).

Low sodium water is highly feasible for irrigation as it has the least chance for the development of harmful exchangeable sodium. Medium sodium water (S2) under low leaching conditions has an appreciable sodium hazard in fine textured soil of high cation exchange capacity. This water can be used on coarse-textured or organic soils that have good permeability. High sodium water (S3) produces exchangeable levels of sodium in soils to harmful levels. High leaching, good drainage, special soil management and addition of organic matter is required for reducing this high exchangeable sodium in soil. Gypsiferous soils may not develop harmful levels of exchangeable sodium from such waters. Very high sodium water (S4) is generally unsatisfactory for irrigation purposes except at low and perhaps medium salinity where the solution of calcium from the soil or use of gypsum or other amendments may make the use of these waters feasible.

According to the USSL classification of irrigation water the coastal/inland alluvial dug wells during the pre and post monsoon season is distributed across C2S1,C3S1,C4S1,C3S2,C4S2,C3S3,C4S3 and C4S4 water type. The coastal/inland alluvial bore wells for pre and post monsoon are distributed along C2S1, C3S1, C3S2, C3S3, C4S3, C3S4 and C4S4 water types, while a transformation from C4S2 to C3S2 water type is observed from pre monsoon to post monsoon season. The inland bore well is classified into C2S1, C3S1, C4S1, C3S2, C4S2, C3S3, C4S3 and C4S4 water type for both pre and post monsoon season. Inland dug wells is classified into C2S1, C3S1, C4S3 and C4S4 water type. Temporal transformation from C4S3 to C4S2 is also observed.

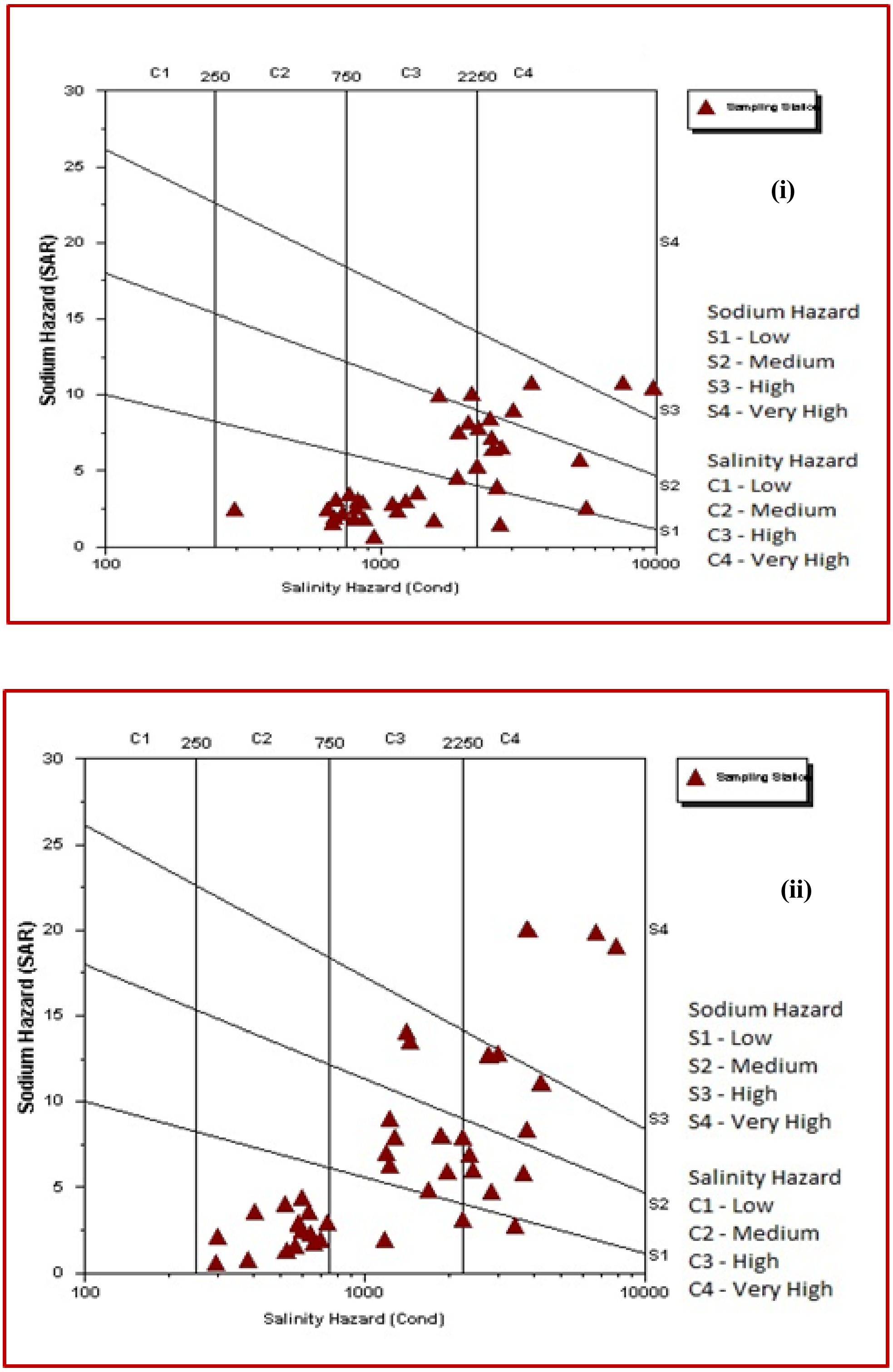


Fig 3.16a. Groundwater classification based on USSL method for coastal/inland alluvial dug wells during (i) pre monsoon (ii) post monsoon

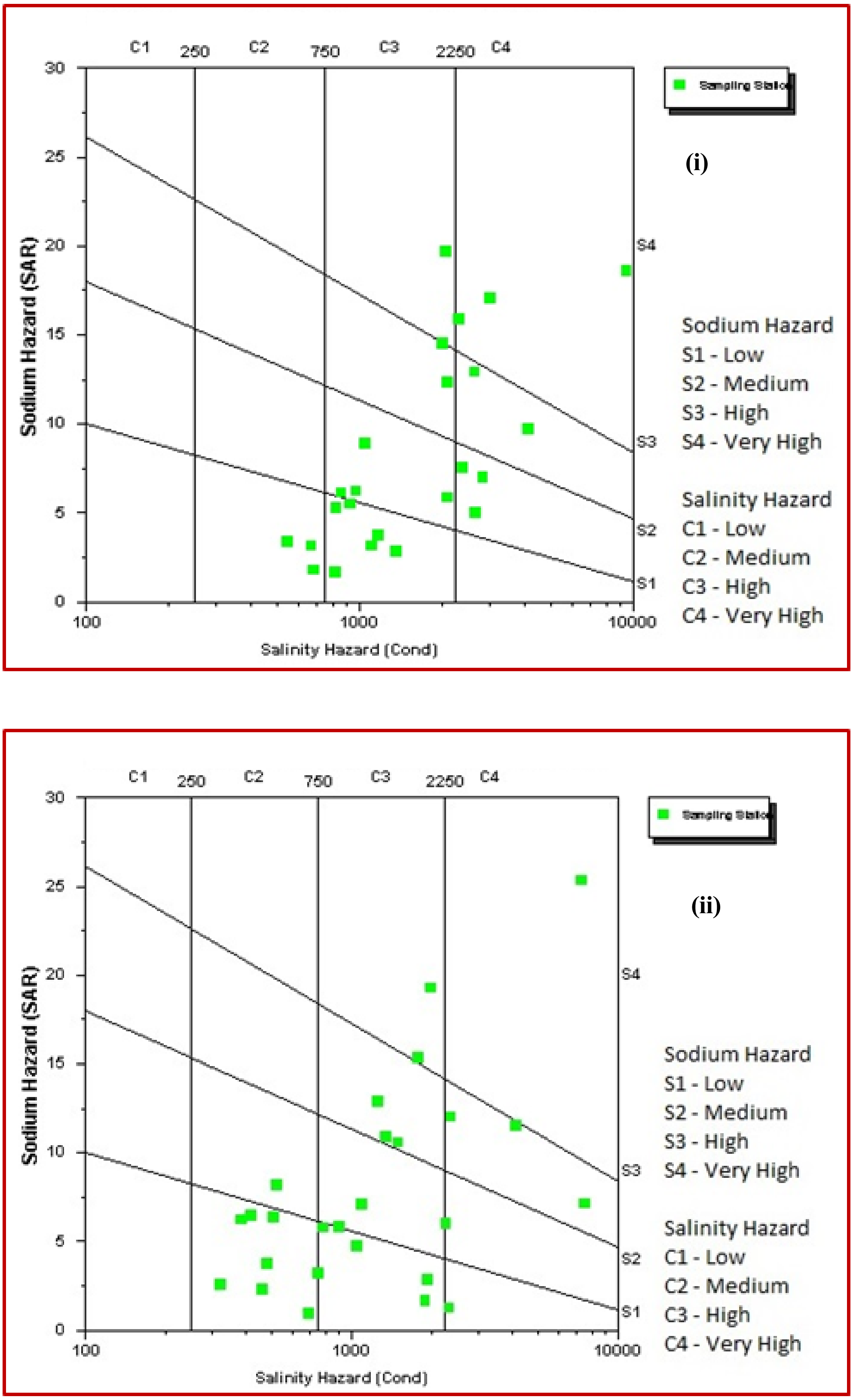


Fig 3.16b. Groundwater classification based on USSL method for coastal/inland alluvial tube wells during (i) pre monsoon (ii) post monsoon

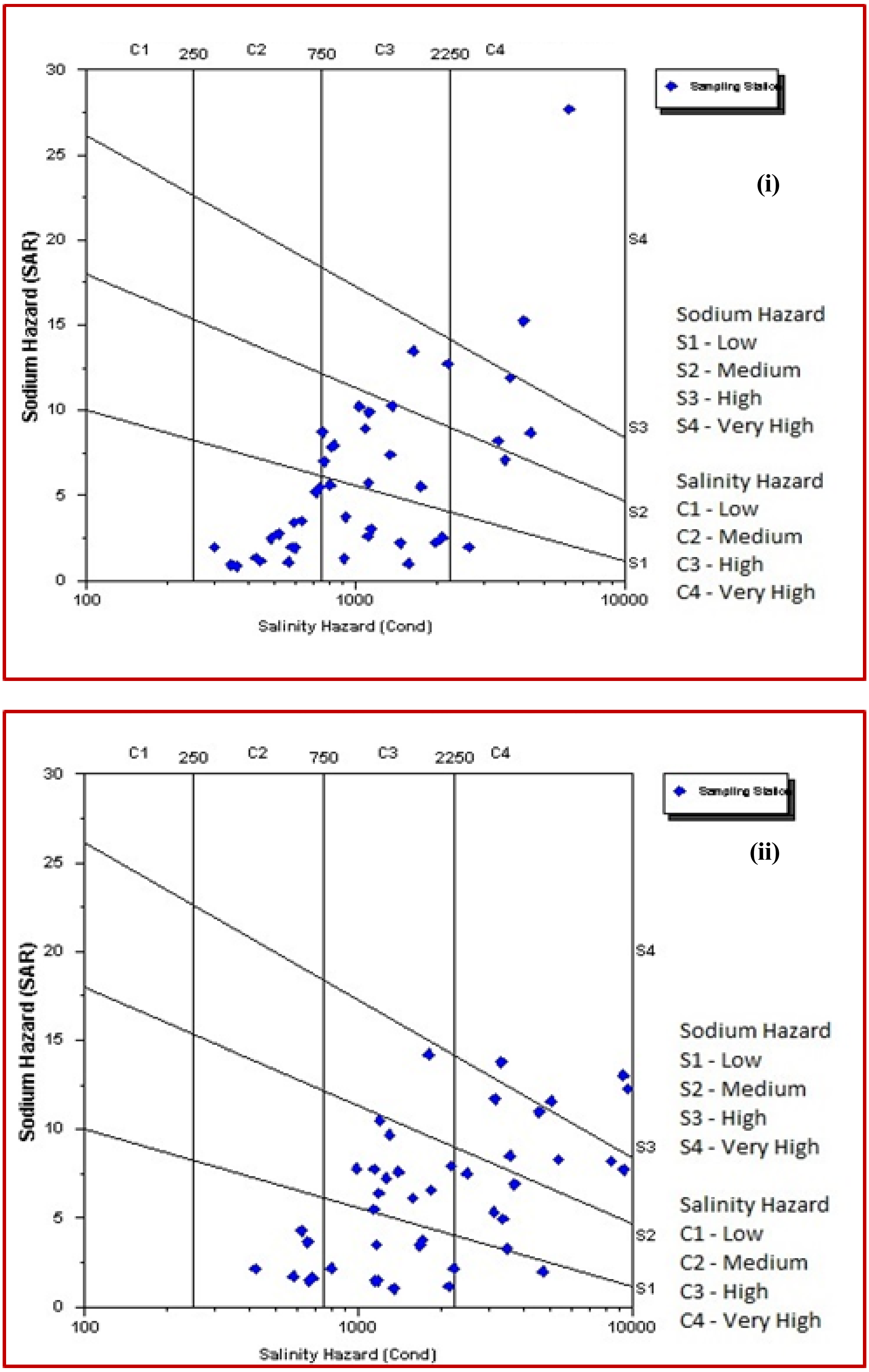


Fig 3.16c. Groundwater classification based on USSL method for inland bore wells during (i) pre monsoon (ii) post monsoon

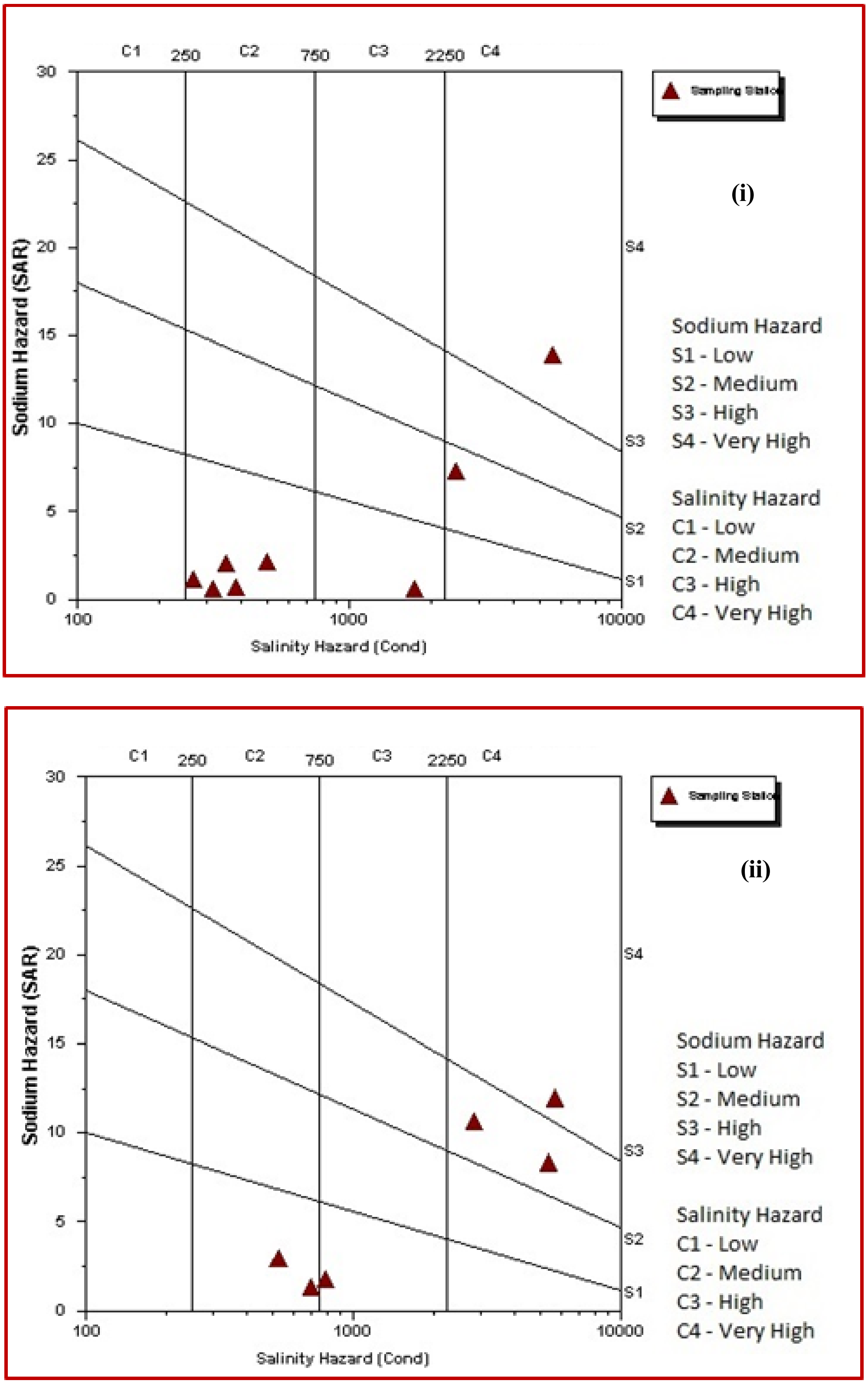


Fig 3.16d. Groundwater classification based on USSL method for inland dug wells during (i) pre monsoon (ii) post monsoon

3.6 Hydrochemical mechanism and processes

The correlation between ions and ion chemistry of water deciphers the source of solute and evolution of groundwater. The major ion chemistry of groundwater and compositional relations among ionic species can reveal the origin of solutes and processes that generated an observed water composition (Rajmohan et al. 2000; Demlie et al. 2007 and Cendon et al. 2011). The ionic correlation, abundance and chemical facies of groundwater were discussed below.

3.6.1 Ionic abundance

The abundance of ion in groundwater helps in deciphering the predominant cation and anion solute in them. The predominant cation in all well categories for both pre and post monsoon seasons were sodium (Fig 3.17a and 3.17b). Chloride was the major anion found in coastal well for both the season and sulphate was the predominant anion for inland wells.

The order of abundance of cations and anions in the pre and post monsoon seasons were as follows:

Coastal/inland alluvial dug well

Pre monsoon	Cation: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$	Anion: $Cl^- > SO_4^{2-} > HCO_3^-$
Post monsoon	Cation: $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	Anion: $Cl^- > HCO_3^- > SO_4^{2-}$

Coastal/inland alluvial tube well

Pre monsoon	Cation: $Na^+ > K^+ > Mg^{2+} > Ca^{2+}$	Anion: $Cl^- > SO_4^{2-} > HCO_3^-$
Post monsoon	Cation: $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$	Anion: $Cl^- > HCO_3^- > SO_4^{2-}$

Inland bore well

Pre monsoon	Cation: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$	Anion: $SO_4^{2-} > Cl^- > HCO_3^-$
Post monsoon	Cation: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$	Anion: $Cl^- > HCO_3^- > SO_4^{2-}$

Inland dug well

Pre monsoon	Cation: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$	Anion: $SO_4^{2-} > Cl^- > HCO_3^-$
Post monsoon	Cation: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$	Anion: $Cl^- > HCO_3^- > SO_4^{2-}$

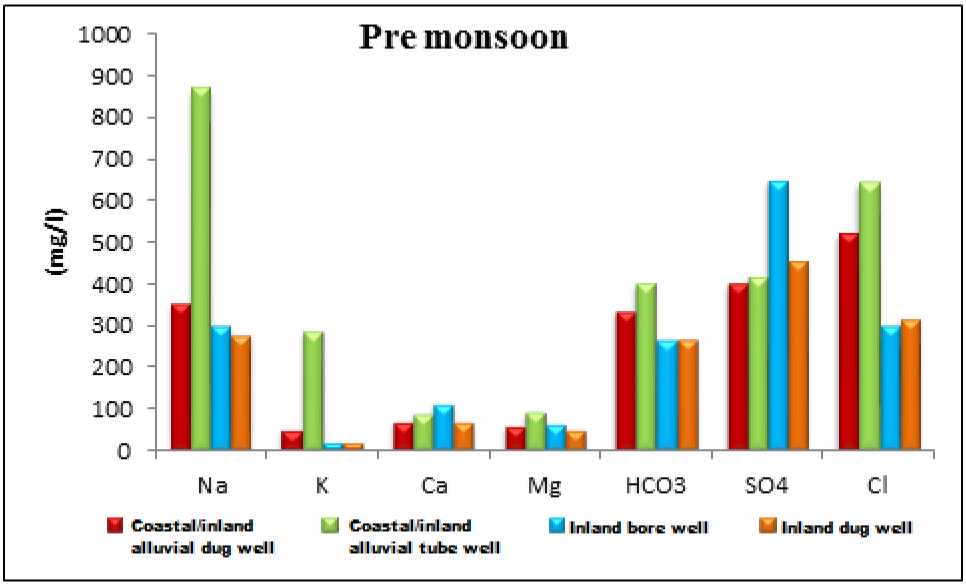


Fig 3.17a. Ionic abundance graph of the study area during pre monsoon season

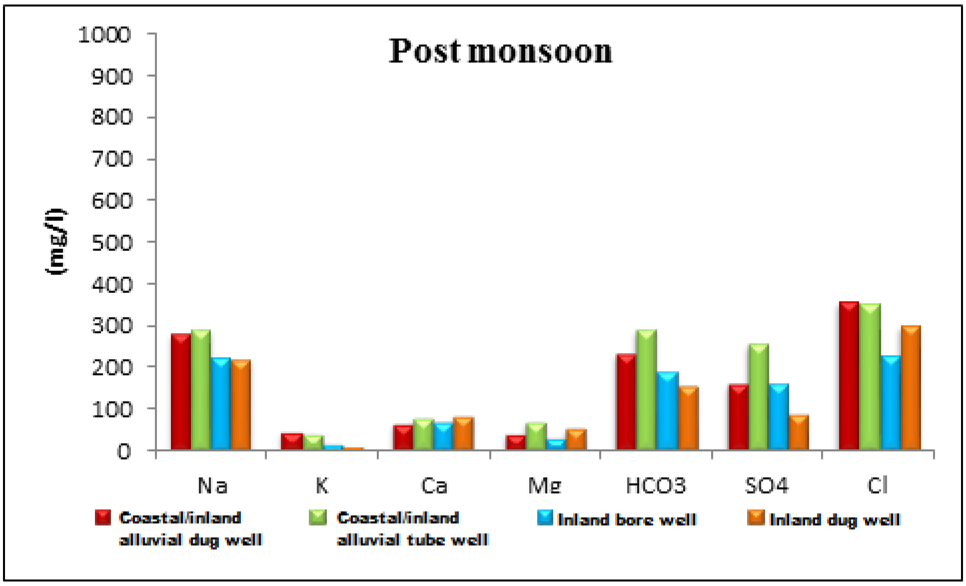


Fig 3.17b. Ionic abundance graph of the study area during post monsoon season

Seasonally average variations were plotted on graph to identify the temporal variation of ions for coastal/inland alluvial dug well, coastal/inland alluvial tube well, inland bore well and inland dug well (Fig 3.18). Sulphate show significant temporal variation in all well types. Chloride ions in tube well have great temporal fluctuation. The ion concentrations for all well types near to salt pans are well above the drinking water quality standards (BIS, 2012) leaving them as the least potable water.

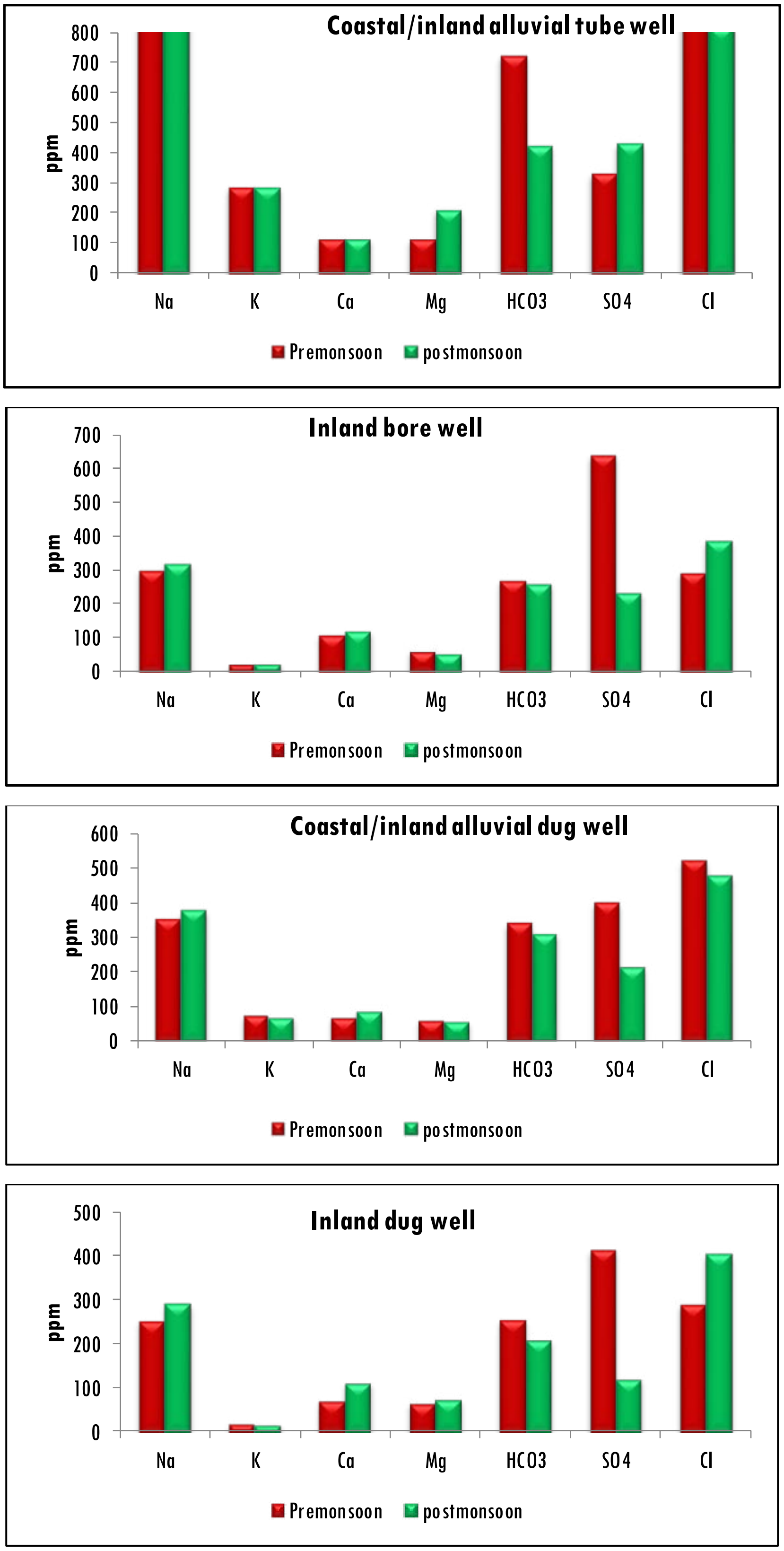


Fig 3.18: Seasonally average ionic concentration of study area during pre and post monsoon season

3.6.2 Ionic Correlations

Groundwater during its course of evolution and movement absorbs and dissolves many solutes changing the ionic chemistry of groundwater. Minerals inside the aquifer and other sedimentary formations change the chemical property of groundwater. The ratio between the dissolved ionic species in groundwater has been studied to elucidate the chemical changes of groundwater. The study area is known for its high salinity concentration, ionic ratios of the study area aids in understanding the extent of salinity. According to various publications (Vengosh et al. 2002; Mondal et al. 2010; Thilagavathi et al. 2012) sea water has a unique ionic ratio.

Na/Cl molar ratio has a critical role in identifying the geochemical process occurring in groundwater to elucidate the salinization pattern. Salinity of groundwater occurs due to many factors such as saline water ingress and leaching of aquifer material into the water sources. High levels of Na/Cl ratios ie Na/Cl >1 will be due to limited atmospheric precipitation contribution and weathering of rocks. Na/Cl ratio < 0.86 indicates the effect of salt water ingress into the fresh groundwater (Vengosh et al. 2002). In the present study 12.5% of pre and post monsoon coastal/inland alluvial dug well has a Na/Cl < 0.86 ratio, the coastal/inland alluvial tube well for pre monsoon has 20% and post monsoon 11% < 0.86 Na/Cl ratio. Less than 0.86 Na/Cl ratio is seen in 12% inland bore well for pre monsoon and 16% during post monsoon, 25% of inland dug well during post monsoon and 12.5% in the pre monsoon sample recorded Na/Cl ratio less than 0.86. The covariance diagram of Na/Cl ratio shows a high correlation for the coastal/inland alluvial dug well in the pre monsoon and inland dug well of post monsoon (Fig 3.19). Na/Cl ratio >1 signifies the occurrence of leaching from aquifer material into the groundwater.

Table 3.8: Na/Cl percentage of groundwater

Type of Aquifer	No. of Samples	Na/Cl < 0.86 pre monsoon (%)	Na/Cl < 0.86 post monsoon (%)	Na/Cl >1 Pre monsoon (%)	Na/Cl >1 post monsoon (%)
Coastal/inland alluvial dug well	40	12	12.5	70	67
Coastal/inland alluvial tube well	27	19	11	69	85
Inland bore well	43	11	16	81	79
Inland dug well	8	12.5	25	87.5	75

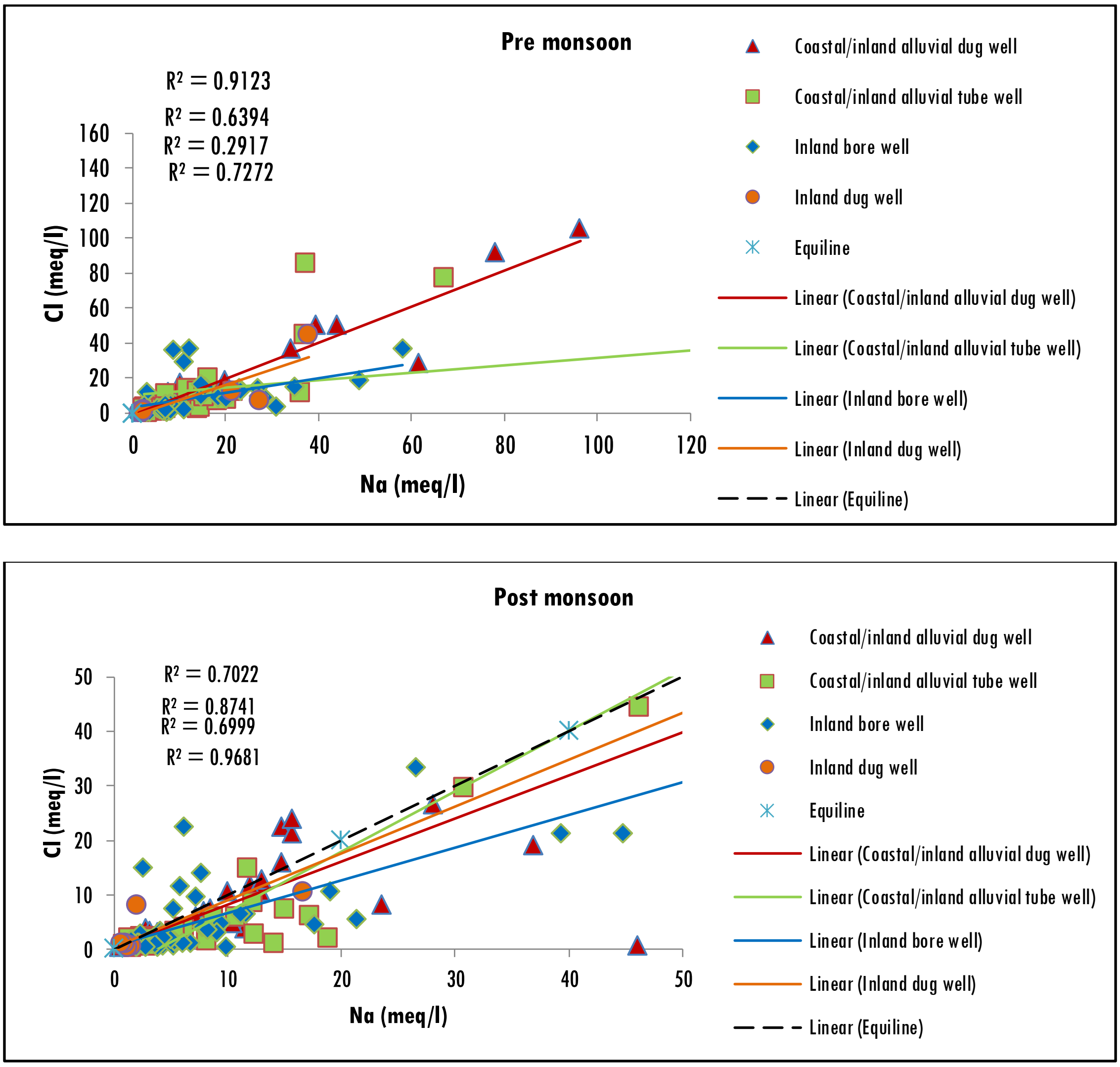


Fig 3.19: Na/Cl covariance graph of coastal/inland alluvial dug wells, coastal/inland alluvial tube wells, inland bore wells and inland dug wells for pre and post monsoon

The SO_4/Cl^- molar ratio of coastal/inland alluvial tube wells of pre monsoon season has the highest covariance followed by coastal/inland alluvial dug wells. In the post monsoon season also coastal/inland alluvial tube wells has the highest SO_4/Cl^- covariance (Fig 3.20). The coastal/inland alluvial tube well during pre monsoon season has a higher Na+K/TZ$^+$ linear relationship, while in the post monsoon season coastal/inland alluvial dug wells has the highest linear relationship (Fig 3.21). The inland dug wells during the pre monsoon season show the highest covariance with Ca+Mg/ TZ$^+$ molar ratio and in the post monsoon similar trend is shown by the coastal/inland alluvial tube well (Fig 3.22).

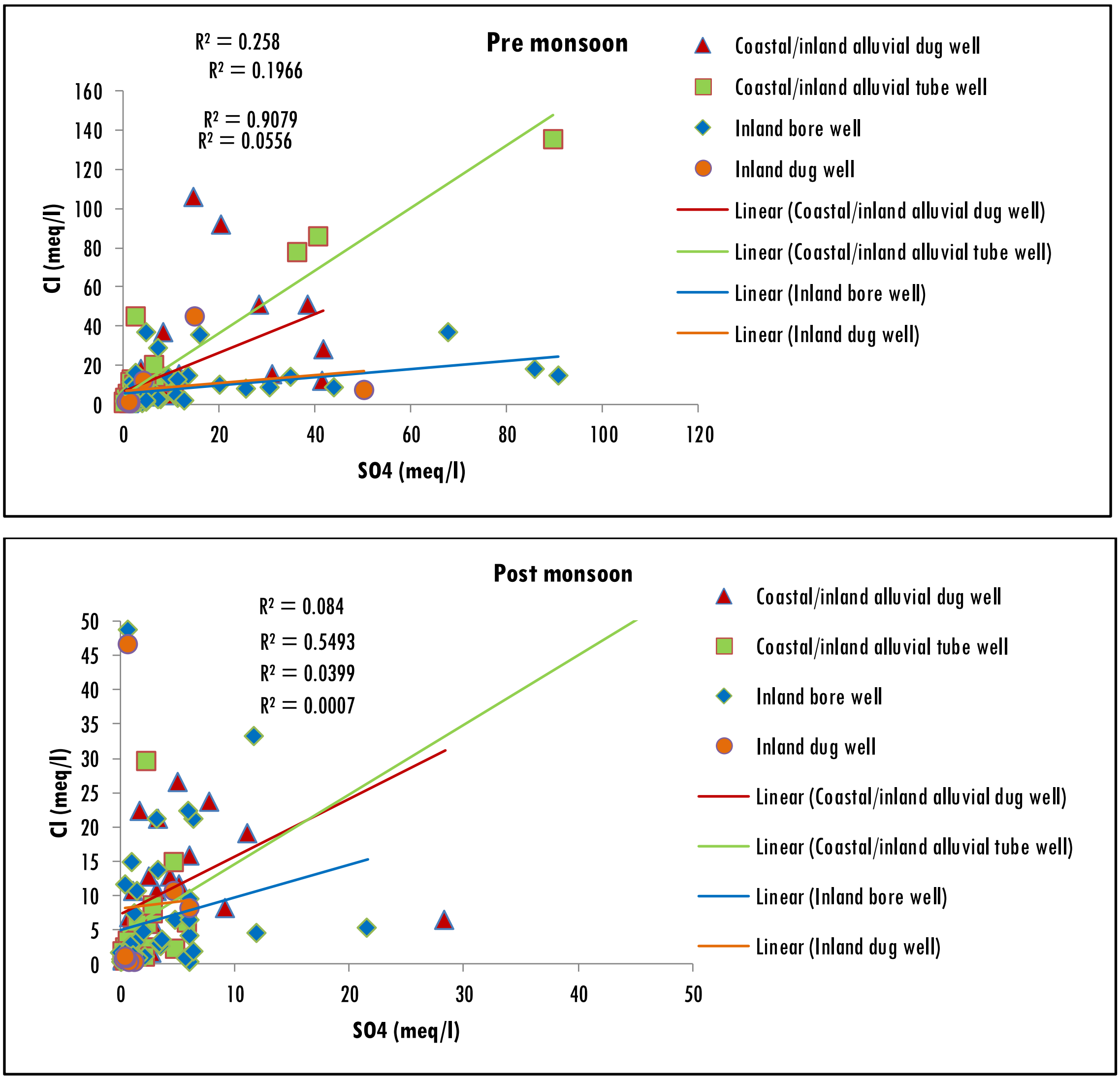


Fig 3.20: SO_4/Cl^- covariance graph of coastal/inland alluvial dug well, coastal/inland alluvial tube well, inland bore well and inland dug well for pre and post monsoon

The covariance of SO_4/Cl^- elucidates the fact that coastal/inland alluvial tube wells are affected by the saline water ingress (Fig 3.20). In the linear relationship of alkali ions (Na+K) and alkaline earth ions (Ca+Mg) with total cations, dominance of alkali metal ions in the coastal/inland alluvial tube wells and coastal/inland alluvial dug wells in both season indicates the sea water ingress (Fig 3.21 & Fig 3.22).

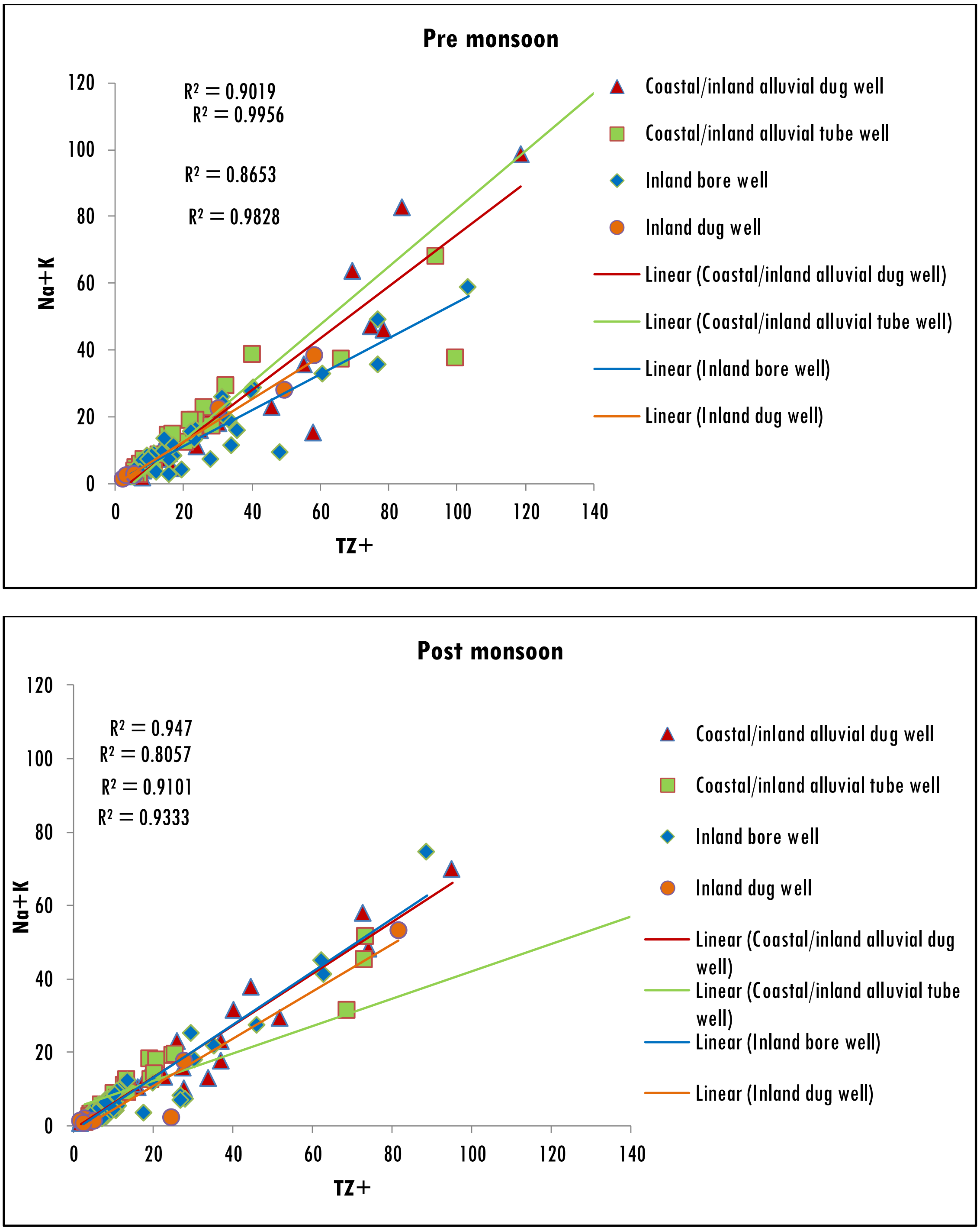
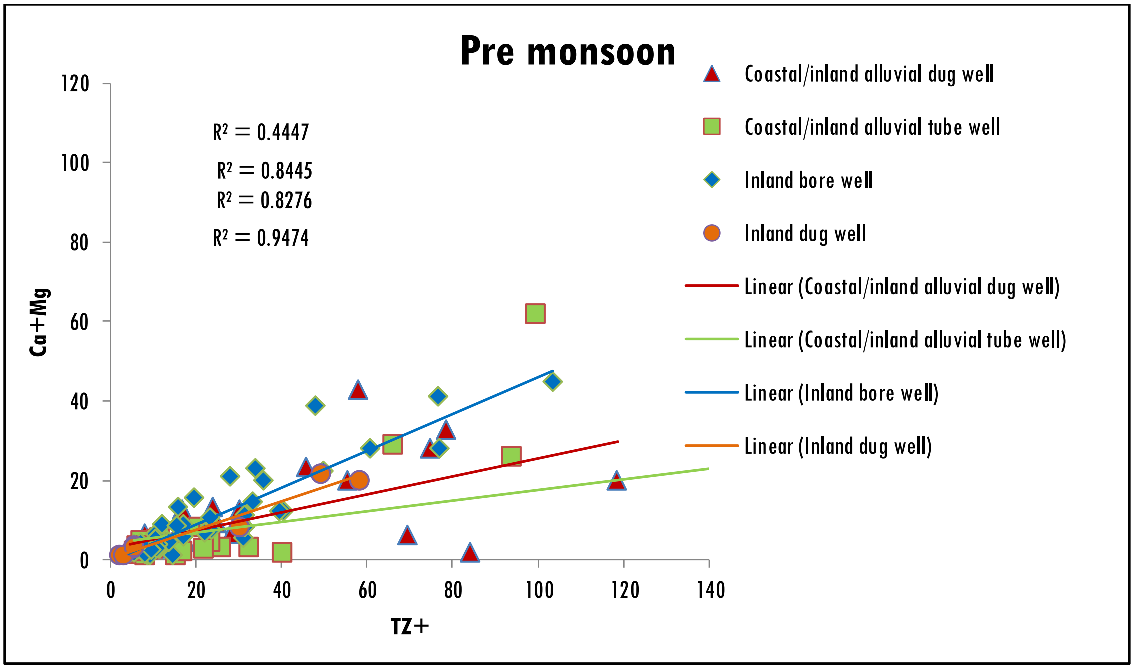


Fig 3.21: Na+K / TZ^+ covariance graph of coastal/inland alluvial dug well, coastal/inland alluvial tube well, inland bore well and inland dug well for pre and post monsoon



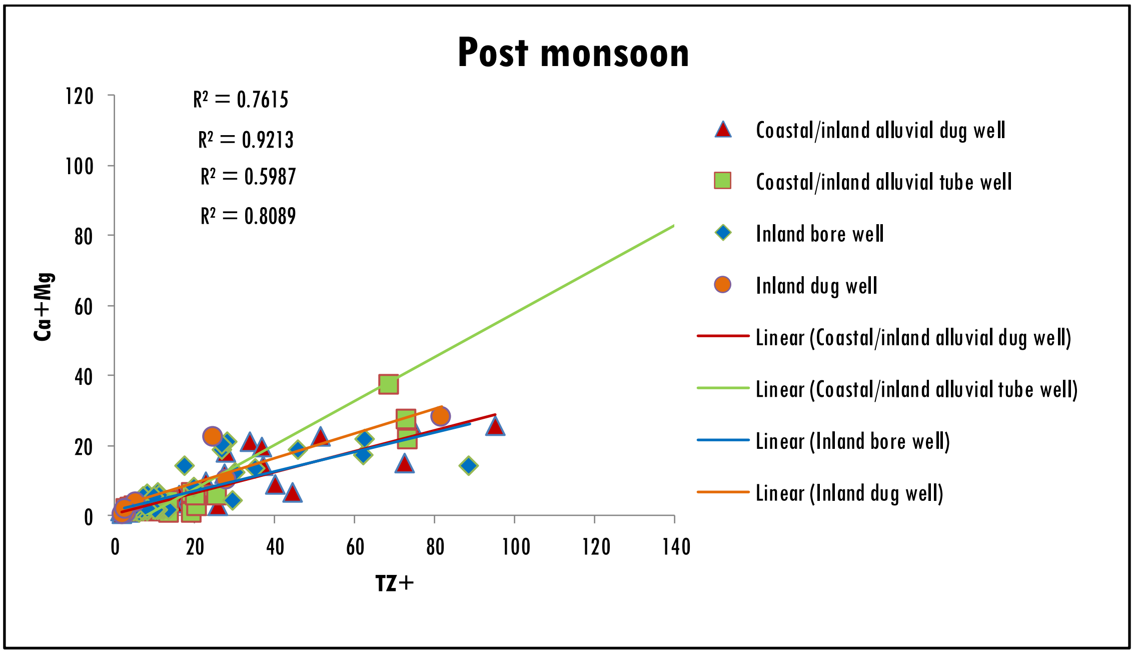


Fig 3.22: Ca+Mg/ TZ^+ covariance graph of coastal/inland alluvial dug well, coastal/inland alluvial tube well, inland bore well and inland dug well for pre and post monsoon

3.6.3 Hydrochemical Facies

Hydrochemical facies is defined as distinct zones that have cation and anion concentrations of diagnostic chemical character of water solutions in hydrological systems which is describable within defined composition categories. During the journey of formation of groundwater the chemistry of this water is interfered with the surrounding lithological framework. This variation in chemical characteristics of water is used to subdivide them into various zones .The chemical characteristics of surface and groundwater is assessed by means of hydrochemical facies for several decades and for this the piper (1944) and modified piper by Chadha (1999) is used in this study.

HILL PIPER DIAGRAM: - This diagram for disseminating hydrochemical facies was introduced by Hill (1940) and later improved by Piper(1944). The trillinear graph constitutes of three major component a ternary diagram on the left with the cations (magnesium, calcium, and sodium plus potassium), the one on right with the anions (chloride, sulfate, and carbonate plus bicarbonate) and a diamond plot in the centre, which is a matrix transformation of the two ternary diagrams. The diamond plot in the centre reveals the type of water. Samples in the top quadrant are calcium sulfate waters, samples in the left quadrant are calcium bicarbonate waters, samples in the right quadrant are sodium chloride waters, and samples in the bottom quadrant are sodium bicarbonate waters.

The trilinear piper plot of the study area reveals the fact that the coastal/inland alluvial dug well of pre and post monsoon season Na-K-Cl-SO_4 type of water as the predominant followed by Na-K-HCO_3 (Fig 3.23a). In the coastal/inland alluvial tube well Na-K-HCO_3 as the predominant type followed by Na-K-Cl-SO_4 (Fig 3.23b). During the pre and post monsoon season, the inland bore well the predominant water type is Na-K-HCO_3, a reduction in Na-K-Cl-SO_4 is observed in the post monsoon season (Fig 3.23c). During the post monsoon, reduction in Na-K-HCO_3 water type is observed in the inland dug well and the other predominant water type is Na-K-Cl-SO_4 for both seasons (Fig 3.23d). Na-Cl water type is the predominant type in all the wells during pre and post monsoon. The alkali exceeds the alkaline earth in all the wells for both the seasons.

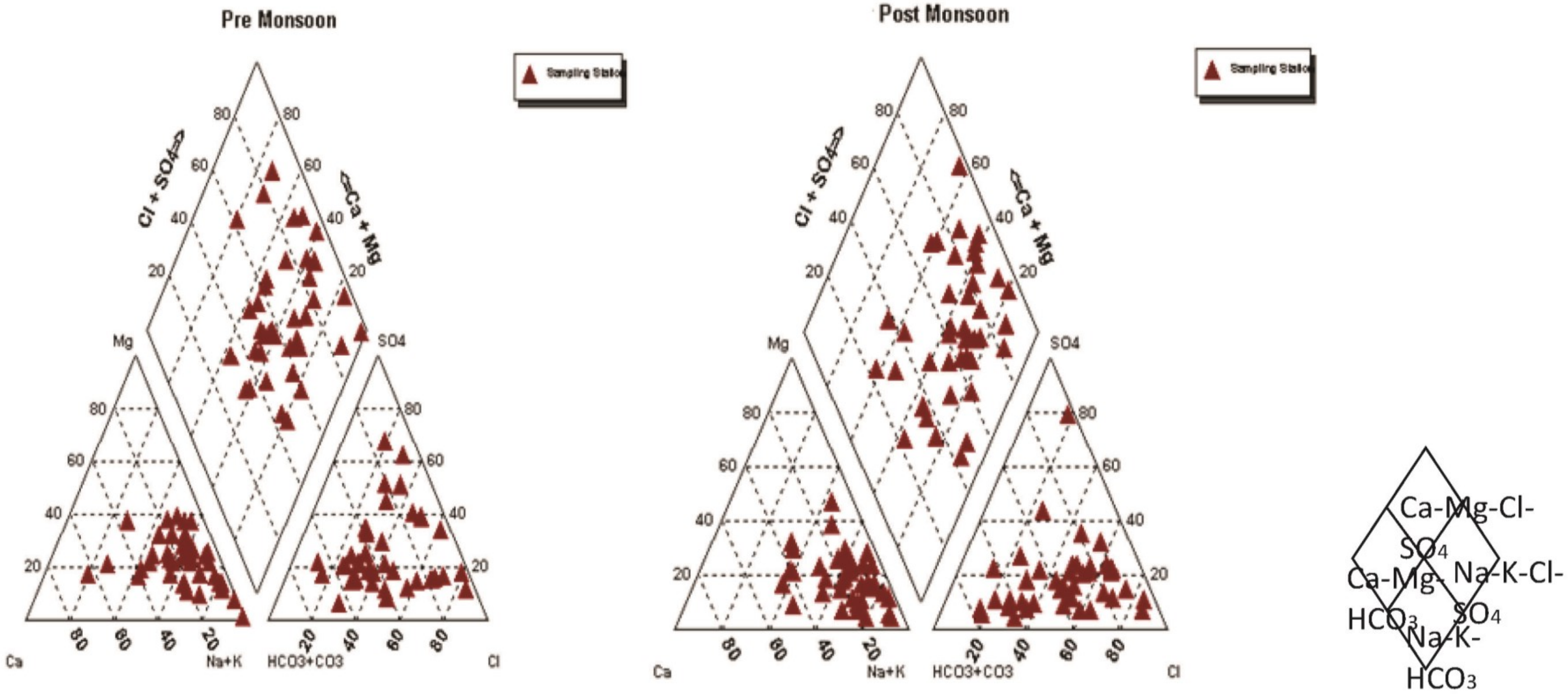


Fig 3.23a. Hill Piper trillinear diagram of coastal/inland alluvial dug well

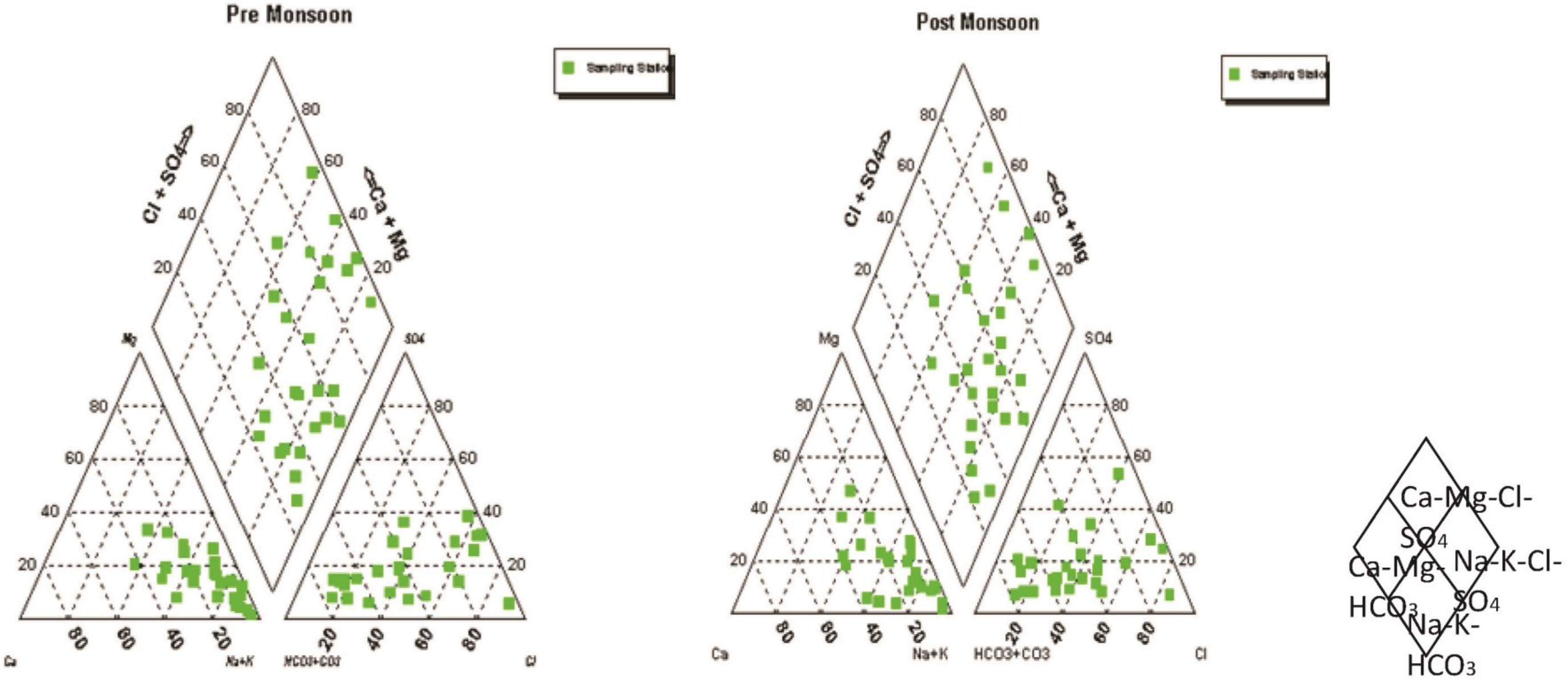


Fig 3.23b. Hill Piper trillinear diagram of coastal/inland alluvial tube well

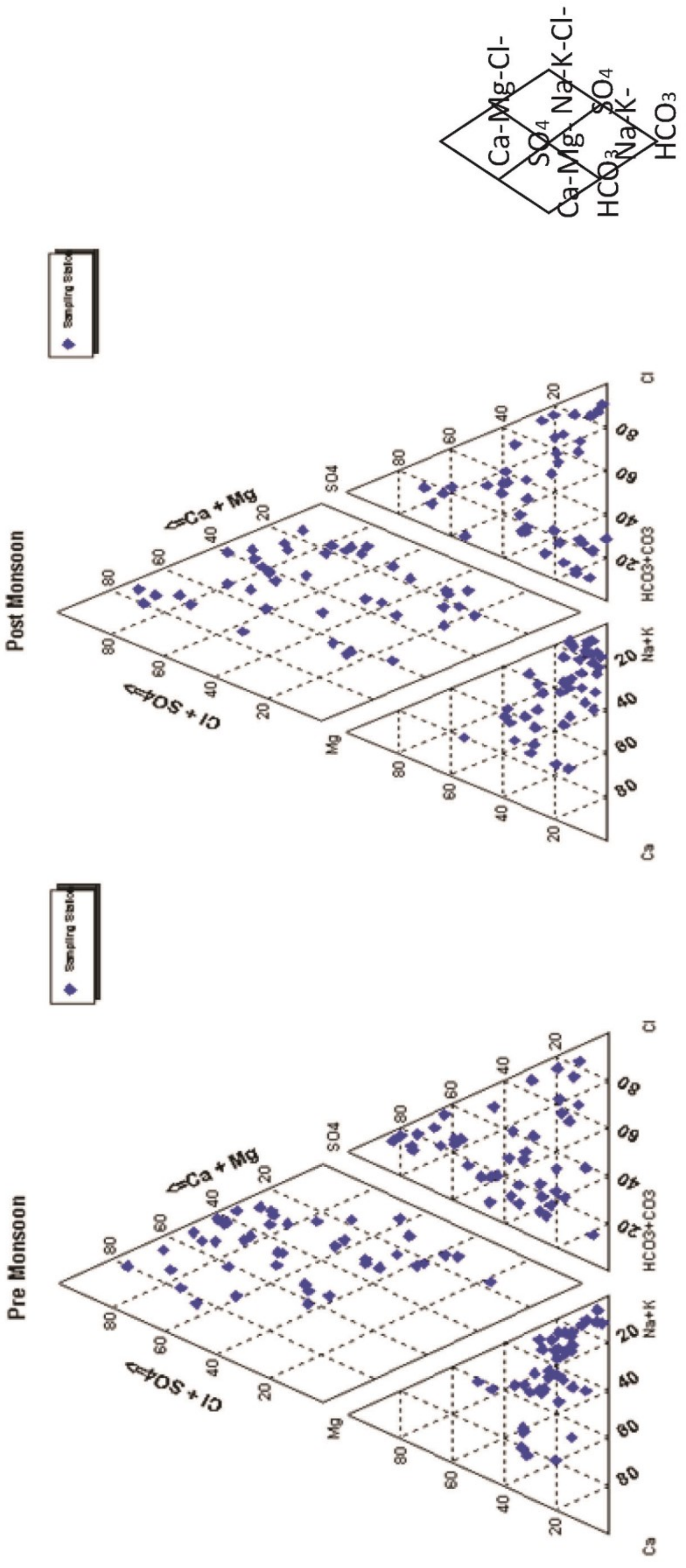


Fig 3.23c. Hill Piper trillinear diagram of inland bore well

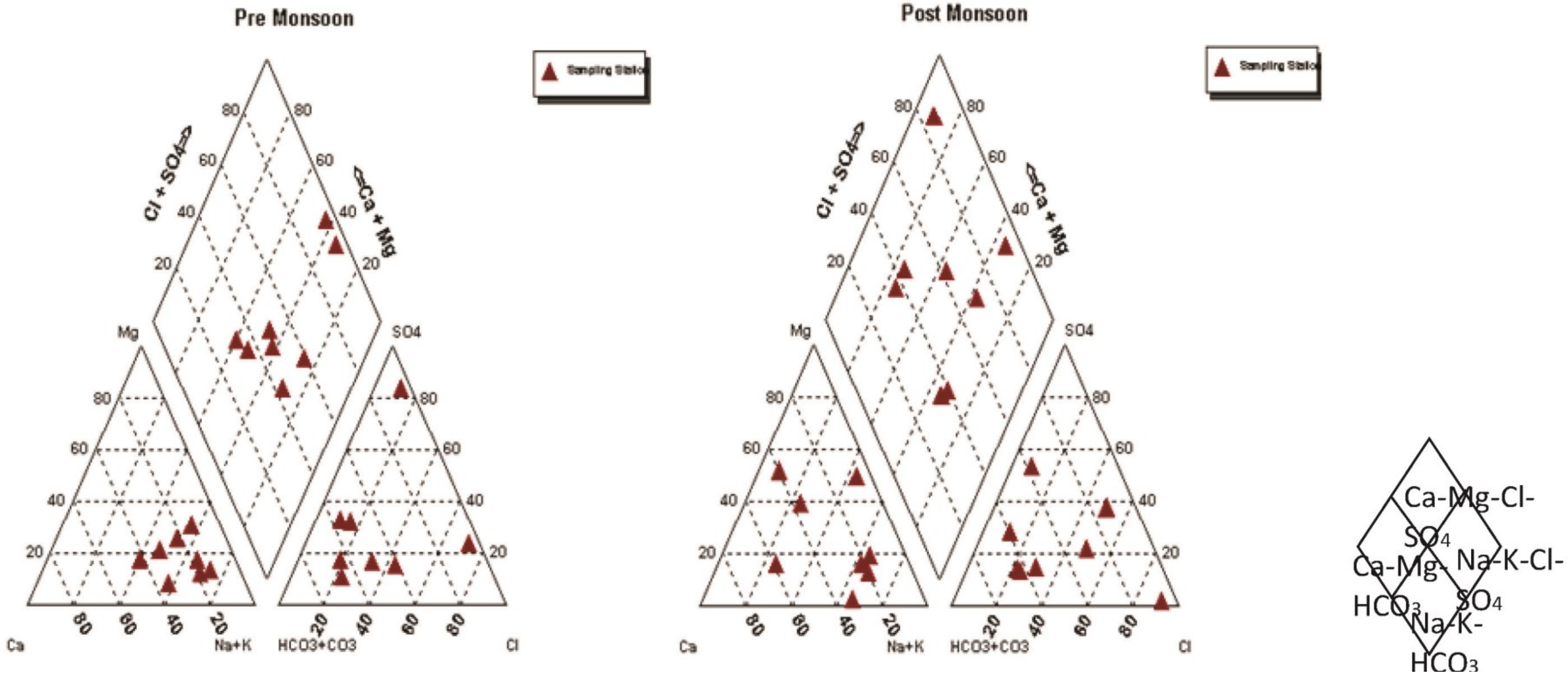


Fig 3.23d. Hill Piper Trillinear diagram of inland dug well

CHADHAS PLOT: In order to derive a better understanding about the hydrochemical process and facies modified chadha plot was used. According to Chadha the graph is divided into four quadrants and eight zones and the eight zones depicts the following.

Table 3.9: Characteristics of various zones as suggested by Chadhas plot

Zone No.	Characteristics
1	Alkaline earths exceed alkali metals.
2	Alkali metals exceed alkaline earths.
3	Weak acidic anions exceed strong acidic anions.
4	Strong acidic anions exceed weak acidic anions.
5	Alkaline earths and weak acidic anions exceed alkali metals and strong acidic anions.
6	Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions.
7	Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions.
8	Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions.

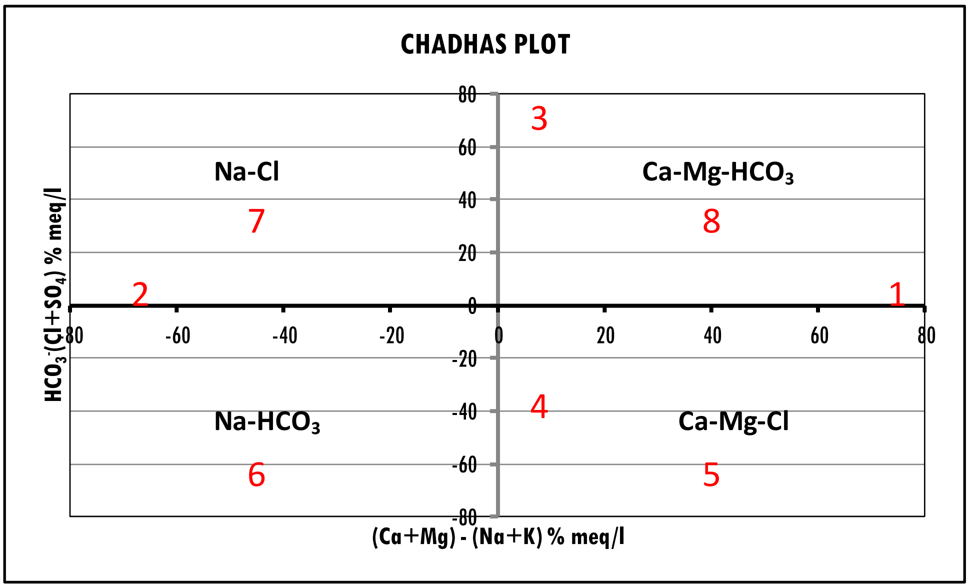


Fig 3.24: Chadhas plot zonation

In the present study, alkaline earth metals exceed alkali metals and strong acidic anions exceed weak acidic anions in coastal/inland alluvial dug well for both the season. The predominant water type observed is Na-HCO_3^- type (Fig 3.25a). The coastal/inland alluvial tube well shows a tendency in migrating from Na-HCO_3^- type to Na-Cl type from post monsoon to pre monsoon (Fig 3.25b). Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions during the pre monsoon season for coastal/inland alluvial tube well (Fig 3.25b). Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions during the post monsoon for inland bore well samples. A reduction from Na-Cl type to Na-HCO_3^- type is observed in the inland bore well samples from pre monsoon to post monsoon (Fig 3.25c). Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions in the inland dug wells for both the season (Fig 3.25d).

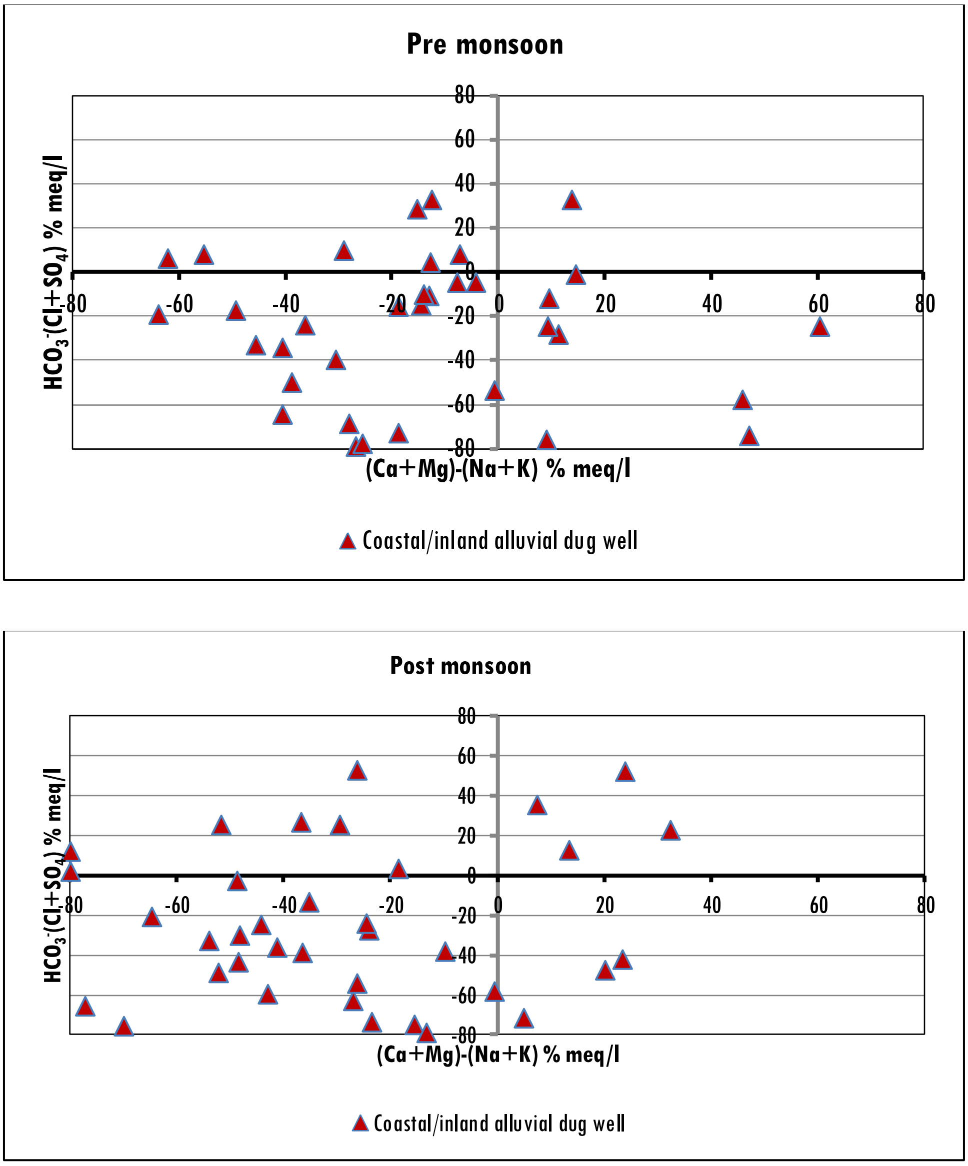


Fig 3.25a. Chadhas classification of coastal/inland alluvial dug well

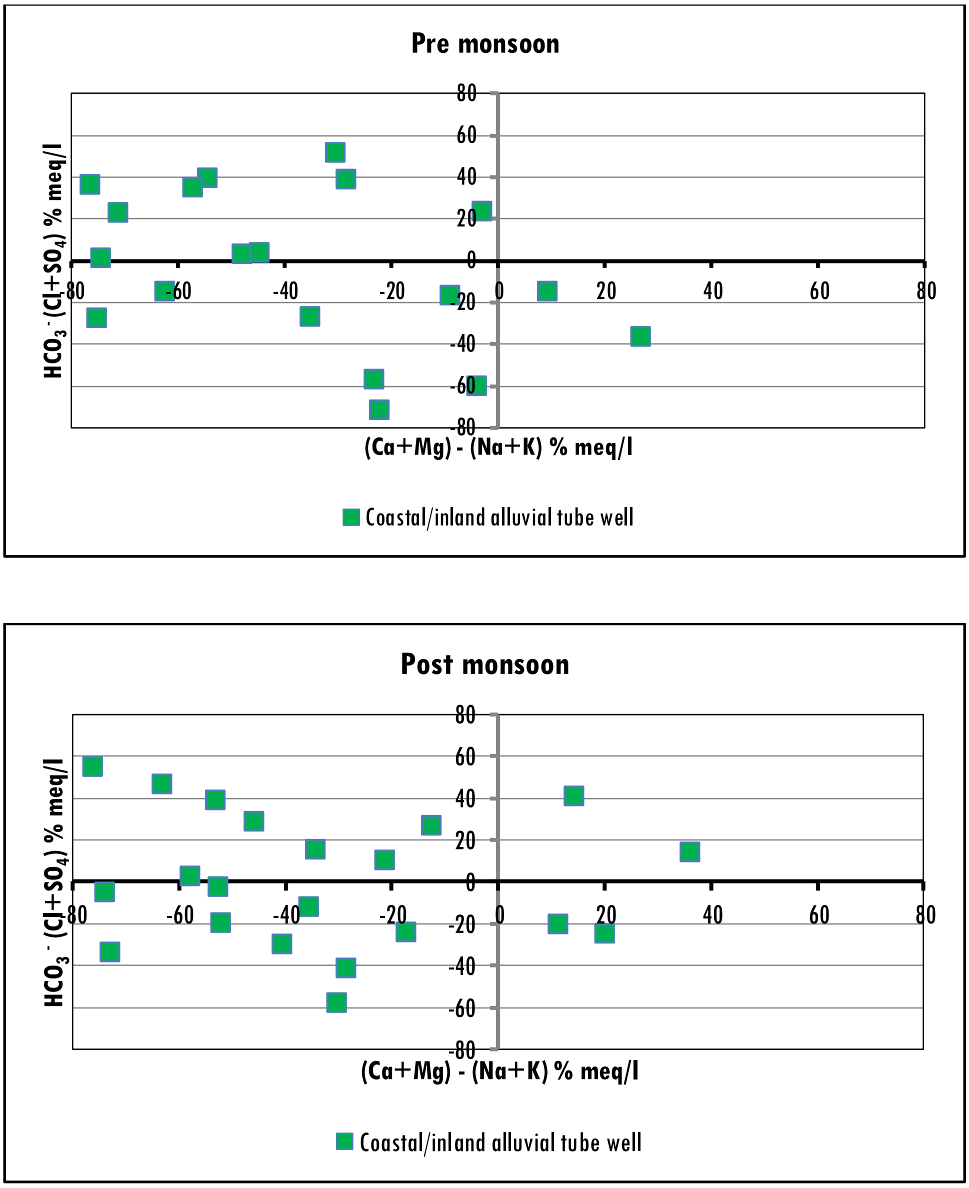


Fig 3.25b. Chadhas classification of coastal/inland alluvial tube well

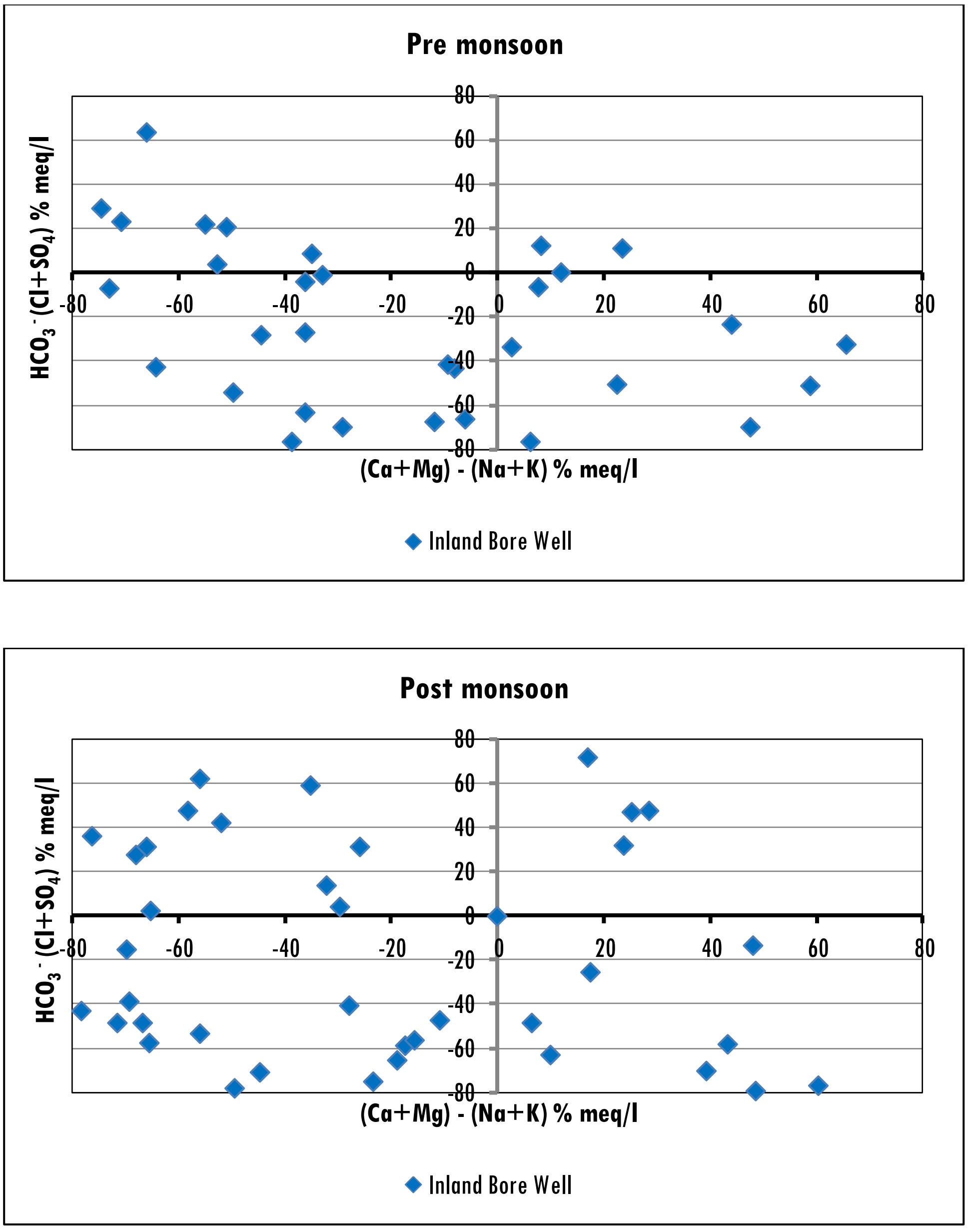
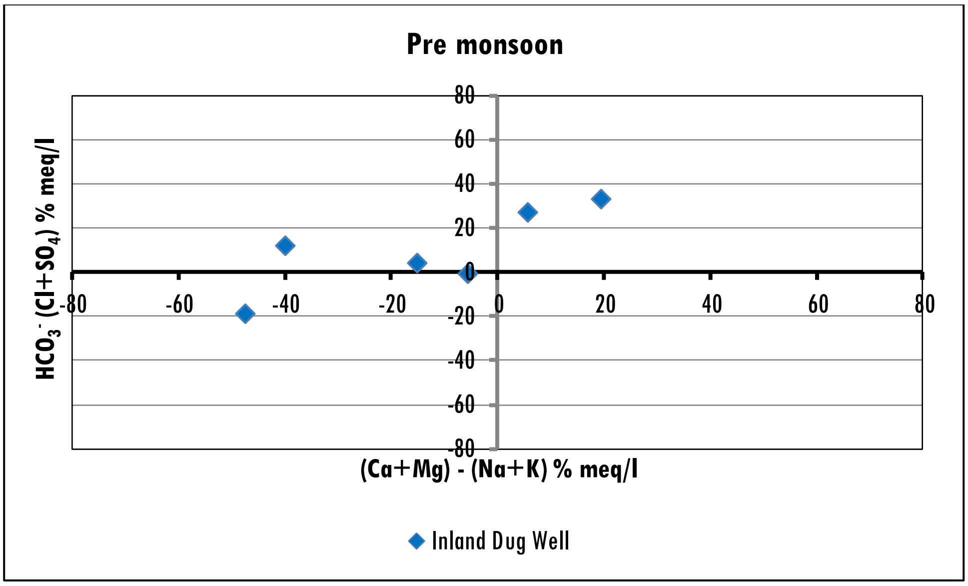


Fig 3.25c. Chadhas classification of inland bore well



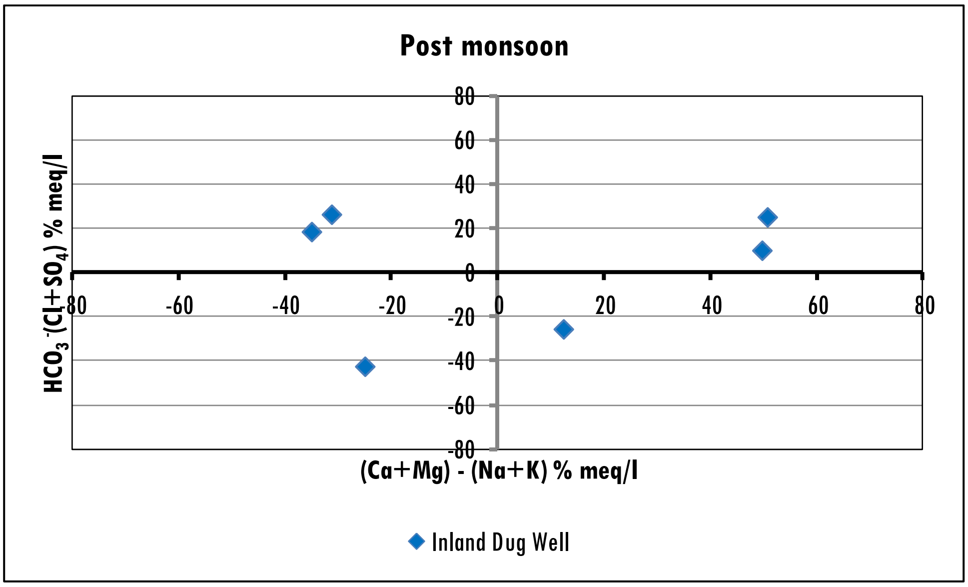


Fig 3.25d: Chadhas classification of inland dug well

GIBBS DIAGRAM:

The study on hydrochemical water quality explains the relationship of groundwater chemistry with the containing aquifer lithology (Viswanathiah and Sastri, 1973; Sastri, 1975). Such relations would help not only to explain the origin and distribution of the dissolved constituents but also to elucidate the factors controlling the groundwater chemistry (Rangarajan and Balasubramanian, 1990). Gibbs (1970) formulated a model for understanding the hydrochemistry of groundwater, which helps in identifying the factors such as evaporation, precipitation and rock interaction dominance in the hydrochemistry of groundwater.

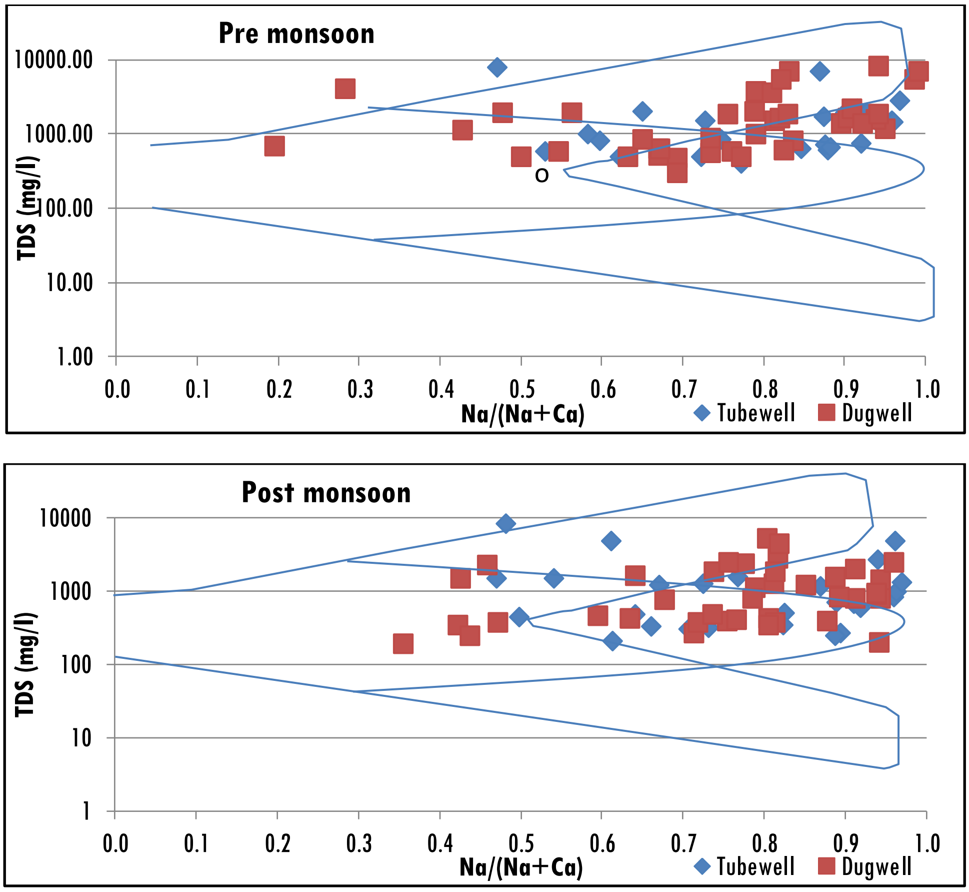


Fig 3.26a. Gibbs plot for pre and post monsoon coastal/inland alluvial tube and dug well

The mechanism controlling the hydrochemistry of groundwater in the study area using Gibbs plot for coastal and inland groundwater (Fig 3.26a and Fig 3.26b). In the present study no precipitation dominance was found in coastal and inland groundwater for all the season. No samples were found in the precipitation zone deciphering the fact that precipitation has little or no influence in controlling the hydrochemistry of the study area and the area is highly deprived of from rainfall. Highest sampling cluster in the evaporation zone is observed for the pre monsoon coastal/inland alluvial dug well. During the post monsoon season, clustering of samples is seen within the rock water interaction dominance for both coastal and inland wells. Similar observation was found in groundwater quality of Paravanar river sub basin, Cuddalore district, Tamil Nadu that the study area is controlled by rock-water interaction (Shankar et al. 2011). This reveals the fact that aquifer lithology also controls the hydrogeochemistry of the study area.

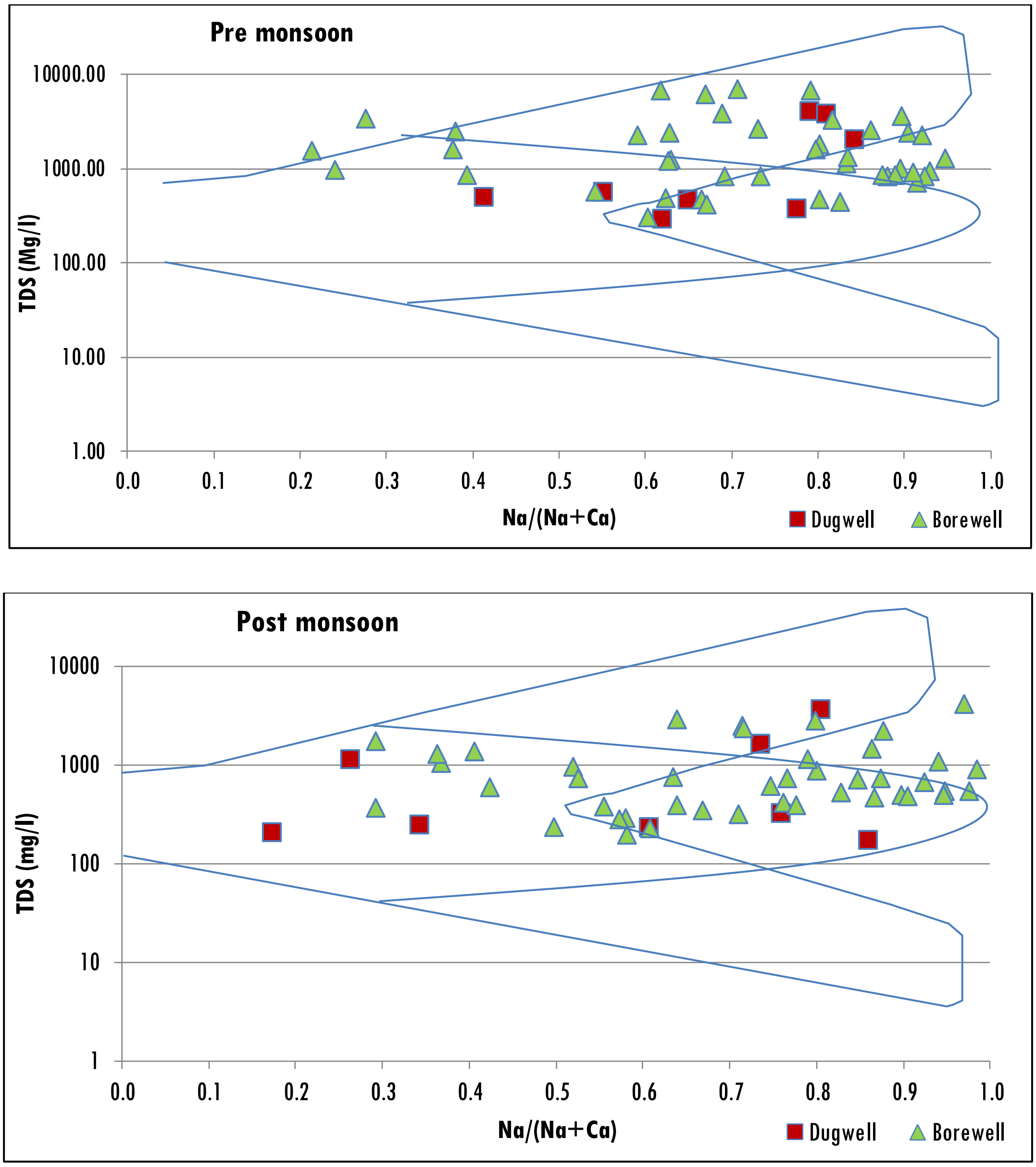


Fig 3.26b. Gibbs plot for pre and post monsoon inland dug and bore well

3.7 Multivariate statistical analysis

Multivariate statistical methods including factor analysis (FA), cluster analysis (CA), and correlation analysis have been used to evaluate the spatial variations and the interpretation of water quality data.

3.7.1 Correlation coefficient matrix

Pearson correlation coefficient matrix is applied to perform principal component analysis. Correlation matrix analysis is used to account for the degree of mutually shared variability between individual pairs of groundwater quality variables. Correlation coefficient (r) of correlation matrix is a measure of interrelationship for all pairs of constituents were determined in correlation analysis and it was expressed the extent to which two variables are statistically associated (Ashley and Lloyd, 1978). Perfect correlation coefficient is ranging 0.99 to 1.00. Strong correlation coefficient is ranging 0.80 to 0.98. Parameters showing correlation coefficients of $r>0.5-0.8$ are considered to be moderate correlation. Weak correlation coefficient is considered when $r<0.5$. The negative values show inverse relationships between chemical parameters. The strong to perfect correlation between the chemical parameters is an indication of common source. The correlations between various ions in groundwater of the entire study area are presented in Table 3.10, 3.11, 3.12 and 3.13.

Table 3.10: Correlation matrix for the hydrogeochemical parameters in coastal/inland alluvial dug well during pre monsoon and post monsoon period

Pre Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	1.00									
pH	0.09	1.00								
TDS	**0.99**	0.08	1.00							
Na^+	**0.90**	0.11	**0.92**	1.00						
K^+	0.69	0.23	0.67	0.51	1.00					
Ca^{2+}	0.39	-0.01	0.38	0.15	0.31	1.00				
Mg^{2+}	0.72	0.03	0.71	0.50	0.54	0.56	1.00			
HCO_3^-	0.24	0.27	0.29	0.23	0.44	0.13	0.20	1.00		
SO_4^{2-}	0.75	0.01	0.79	0.59	0.61	0.60	0.74	0.29	1.00	
Cl^-	**0.92**	0.07	**0.91**	**0.96**	0.52	0.20	0.53	0.09	0.51	1.00
Post Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	**1.00**									
pH	**0.21**	1.00								
TDS	**1.00**	0.21	**1.00**							
Na^+	**0.91**	0.18	**0.91**	**1.00**						
K^+	**0.50**	0.01	**0.50**	**0.33**	1.00					
Ca^{2+}	**0.79**	0.07	**0.79**	**0.75**	0.35	1.00				
Mg^{2+}	**0.59**	-0.14	**0.59**	**0.58**	0.40	0.68	1.00			
HCO_3^-	**0.37**	0.60	**0.37**	**0.24**	0.23	0.06	0.08	1.00		
SO_4^{2-}	**0.53**	-0.12	**0.53**	**0.30**	0.30	0.40	0.41	0.11	1.00	
Cl^-	**0.91**	0.15	**0.91**	**0.84**	0.41	0.71	0.40	0.14	0.29	1.00

Table 3.11: Correlation matrix for the hydrogeochemical parameters in coastal/inland alluvial tube well during pre monsoon and post monsoon period

Pre Monsoon	**EC**	**pH**	**TDS**	**Na**	**K**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	1.00									
pH	0.29	1.00								
TDS	**1.00**	0.29	1.00							
Na^+	**0.98**	0.39	**0.98**	1.00						
K^+	**0.96**	0.44	**0.96**	**0.99**	1.00					
Ca^{2+}	0.40	-0.35	0.40	0.24	0.18	1.00				
Mg^{2+}	**0.99**	0.33	**0.99**	**0.99**	**0.97**	0.38	1.00			
HCO_3^-	0.17	0.03	0.17	0.18	0.19	-0.14	0.08	1.00		
SO_4^{2-}	**0.96**	0.14	**0.96**	**0.90**	**0.85**	0.57	**0.93**	0.09	1.00	
Cl^-	**0.89**	0.01	**0.89**	**0.80**	0.73	0.70	**0.87**	-0.01	**0.95**	1.00
Post Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	**1.00**									
pH	**-0.20**	1.00								
TDS	**1.00**	-0.20	**1.00**							
Na^+	**0.12**	-0.03	**0.12**	**1.00**						
K^+	**-0.09**	0.34	**-0.09**	**0.44**	1.00					
Ca^{2+}	**0.16**	0.18	**0.16**	**0.74**	0.56	1.00				
Mg^{2+}	**0.07**	0.38	**0.07**	**0.68**	0.64	0.95	**1.00**			
HCO_3^-	**-0.10**	0.61	**-0.10**	**0.24**	0.54	0.13	**0.26**	1.00		
SO_4^{2-}	**0.02**	0.28	**0.02**	**0.78**	0.62	0.89	**0.95**	0.25	**1.00**	
Cl^-	**0.10**	-0.17	**0.10**	**0.94**	0.29	0.73	**0.63**	0.01	**0.74**	1.00

Table 3.12: Correlation matrix for the hydrogeochemical parameters in inland bore well during pre monsoon and post monsoon period

Pre Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	1.00									
pH	-0.13	1.00								
TDS	**1.00**	-0.13	1.00							
Na^+	**0.92**	0.02	**0.92**	1.00						
K^+	0.14	0.22	0.14	0.18	1.00					
Ca^{2+}	**0.78**	-0.36	**0.78**	0.59	0.04	1.00				
Mg^{2+}	**0.88**	-0.24	**0.87**	**0.78**	0.04	**0.86**	1.00			
HCO_3^-	-0.04	0.49	-0.04	0.08	0.22	-0.31	-0.21	1.00		
SO_4^{2-}	**0.88**	-0.08	**0.88**	**0.85**	-0.02	0.61	**0.81**	-0.12	1.00	
Cl^-	0.62	-0.12	0.62	0.54	0.12	0.74	0.58	-0.24	0.44	1.00
Post Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	1.00									
pH	-0.23	1.00								
TDS	**1.00**	-0.23	1.00							
Na^+	**0.91**	-0.22	**0.91**	1.00						
K^+	0.38	-0.21	0.38	0.37	1.00					
Ca^{2+}	0.63	-0.14	0.63	0.39	0.30	1.00				
Mg^{2+}	**0.77**	-0.26	0.77	0.62	0.24	0.56	1.00			
HCO_3^-	0.18	0.38	0.18	0.23	-0.14	-0.20	0.06	1.00		
SO_4^{2-}	0.53	-0.06	0.53	0.28	0.04	0.40	0.48	0.01	1.00	
Cl^-	**0.88**	-0.32	**0.88**	0.84	0.39	0.61	0.68	0.00	0.20	1.00

Table 3.13: Correlation matrix for the hydrogeochemical parameters in inland dug well during pre monsoon and post monsoon period

Pre Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	1.00									
pH	-0.51	1.00								
TDS	**1.00**	-0.51	1.00							
Na^+	**0.98**	-0.46	**0.98**	1.00						
K^+	0.31	-0.55	0.31	0.39	1.00					
Ca^{2+}	**0.95**	-0.41	**0.96**	**0.96**	0.34	1.00				
Mg^{2+}	**0.94**	-0.54	**0.95**	**0.86**	0.19	**0.84**	1.00			
HCO_3^-	0.02	-0.27	-0.01	0.12	0.74	-0.02	-0.15	1.00		
SO_4^{2-}	**0.77**	-0.48	**0.78**	0.65	0.00	0.60	**0.94**	-0.26	1.00	
Cl^-	**0.77**	-0.22	**0.77**	**0.85**	0.30	**0.90**	0.55	0.01	0.24	1.00
Post Monsoon	**EC**	**pH**	**TDS**	**Na^+**	**K^+**	**Ca^{2+}**	**Mg^{2+}**	**HCO_3^-**	**SO_4^{2-}**	**Cl^-**
EC	**1.00**									
pH	**0.51**	1.00								
TDS	**1.00**	0.51	**1.00**							
Na^+	**0.96**	0.59	**0.96**	**1.00**						
K^+	**0.75**	0.87	**0.75**	**0.77**	1.00					
Ca^{2+}	**0.72**	0.28	**0.72**	**0.78**	0.49	**1.00**				
Mg^{2+}	**0.64**	0.18	**0.64**	**0.74**	0.36	**0.98**	1.00			
HCO_3^-	**0.50**	0.58	**0.50**	**0.45**	0.76	**0.44**	0.27	1.00		
SO_4^{2-}	**-0.08**	-0.01	**-0.08**	**-0.04**	-0.02	**0.49**	0.46	0.45	1.00	
Cl^-	**0.93**	0.48	**0.93**	**0.98**	0.68	**0.85**	0.83	0.37	0.03	1.00

From all the Tables (Table 3.10, 3.11, 3.12 and 3.13.) perfect correlation is found between TDS and EC and in coastal/inland alluvial dug well during pre- monsoon with K^+ and Na^+, and with Mg^{2+}, EC, TDS and Na^+. The correlation coefficient of Na^+ and Cl^- is fairly high, it can be deduced that for most of the groundwater samples Na^+ and Cl^- originate from a common source (Asna Rani et al. 2008).

3.7.2 Factor analysis

Factor analysis exposes the important factor responsible for variation in groundwater quality eventually leads to sources identification of groundwater pollution. Therefore, the factor analysis is applied to extract the most significant factors and to reduce the contribution of less significant variables to simplify even more of the data structure coming from factor analysis. In the present work, factor extraction (2 factors) was done by principal components; whereas, varimax rotation with Kaiser-Mayer-Olkin test (KMO) was performed. KMO was showed a value of 0.8, indicated the meritorious adequacy for factor analysis. Variable loadings, explaining variance and corresponding factors are in Table 3.14, 3.15, 3.16 and 3.17.

Table 3.14: Factor pattern for coastal/inland alluvial dug well

Coastal/inland alluvial dug well	**Pre monsoon**		**Post monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
EC (µS/Cm)	**0.975**	-0.072	**0.986**	0.056
pH	0.025	**0.825**	0.127	**0.845**
TDS (mg/l)	**0.981**	-0.041	**0.986**	0.056
Na^+(mg/l)	**0.869**	0.018	**0.903**	0.032
K^+(mg/l)	**0.745**	0.285	**0.559**	0.106
Ca^{2+}(mg/l)	0.490	-0.128	**0.845**	-0.190
Mg^{2+}(mg/l)	**0.786**	-0.204	**0.691**	-0.302
HCO_3^- (mg/l)	0.344	**0.731**	0.318	**0.723**
SO_4^{2-}(mg/l)	**0.837**	-0.087	0.537	-0.351
Cl^-(mg/l)	**0.856**	-0.107	**0.871**	0.025
Variability %	56.332	13.808	54.299	15.073
Cumulative %	56.332	70.140	54.299	69.372

Table 3.15: Factor pattern for coastal/inland alluvial tube well

Coastal/inland alluvial tube well	**Pre monsoon**		**Post monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
EC (µS/Cm)	**0.998**	0.042	0.108	**0.969**
pH	0.242	**0.82**	0.265	0.106
TDS(mg/l)	**0.998**	0.042	0.108	**0.969**
Na^+(mg/l)	**0.971**	0.177	**0.863**	0.065
K^+(mg/l)	**0.945**	0.243	**0.693**	-0.285
Ca^{2+}(mg/l)	0.452	-0.743	**0.933**	0.096
Mg^{2+}(mg/l)	**0.988**	0.033	**0.945**	-0.021
HCO_3^- (mg/l)	0.149	**0.577**	0.332	-0.320
SO_4^{2-}(mg/l)	**0.969**	-0.156	**0.956**	-0.066
Cl^-(mg/l)	**0.911**	-0.348	**0.794**	0.093
Variability %	68.559	17.980	47.364	47.364
Cumulative %	68.559	86.539	20.984	68.348

For inland dug and bore well the variability percentage of factor 1 is 58% and 53% - 66% and 65% in pre and post monsoon respectively. The total variance had strong positive loading on EC, TDS, Na^+, Ca^{2+}, Mg^{2+}, SO_4^{2-} and Cl^-. The high loading of TDS, Ca^{2+}, Na^+, and Cl^- is due to saltwater intrusion (Asaad et al. 2016). The high loading of SO_4 is related to the long-history of evaporation process. In both the season Factor 2 represented by high loading of HCO_3^-, and pH except in inland bore well during pre monsoon represented by the variables K^+ and HCO_3^- with 19% variance. The high value of K^+ suggests pollution from application of potash fertilizers to agricultural lands.

Table 3.16: Factor pattern for Inland bore well

Inland bore well	**Pre monsoon**		**Post monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
EC(µS/Cm)	**0.972**	0.154	**0.978**	0.168
pH	-0.372	**0.578**	-0.360	**0.775**
TDS(mg/l)	**0.971**	0.155	**0.978**	0.168
Na^+(mg/l)	**0.889**	0.308	**0.871**	0.204
K^+(mg/l)	0.099	**0.617**	0.450	-0.315
Ca^{2+}(mg/l)	**0.862**	-0.212	**0.712**	-0.256
Mg^{2+}(mg/l)	**0.930**	-0.054	**0.830**	-0.009
HCO_3^- (mg/l)	-0.173	**0.785**	0.050	**0.883**
SO_4^{2-}(mg/l)	**0.880**	0.058	0.505	0.204
Cl^-(mg/l)	**0.717**	-0.143	**0.901**	-0.048
Variability %	57.526	15.449	52.710	16.882
Cumulative %	57.526	72.975	52.710	69.592

Table 3.1: Factor pattern for Inland dug well

Inland dug well	**Pre Monsoon**		**Post Monsoon**	
	Factor 1	**Factor 2**	**Factor 1**	**Factor 2**
EC(µS/Cm)	**0.989**	-0.028	**0.966**	0.119
pH	-0.723	-0.082	**0.576**	0.432
TDS(mg/l)	**0.995**	-0.045	**0.966**	0.119
Na^+(mg/l)	**0.971**	0.096	**0.970**	0.193
K^+(mg/l)	0.373	**0.862**	**0.819**	0.149
Ca^{2+}(mg/l)	**0.954**	0.021	**0.643**	**0.704**
Mg^{2+}(mg/l)	**0.944**	-0.232	**0.582**	**0.675**
HCO_3^- (mg/l)	0.017	**0.926**	0.434	0.485
SO_4^{2-}(mg/l)	**0.772**	-0.412	-0.226	**0.955**
Cl^-(mg/l)	**0.765**	0.132	**0.930**	0.271
Variability %	65.558	18.610	65.294	15.806
Cumulative %	65.558	84.167	65.294	81.099

3.7.3 Cluster Analysis

Clustering of variables was done with the correlation distance measure, single linkage and dendrogram. Dendrogram is suggesting variables which can be combined, possibly by averaging or totaling and the information is demonstrated in the form of a tree diagram (Fig 3.27a, 3.27b, 3.27c and 3.27d).

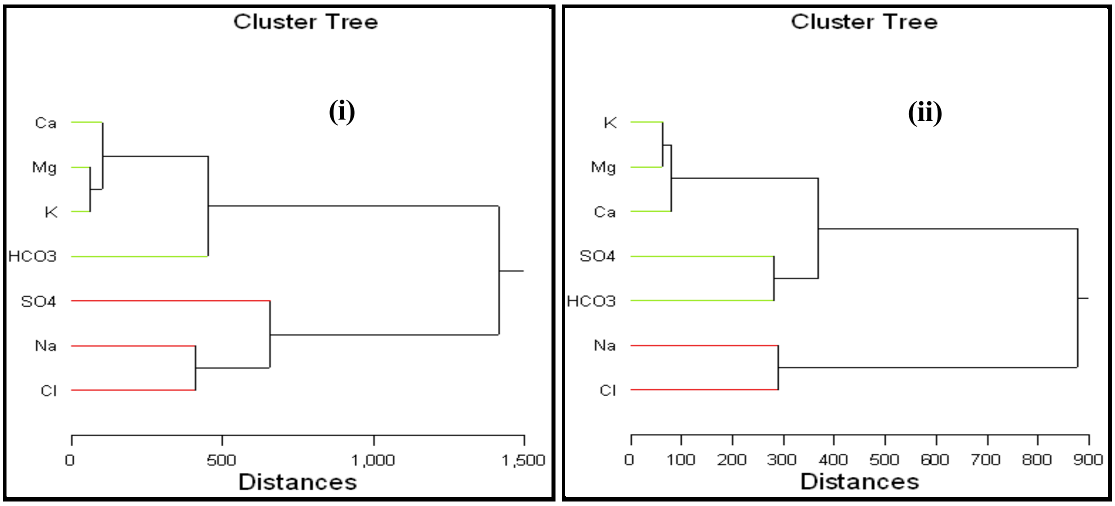


Fig 3.27a. Dendrogram of coastal/inland alluvial dug well during (i) pre monsoon (ii) post monsoon

Sodium and chloride forms a cluster group to indicate relationship intensity between them. It indicates that the seawater (Aris et al. 2007) influenced the groundwater compositions. Bicarbonate and sulphate also forms a strong relationship indicating intensive weathering (Prasanna et al. 2011). The clusters shown in the dendrogram corroborates with the processes explained in factor analysis

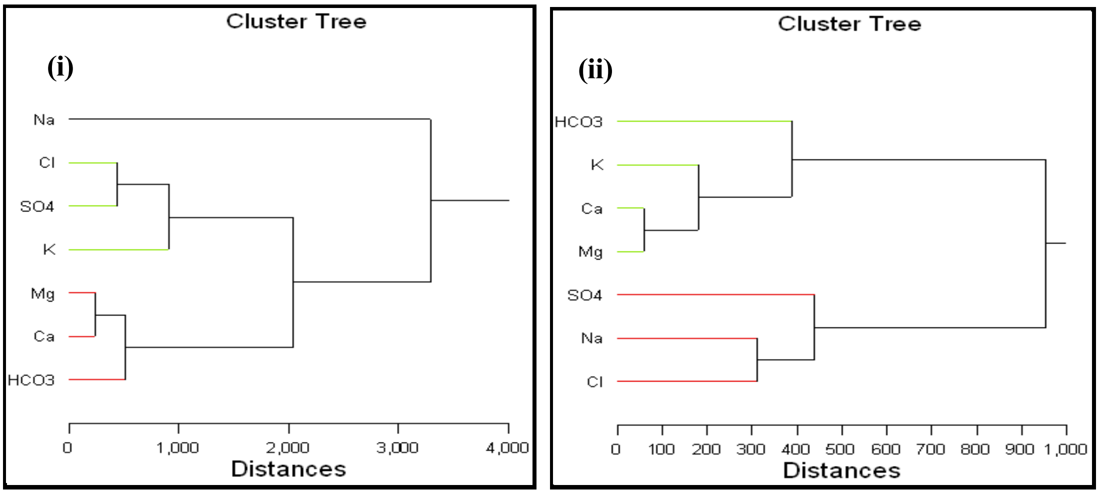


Fig 3.27b. Dendrogram of coastal/inland alluvial tube well during (i) pre monsoon (ii) post monsoon

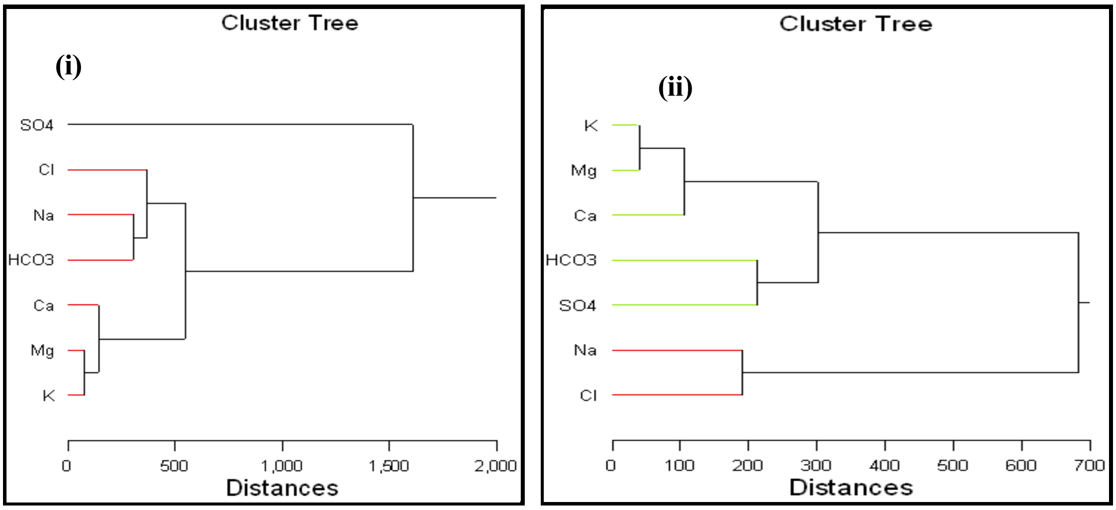


Fig 3.27c. Dendrogram of inland bore well during (i) pre monsoon (ii) post monsoon

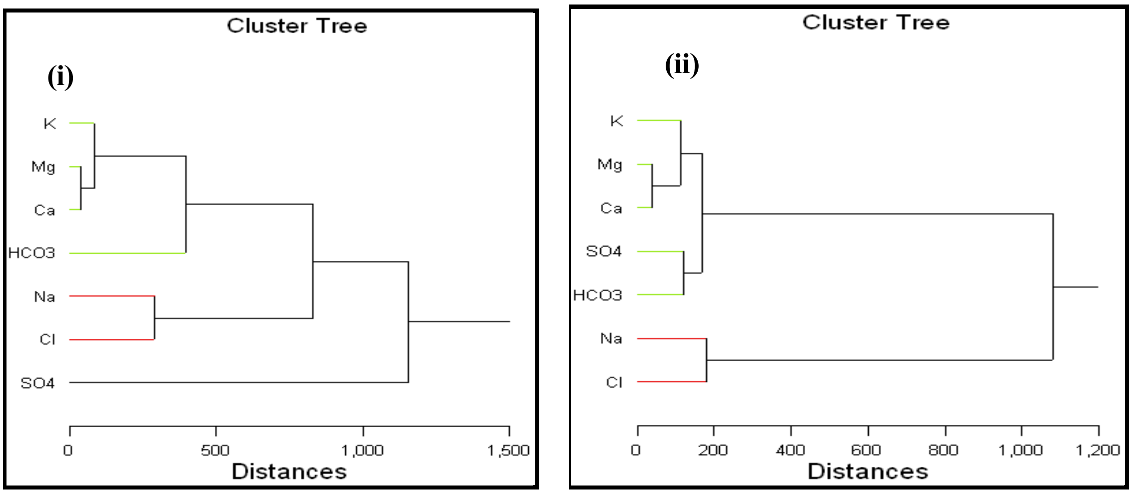


Fig 3.27d. Dendrogram of inland dug well during (i) pre monsoon (ii) post monsoon

******

Chapter 4

ISOTOPIC CHARECTERIZATION TO IDENTIFY THE SALINIZATION MECHANISM OF THE STUDY AREA

4.1 Introduction

Stable isotopes of oxygen and hydrogen are the principal components of a water molecule and is fractionated to solid, liquid and gaseous state during its travel in hydrological cycle, therefore used as the best tracer in hydrological studies. The International Atomic Energy Agency (IAEA) has been monitoring numerous research activities in the isotopic studies envisaging on evaluation of effects of irrigation on groundwater quality, origin and process of groundwater, salinization in coastal and island aquifers. Understanding the processes and factors that control the evolution of saline water in the aquifers over the years is a challenge and at the same time has important practical implications for water resource evaluation and management (Allison et al. 1994; Aunay et al. 2006; Mukherjee et al. 2007; Bouchao et al. 2008). The combination of chemical and isotopic indicators to characterize the behaviour of saline water in the coastal groundwater circulation has previously been applied to determine the origins of groundwater salinity, delineating flow systems and groundwater salinization processes, examine migration of the fresh–salt water interface and understand the mixing relationships between saline water bodies and surrounding freshwater in many coastal aquifers (Epstein and Mayeda, 1953; Bennetts et al. 2006; Hameed et al. 2015; Hameed and Resmi, 2016). Using multiple sources of chemical and isotope data combined with hydrogeological information may significantly improve the current understanding of seawater ingress.

Stable isotopes of water have been proved to be potential tracers to identify origin of recharge in a groundwater system (Zhu, 2000; Zhu et al. 2007; Palmer et al. 2007; Bouchaou et al. 2008) and to find out the salinization of ground water (Freeze and Cherry, 1979, Ghabayen et al. 2006; Saravana Kumar et al. 2009; Gopinath et al. 2018). This chapter focused on interpretation of analyses of stable isotopes of hydrogen and oxygen in groundwater from open/dug wells, tube wells and bore wells from the coastal and inland aquifers of Tuticorin district, rainwater, surface water and seawater to better understand the salinization mechanism in coastal and inland aquifers.

4.2 Stable isotopic composition of rainwater, groundwater and surface water sources

Water samples for stable isotope analysis were collected from different water sources in the study area, which comprises of precipitation water, various groundwater and surface water sources (Fig. 4.1). Groundwater samples for stable isotopic analysis were collected from 25 dug wells (coastal/inland-alluvium/crystalline), 29 bore well (inland crystalline) and 14 tube well (coastal/inland alluvium), two surface water from Thamirabarani river and a sea water sample were also collected. The stable isotope composition of groundwater (collected from dug wells, tube wells and bore wells), surface water and seawater in the pre monsoon and post monsoon periods were presented in Table 4.1.

Table 4.1 Stable isotope data of groundwater/surface water/sea water of the study area in the pre monsoon and post monsoon seasons

Code	Type	Pre monsoon			Post monsoon		
		$\delta^{18}O$	δD	D Excess	$\delta^{18}O$	δD	D Excess
DW1	Dug well (alluvium)	-3.9	-23.8	7.1	-5.3	-36.9	5.2
DW2	Dug well - (crystalline)	-1.4	-10.3	0.8	-1.4	-15.3	-4.5

DW3	Dug well - (alluvium)	-4.1	-31.7	1.0	-4.3	-37.1	-2.7
DW4	-do-	-4.5	-25.7	10.4	-4.5	-34.6	1.6
DW5	-do-	-5.6	-39.3	5.1	-7.2	-48.9	8.4
DW6	-do-	-3.5	-23.5	4.7	-3.2	-25.6	0.4
DW7	-do-	-2.7	-17.4	4.6	-3.8	-26.7	3.3
DW8	-do-	-4.5	-44.1	-8.6	-5.6	-43.3	1.5
DW9	-do-	-4.4	-29.8	5.6	-4.7	-33.2	4.8
DW10	-do-	-4.2	-27.2	6.2	-5.1	-34.7	6.2
DW11	-do-	-2.3	-27.6	-9.3	-2.6	-17.2	3.5
DW12	-do-	-3.2	-20.1	5.7	-3.0	-18.4	5.2
DW13	-do-	-2.9	-16.2	6.7	-5.9	-39.7	7.6
DW14	-do-	-0.8	-4.8	1.4	-3.7	-32.9	-3.6
DW15	-do-	-5.1	-36.3	4.2	-6.5	-51.0	0.8
DW16	-do-	-5.9	-48.7	-1.6	-4.9	-42.6	-3.7
DW17	-do-	-7.2	-52.9	4.7	-6.4	-42.5	8.9
DW18	Dug well (crystalline)	-1.2	-17.8	-8.3	-5.0	-40.2	-0.4
DW19	-do-	0.7	-4.7	-10.2	-5.3	-36.5	5.7
DW20	-do-	-4.0	-32.0	-0.3	-4.8	-40.2	-2.2
DW21	-do-	-3.6	-32.0	-3.6	-7.5	-56.6	3.1
DW22	-do-	-5.6	-40.6	3.8	-5.5	-38.9	5.2
DW23	Dug well - (alluvium)	-4.3	-28.7	5.8	-4.0	-30.6	1.0
DW24	-do-	-4.8	-33.1	5.2	-4.6	-29.6	7.2
DW25	-do-	-5.3	-33.3	9.2	-5.8	-38.9	7.6
TT1	Coastal tube well	-6.0	-43.3	4.6	0.0	-14.7	-14.6
TT2	-do-	-5.5	-42.9	1.3	-5.9	-43.3	3.7
TT3	-do-	-6.9	-54.7	0.1	-5.8	-41.2	5.3
TT4	-do-	-5.7	-41.3	4.7	-5.7	-42.6	2.8
TT5	-do-	-5.6	-41.1	3.3	-5.1	-35.5	5.5
TT6	Inland Tube well	-4.4	-28.8	6.0	-5.2	-35.2	6.7
TT7	-do-	-4.2	-29.6	3.6	-4.1	-25.9	7.0
TT8	-do-	-4.7	-29.7	8.1	-4.6	-30.7	6.3
TT9	-do-	-4.1	-25.6	6.9	-4.0	-26.9	5.2
TT10	Coastal tube well	-4.0	-29.0	3.2	-3.9	-26.2	4.6
TT11	Inland Tube well	-3.9	-24.0	7.5	-3.8	-24.7	5.9
TT12	Coastal tube well	-2.8	-21.9	0.3	-5.1	-36.0	5.2
TT13	Inland Tube well	-6.0	-41.5	6.5	-6.2	-39.2	10.5
TT14	Coastal tube well	0.7	3.8	-1.9	-5.1	-30.9	9.6
TB1	Inland bore well	-6.5	-47.5	4.3	-2.9	-28.3	-5.0
TB2	-do-	-7.0	-50.5	5.7	-6.7	-50.2	3.6
TB3	-do-	-7.5	-51.5	8.3	-7.5	-52.0	8.1

TB4	-do-	-3.6	-31.1	-2.0	-6.9	-50.7	4.6
TB5	-do-	-6.7	-46.9	6.4	-6.3	-46.6	3.5
TB6	-do-	-4.5	-31.3	4.5	-5.6	-36.4	8.2
TB7	-do-	-8.9	-64.7	6.4	-4.6	-32.5	4.6
TB8	-do-	-5.7	-37.1	8.6	-4.8	-35.2	3.5
TB9	-do-	-5.1	-32.9	7.8	-5.2	-37.6	4.2
TB10	-do-	-5.4	-34.8	8.6	-5.0	-34.2	5.6
TB11	-do-	-6.9	-48.3	6.8	-9.2	-67.6	6.0
TB12	-do-	-6.0	-41.9	5.8	-8.7	-65.2	4.1
TB13	-do-	-8.3	-60.6	5.7	-3.3	-30.8	-4.8
TB14	-do-	-6.3	-43.1	6.9	-6.0	-41.1	7.0
TB15	-do-	-4.2	-31.2	2.2	-6.1	-44.0	4.8
TB16	-do-	-2.2	-23.4	-6.0	-5.5	-41.2	2.9
TB17	-do-	-5.4	-38.2	5.2	-7.2	-48.0	9.5
TB18	-do-	-5.1	-37.2	3.8	-6.8	-48.7	5.4
TB19	-do-	-5.9	-38.8	8.3	-7.0	-52.8	3.4
TB20	-do-	-4.2	-32.1	1.2	-4.9	-36.7	2.5
TB21	-do-	-4.9	-34.5	4.4	-4.2	-31.8	2.0
TB22	-do-	-5.5	-36.5	7.5	-5.4	-36.0	6.9
TB23	-do-	-5.9	-42.5	4.9	-5.8	-40.9	5.3
TB24	-do-	-6.9	-48.2	6.8	-6.1	-42.4	6.0
TB25	-do-	-6.1	-42.8	5.6	-5.3	-39.4	2.8
TB26	-do-	-6.4	-45.2	5.7	-6.1	-42.4	6.7
TB27	-do-	-5.5	-39.0	4.9	-8.6	-57.6	10.9
TB28	-do-	-7.4	-52.5	6.9	-6.6	-47.8	5.3
TB29	-do	-5.6	-38.0	7.1	-4.9	-35.1	4.33
SW1	Surface water	-1.3	-10.8	-0.8	-3.0	-26.0	-1.6
SW2	-do-	-4.3	-25.9	8.9	-5.1	-30.9	9.6
Seawater		0.5	3.2	-0.5			

Groundwater from the open dug well varied in isotopic composition as follows: $\delta^{18}O$ between 0.70‰ and-7.20‰ and δ D between -4.60‰ and -53.90‰ in the pre monsoon season; $\delta^{18}O$ between -1.40‰ and -7.50‰ and δD between -15.30‰ and -56.38‰ during post monsoon season. δ values of groundwater collected from tube wells ranged in the following manner: $\delta^{18}O$ from -6.90 to 0.71‰ and δD from -54.70 to 3.80‰ in pre monsoon; and $\delta^{18}O$ from -6.20 to -0.01‰ and δD from -43.30‰ to -14.70‰ in post monsoon season. Deep groundwater from bore wells varied in $\delta^{18}O$ from -8.90 to -2.20‰ in pre monsoon; and $\delta^{18}O$ from -9.20 to -2.90‰ and δD from -67.60 to -28.30‰ in the post monsoon period (Table 4.1).

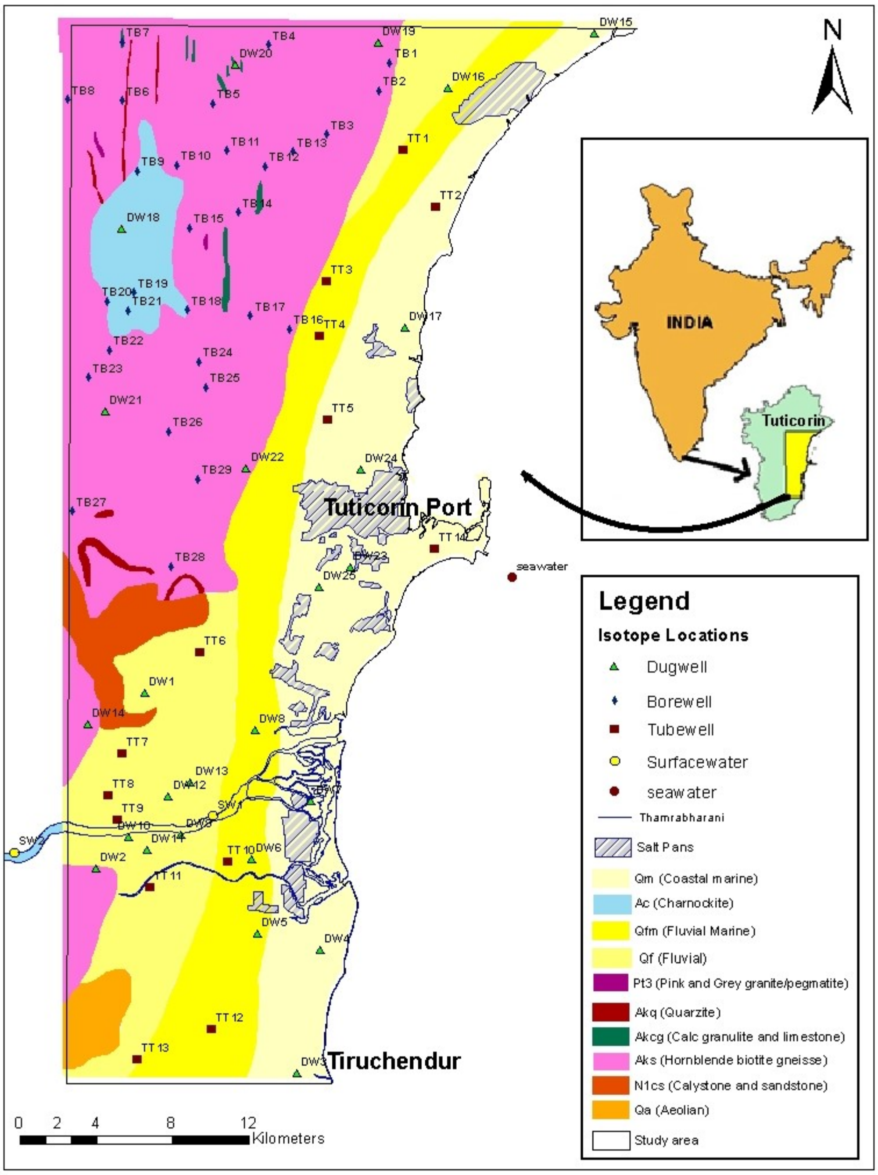


Fig 4.1 Stable isotope sampling sites in the study area

Frequency analysis (Fig 4.2 a & b) shown that that $\delta^{18}O$ of majority of the samples from the dug wells ranged between -3 to -5‰ and samples from tube wells ranged from -4 to -5‰ and bore well samples in the range -5 to -6‰. In general, there is a depletion of 1‰ in $\delta^{18}O$ of groundwater as we go deeper from DW to TT and another 1‰ depletion from TT to BW, in the Tuticorin area during the pre monsoon period. The same observation holds good in the post monsoon season also with an overall decrease of 1‰ in each of the sample sets (dug well: -4 to -6‰; tube well: -5 to -6; and bore well: -6 to -7‰). The dug wells in the study area are mostly in the depth range 0.3-10m bgl and the tube wells ranges from 6 - 40 m bgl. The bore wells in the region are ~30-200m bgl. The depletion in δ values of dug well samples to tube well samples to bore well samples may be actually the evaporative enrichment of heavier isotopes in the shallow well water samples.

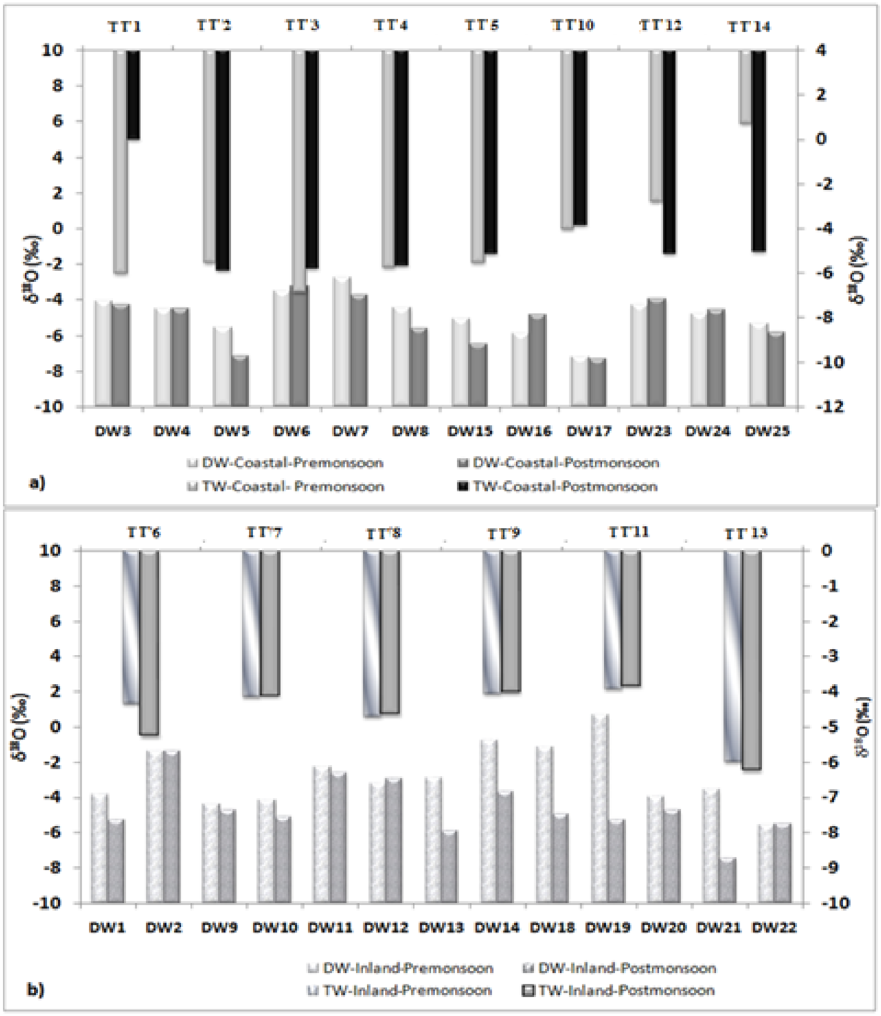


Fig 4.2: $\delta^{18}O$ variation of the groundwater from dug wells and tube wells in the alluvial region of the study area during (a) pre monsoon season (b) post monsoon season

Seasonal variation of $\delta^{18}O$ by taking the average for each sample sets are shown in Figure 4.3 and Summary statistics of stable isotope composition of groundwater of the study area in the pre monsoon and post monsoon seasons were shown in Table 4.2. After monsoon, depletion in $\delta^{18}O$ can be visualized in all sample sets in varied extents. The rainwater during the northeast winter monsoon period is found to be depleted in heavier isotopes in this region and correspondingly the groundwater also showed depleted δ values than the pre monsoon period. Groundwater abstracted from dug wells showed more seasonal variation than the tube well and bore well samples may be due to the difference in evaporation rate from the shallow dug wells, tube wells and bore wells.

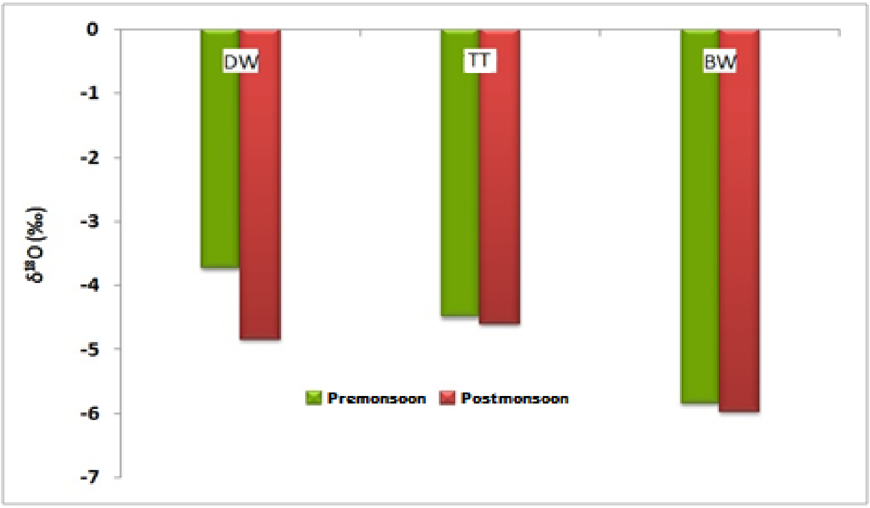


Fig 4.3: Seasonal variation of averaged $\delta^{18}O$ of groundwater from dug well, tube well and bore well of the study area

The groundwater in the area can be further classified as coastal and inland based on the distance from the shore. Wells up to approximately 8km from the coast are considered as coastal, which are in the coastal marine or fluvial marine lithology. Wells beyond 8km from coast are considered as inland alluvium which are of fluvial origin. Further to inland alluvium presence of crystalline rock of Charnockite and Hornblende Biotite Gneiss were considered as inland aquifer. Dug wells in the coastal region are found to be more depleted than those of the inland. During pre monsoon, the depletion of ~2‰ is observed, and in the post monsoon, it is reduced to ~1‰ between the coastal and inland samples. This can be an imprint of less evaporation in coastal zone where relative humidity is high. On the contrary, the tube well samples showed similar isotopic composition irrespective of the distance from the shore/lithology in the two seasons (Fig 4.2 a & b). Seasonal variation in isotopic composition in the hard rock aquifer (bore well) is random compared to the other aquifers (Fig 4.4).

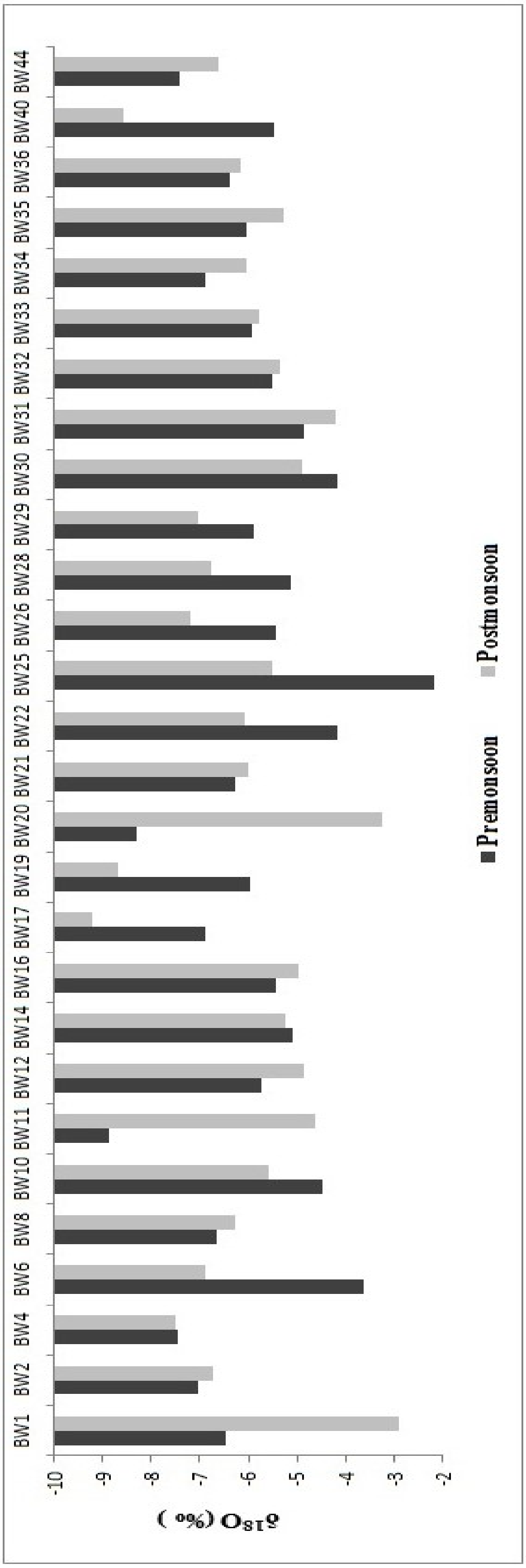


Fig 4.4: Seasonal variation of $\delta^{18}O$ of the groundwater of bore wells in the study area

Deeper waters are not influenced by processes in the shallow surface. In fact, seasonal fluctuations are attenuated beyond a certain depth and hence there is not much seasonal variation is seen in bore well samples. The bore wells sampled in the study area were located in/near the fractures, faults etc. as can be ascertained from the lineament map (not shown). In hard rock aquifers, there are preferential migratory pathways through faults, fractures and fissures which quickly transport waters of different origins, both laterally and vertically.

Table 4.2: Summary statistics of stable isotope composition of groundwater of the study area in the pre monsoon and post monsoon seasons

Pre monsoon									
	Dug well (Alluvium)			**Tube well (Alluvium)**			**Inland Bore well**		
	$\delta^{18}O$ (‰)	**δD (‰)**	**d-excess (‰)**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**d-excess (‰)**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**d-excess (‰)**
Mean	-3.77	-28.06	2.01	-4.51	-32.11	3.87	-5.85	-41.46	5.25
Standard Deviation	1.78	12.29	5.87	1.86	13.98	3.05	1.39	9.22	3.16
Minimum	-7.20	-52.90	-10.20	-6.90	-54.70	-1.90	-8.90	-64.70	-6.00
Maximum	0.70	-4.70	10.40	0.70	3.80	8.10	-2.20	-23.40	8.60
Post monsoon									
	Dug well (Alluvium)			**Tube well (Alluvium)**			**Inland Bore well**		
	$\delta^{18}O$ (‰)	**δD (‰)**	**d-excess ((‰)**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**d-excess (‰)**	**$\delta^{18}O$ (‰)**	**δD (‰)**	**d-excess (‰)**
Mean	-4.82	-35.68	2.80	-4.96	-33.72	6.02	-6.08	-43.75	4.89
Standard Deviation	1.41	10.00	4.05	0.82	6.64	2.13	1.37	9.53	2.85
Minimum	-7.50	-56.60	-4.50	-6.20	-43.30	2.80	-9.20	-67.60	-4.80
Maximum	-1.40	-15.30	8.90	-3.80	-24.70	10.50	-3.30	-30.80	10.90

4.3 Local Meteoric Water Line (LMWL) of the study area

The Global Meteoric Water Line (GMWL) described the relation between δD and $\delta^{18}O$ in global meteoric water (derived from precipitation) developed by Craig (1961) and expressed by the equation:

$$\delta D = 8\ \delta^{18}O + 10\ ‰.$$

This relation was developed as an average of many local water lines which differ from the GMWL as a result of climatic and geographic factors. GMWL used as a reference for interpreting the hydrological processes and origin of different water masses in the study area. Linear-regression analysis was carried out using the δD and $\delta^{18}O$ composition of the monthly composite rainwater samples collected during the period of SW and NE monsoons to determine the local meteoric water line (LMWL) for the study area (Fig 4.5).

Defining the LMWL for precipitation is an important part of ground-water investigations and the equation derived for LMWL in the study area is:

$$\mathbf{\delta D = 6.9\ \delta^{18}O + 3.5}$$

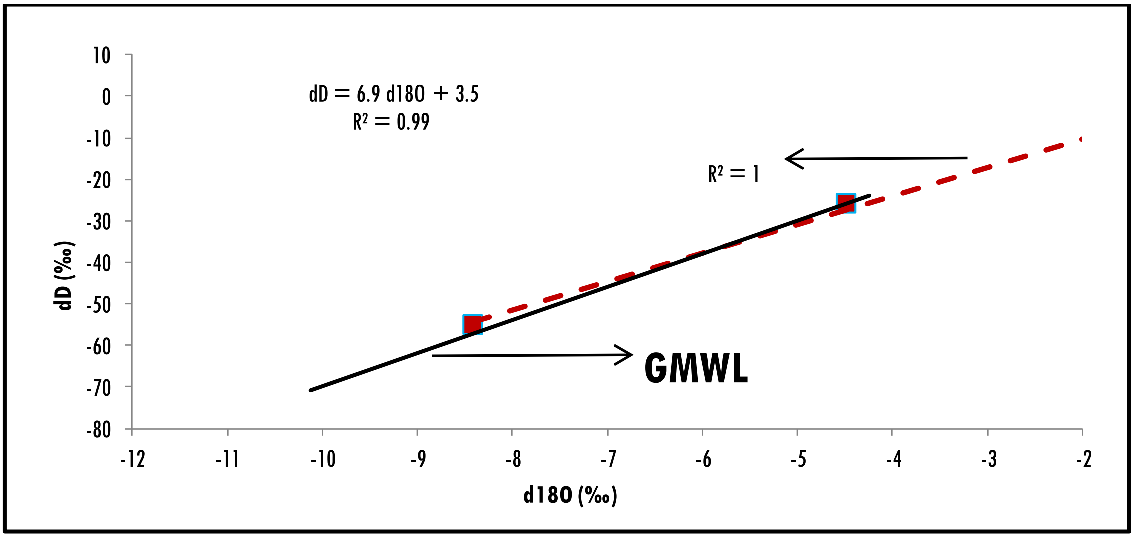


Fig 4.5: δD vs $\delta^{18}O$ Regression analysis from rainfall data for deriving LMWL

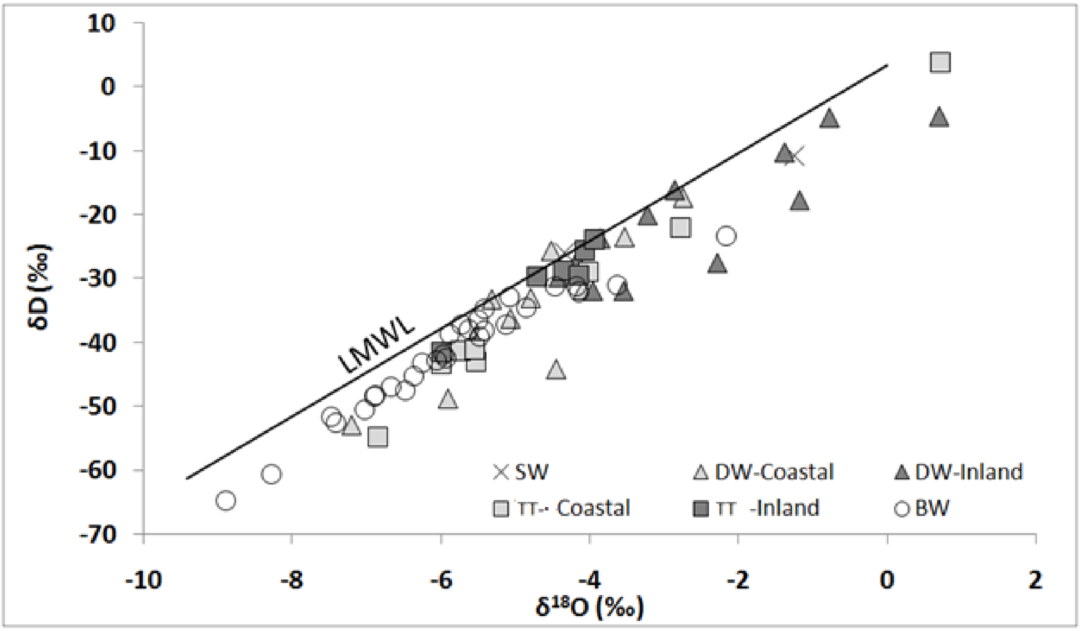


Fig 4.6: δ D Vs $\delta^{18}O$ regression plot of water samples of the study area (Pre monsoon)

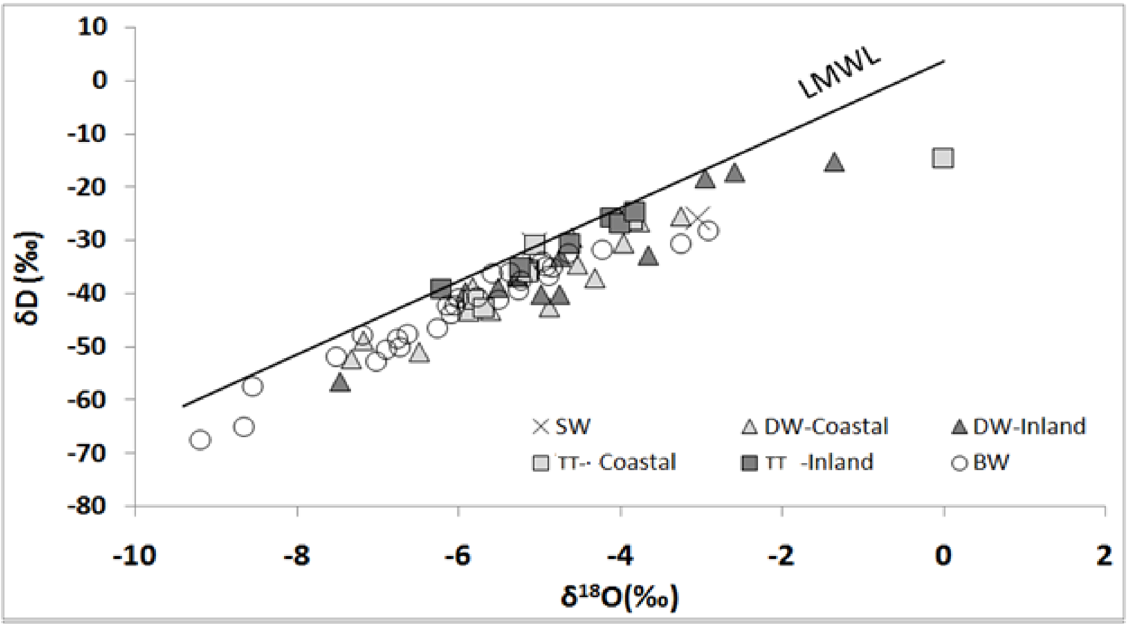


Fig 4.7: δ D Vs δ^{18}O regression plot of water samples of the study area (Post monsoon)

Regression lines were computed separately for the coastal and inland regions for each well type (Fig 4.7 & Fig 4.8). Groundwater and surface water data points were plotted below the local meteoric water line due to evaporative enrichment. The slope, y-intercept and regression coefficients in the pre monsoon and post monsoon periods are given in Table 4.3.

Table 4.3: Regression parameters of the different groundwater, surface water and LMWL of the study area

	Slope (m)		**y-intercept**		**R^2**	
	Pre monsoon	**Post monsoon**	**Pre monsoon**	**Post monsoon**	**Pre monsoon**	**Post monsoon**
LMWL	6.9		3.5		0.998	
SW	4.9	2.4	-4.8	-18.5	1	1
DW	6.3	6.8	-4.1	-3.2	0.829	0.889
TT	7.4	4.8	1.1	-10.3	0.959	0.892
BW	6.4	6.5	-3.9	-4.6	0.938	0.935

Isotopic values of rainwater in Tuticorin region ranged from -0.4 to -8.41‰ in oxygen isotope ratios and from 0.05 to -55.1‰ in hydrogen isotope ratio. In this region, during the study period, only north east winter monsoon (October-January) was active. Accordingly, due to rainout of the air masses carrying moisture, the first rains are depleted and has d-excess value above 10‰. However, the rains showed progressive enrichment in heavier isotopes as the season advances from October to December. Evaporative enrichment of heavier isotopes in the falling raindrops is very obvious from the low d-excess ($\delta D - 8*\delta^{18}O$) value (3.3‰) and enriched $\delta^{18}O$. The slope and y-intercept of the regression line of the LMWL also emphasizes that evaporative enrichment and rain from the progressively depleted air masses are the main controls over the isotopic evolution of precipitation in this region (Table 4.3, Fig 4.6 and 4.7). Contribution from the recycled vapour to the precipitation is not significant enough to impart any isotopic modification of rain water or in other words, evaporation from the rain drops is so intense that, in effect, the resultant rain is highly enriched in heavier isotopes.

The main recharge source for the groundwater and surface water for the region is rain water as can be seen from the regression plots (Fig 4.6 & 4.7). However, the groundwater and surface water samples were found to plot below/on the LMWL, showing different degrees of evaporation. In addition, each of the sample types is characterized by different slope values in different seasons. The surface water samples had slope values much less than that of LMWL in the two seasons. The surface water was enriched during post monsoon season either due to evaporative enrichment/saline water ingression in the downstream area.

Groundwater from the tube wells were found to behave differently from rest of the samples in that the slope values were considerably different in the pre and post monsoon seasons. In the pre monsoon season (May, 2013), the value was close to that of GMWL (7.4), and in the post monsoon season (Dec, 2013), drops to 4.8. It may be noted that the rainwater, which was mainly from the northeast monsoon (Oct-Dec) had a slope value of 6.9. Hence it can be assumed that the groundwater was recharged by the rains occurred in the previous north east monsoon (slope value probably between 6.5 and 7) and correspondingly the slope obtained for the groundwater during the pre monsoon period (May, 2013) of the study, corresponds to that of the rainwater. It can further be assumed that during the non-rainy period of June to September in the study area, the groundwater is mixed with water with different isotopic composition, probably seawater and the groundwater sampled during the post monsoon season has lower slope value. In the case of dug well samples, the slope was similar in both seasons and close to that of LMWL. The shallow groundwater even though showed evaporative enrichment, is being recharged rapidly by the infiltrating rainwater. The deeper groundwater (bore well) on the other hand showed more depleted isotopic composition than the rainwater and the slope is not changing over seasons.

On a closer look, it can be seen that the slope values increases from 4.9 for surface water, 6.3 for dug well samples, 6.4 for bore well samples and 7.4 for tube well samples, which clearly indicates progressively greater extent of evaporation from surface water (SW) to dug well samples (DW) to bore well samples (BW) to tube well samples (TT). The source water for SW, DW and BW seems to be local contemporary precipitation with slope 6.9 because SW, DW and BW have lower slope than LMWL. The TT has slope > LMWL which indicates that deep water of TT may be of different origin (old water of different climate regime or recharged from different precipitation regime or long distance transport of water).

4.4 Spatio-temporal variations in d-excess of groundwater

Deuterium excess (d-excess) is a derived secondary parameter which shows the magnitude of evaporative enrichment of heavier isotopes in a water body. Seasonal variation of d-excess in the groundwater and surface water of the study area are depicted in Fig 4.8.

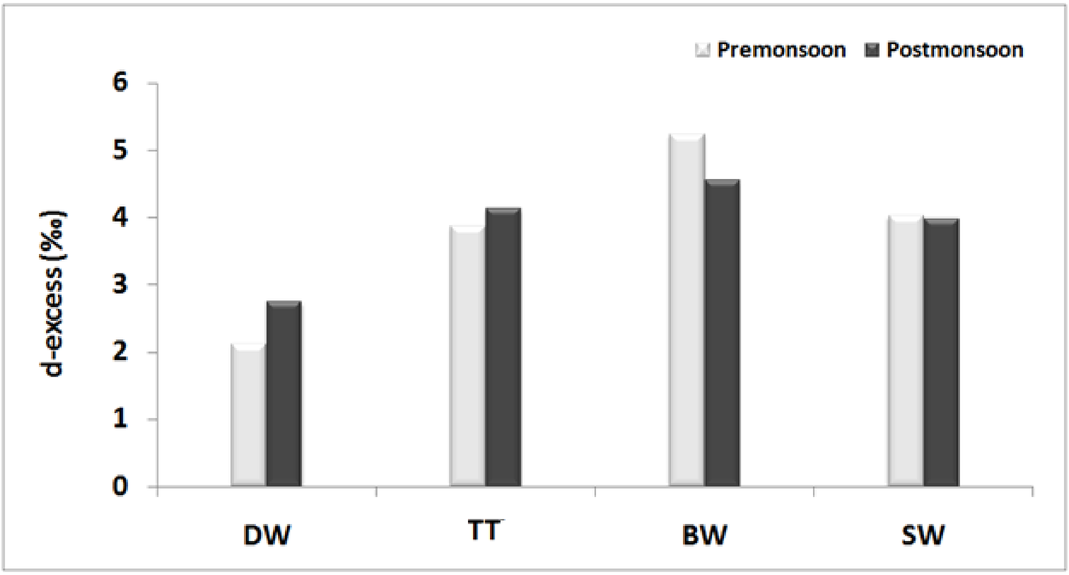


Fig 4.8: Seasonally averaged d-excess values in the different water resources of the area

The average d-excess values in all 4 types of samples, and in both the seasons, are <6. In groundwater samples, there can be various reasons for such low d-excess values. Sea water has d-excess close to zero because its $\delta^{18}O$ and δD are close to 0. Admixture of sea water in groundwater can lower d-excess. Low d-excess in DW can be due to infiltration of sea water in shallow aquifers through back waters, high-tide waters or salinity ingression due to pumping of shallow waters in coastal areas. If evaporation is occurring from a water body, its d-excess will be less than 10‰. Lowest d-excess values obtained in the dug well samples for the two seasons and highest values obtained for the bore well samples Indicates that evaporation was more in the shallow aquifers than either in the tube well or bore well samples. Seasonal variation was marginal in the surface water samples suggesting evaporative enrichment of heavier isotopes.

4.5 Salinization Mechanism of Coastal and Inland Aquifers

The sea water of the Tuticorin coast has $\delta^{18}O$ value of 0.47‰ and chloride concentration of 21993 ppm. The surface water of the Thamirabharani River draining through the area has a mean $\delta^{18}O$ of -2.79‰ and -4.05‰ in the pre monsoon and post monsoon seasons and chloride concentration of 102 and 180ppm respectively.

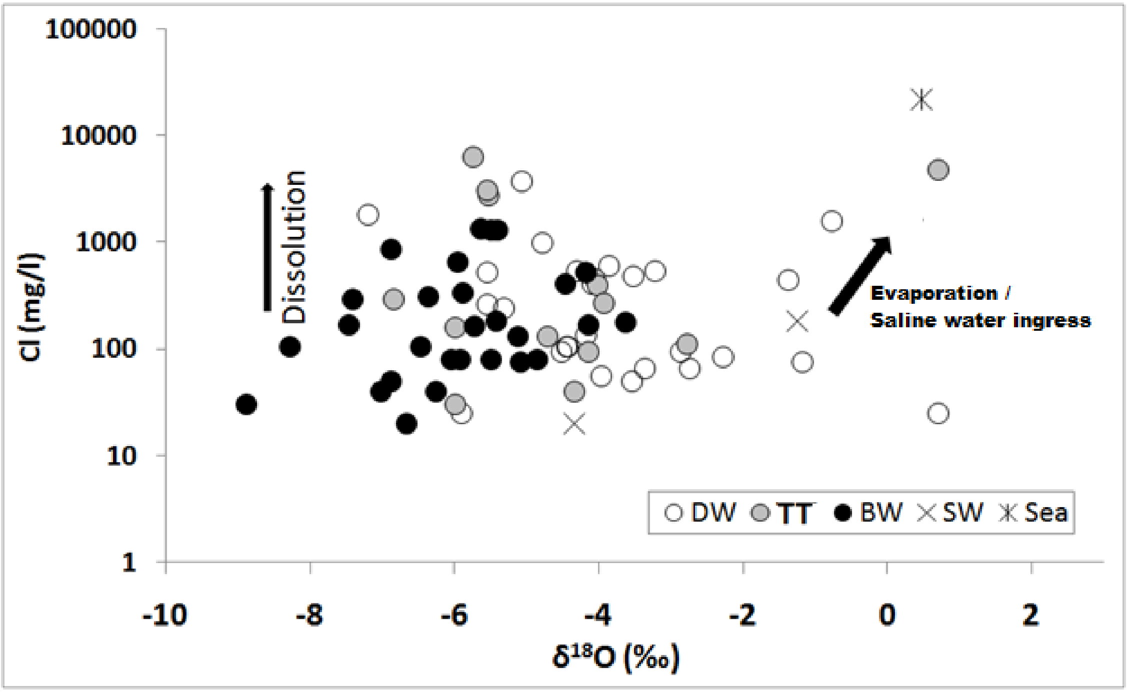


Fig 4.9: $\delta^{18}O$ relationships with chloride in the pre monsoon season

The groundwater had mean $\delta^{18}O$ of -3.74, -4.5, and -5.84 for dug well, tube well and bore well samples in the pre monsoon with corresponding chloride concentration of 2493, 4604 and 1463ppm of chloride. During post monsoon, the $\delta^{18}O$ were -4.84, -4.61 and -5.97 ‰ and chloride concentration were 465, 923 and 353 ppm for dug well, tube well and bore well respectively.

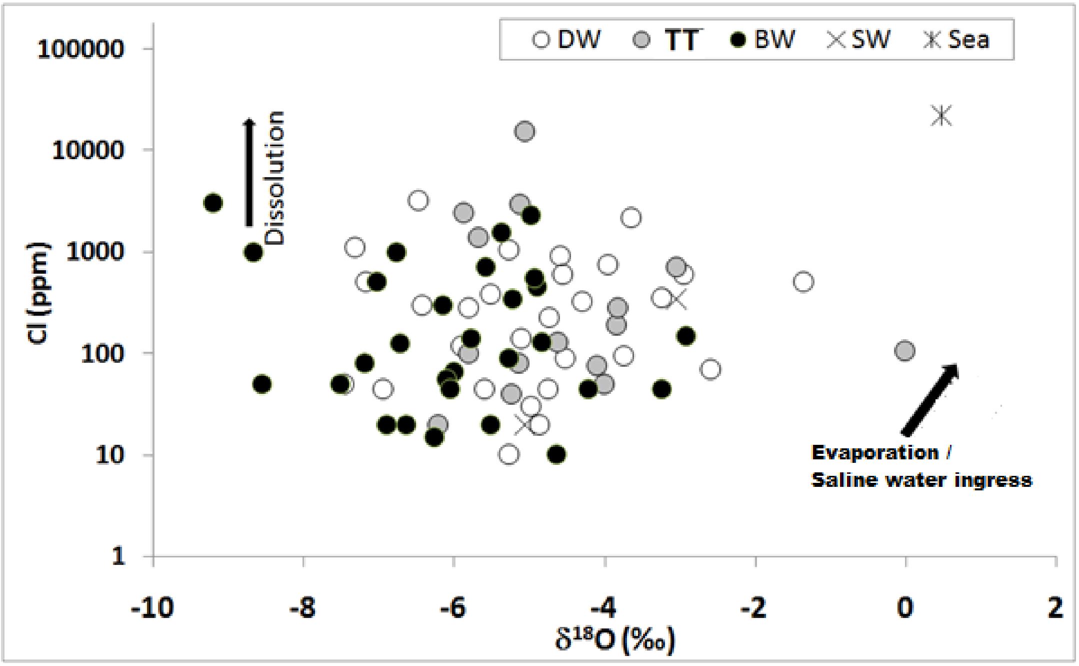


Fig 4.10: $\delta^{18}O$ relationships with chloride in the post monsoon season

The scatter diagram of $\delta^{18}O$ and chloride concentration was plotted for groundwater and surface water for two seasons separately (Fig 4.9 & 4.10.). The plot depicts different mechanisms of salinization in the coastal aquifers. As can be seen from the Figure, apart from direct influence of the sea water, concentrations of ions by evaporation also contribute to the observed salinity in the area. The dissolution or leaching from the aquifer material is also imparting salinity to groundwater in this area. The tube well and dug well samples are found to be more affected by salinity than the bore well samples. The bore well samples are found to least interacting with sea water. Dissolution/leaching is the main mechanism for the salinity in deep groundwater. The deep groundwater is most depleted and showed only marginal seasonal variation. Spatial distribution of the salinization patterns for the study area shown in Figure 4.11.

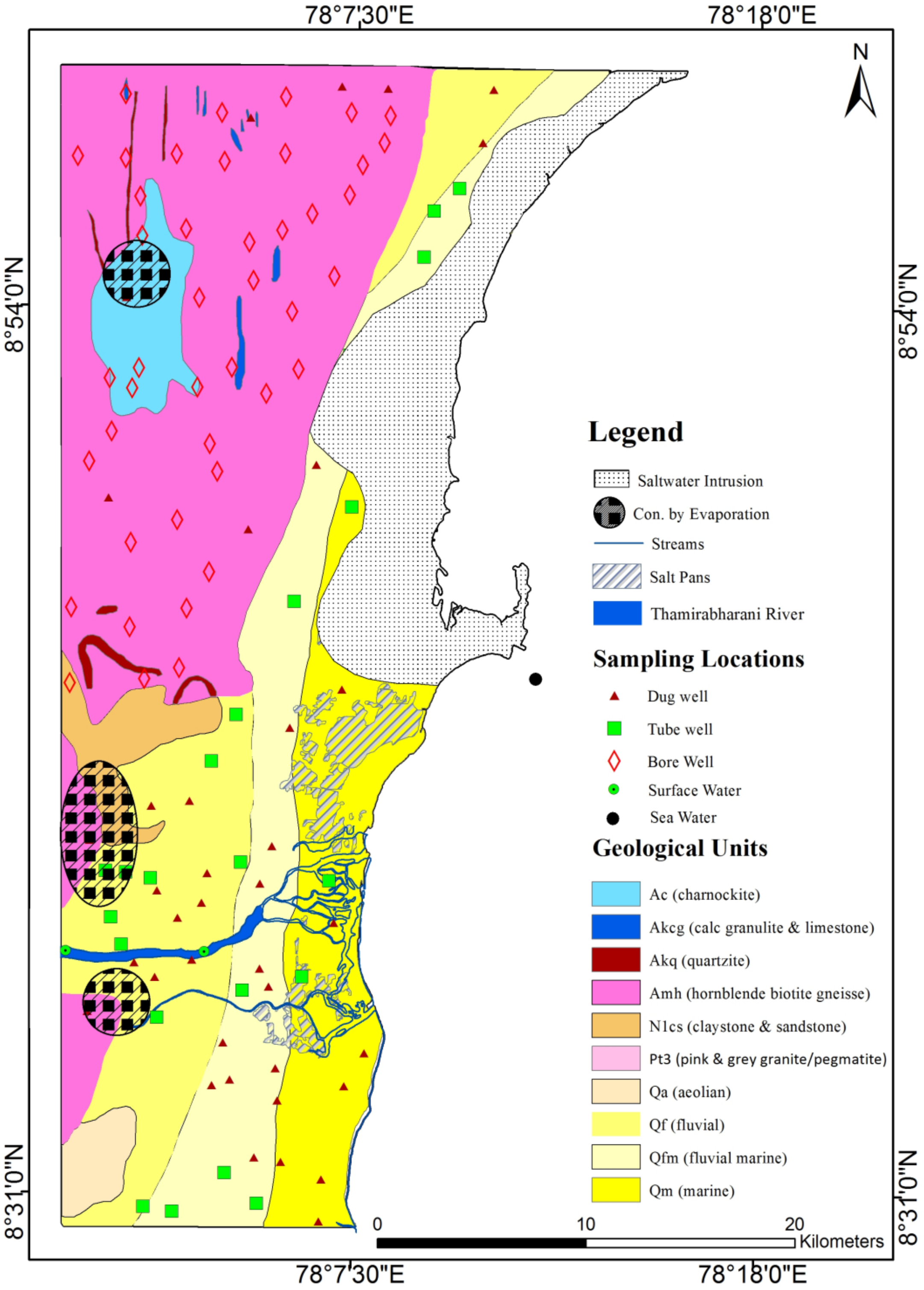


Fig 4.11: Salinization pattern in groundwater of the study area

******

Chapter 5

SUITABILITY AND VULNERABILITY ZONATION OF AQUIFERS BY INTEGRATING GEOSPATIAL TECHNIQUES AND MULTI CRITERIA DECISION MAKING TECHNIQUES

5.1 Introduction

Conviction of groundwater as a major source of fresh water supply has been widely accepted globally, precise site selection for extracting groundwater helps in cost effective, productive and long lifespan of this resource. Groundwater suitability and vulnerable zonation is an effective method to characterize the trend in quality of groundwater and its vulnerability towards contamination. The suitability of groundwater is extensively appraised using the water quality index calculation developed by Horton (1965) further developed by Brown et al. 1972, this method has been appraised as an effective method in estimating the quality of groundwater. Water quality index transforms the inclusive water quality data into a single number which can be transmitted to citizens and planners of concern (Stambuck Giljanovic, 1999; Stigter et al. 2006; Ambiga K et al. 2013; Abtahi et al. 2015). Groundwater is innately considerate to contamination by anthropogenic and naturogenic effects, relative exposure of groundwater to these effects are defined as vulnerability of this resource (Thirumalaivasan D, 2003; AWRC-National Water Quality Management Strategy, 1992). Aquifer vulnerability assessment techniques helps researchers in this field to predict the likeliness of future contamination of this resource by anthropogenic and naturogenic effects, various aquifer vulnerability assessment techniques has been formulated ever since and is broadly classified into overlay and index, process and statistical methods (Mogaji, 2018), DRASTIC method developed by USEPA 1993 is the widely used vulnerability assessment technique at regional scale.

This chapter envisages on the derivation of groundwater suitability zonation for the inland and coastal aquifers of Tuticorin coast integrating GIS and Multi Criteria Decision Making (MCDM) technique. Aquifer vulnerability assessment of the study area is deciphered using DRASTIC method with GIS support. The GIS-MCDM integrations method will help in identification of groundwater vulnerable zone in the study area and will help the future mitigation measures for this natural resource.

5.2 Multi Criteria Decision Making Technique (MCDM) for weights and priority

The MCDM in this study is a process of assigning weights to various criteria and sub criteria of various water quality parameters for suitability assessment and vulnerability parameters based on Analytical Hierarchy Process (AHP). AHP is a method to derive priority scales through pairwise comparisons and relies on the judgments of experts (Saaty, 2005), moreover qualitative and quantitative approaches are aggregated in MCDM and AHP (Saaty, 1980). Multi Criteria Decision Making (MCDM) techniques serve as an effective tool in the management and optimization of groundwater resources by adding structure, auditability, transparency and rigor to reach decisions (Dunning, Ross and Merkhofer, 2000; Flug, Seitz, and Scott, 2000; Joubert, Stewart, and Eberhard, 2003; Machiwal, Jha, and Mal 2011).

The conventional water quality index developed by Brown et al. (1972) derives a single dimensionless number which is used to assess the suitability of water quality based on groundwater chemistry parameters for various needs like agriculture, drinking etc (Jesiya and Gopinath, 2019 a). The major drawback of this WQI is that higher WQI value will be derived for a water source possibly because of higher concentration in much weighted chemical parameter (Zahedi, 2017). The GIS-MCDM method adopted in this study helps to mitigate this drawback by converting the concentration of hydrochemical parameters to an index score and transformed to a normalised weight on saaty's scale within a range of 1-9 (Saaty, 2005; Krishnan et al. 2016).

5.2.1 Deriving normalised weight using MCDM technique

The 10 major chemical parameters evaluated through hydrochemical analysis and their 53 sub criteria (Table 5.1) is used in deriving normalised weight for groundwater suitability assessment, whereas seven layers of DRASTIC and 28 sub criteria (Table 5.4) were involved in the vulnerability assessment of the study. BIS and WHO standards were used in deriving normalised weight for groundwater suitability assessment. According to the BIS and WHO standards for drinking water quality the hydrochemical thematic layers derived were categorized into good, moderate, poor and very poor and relative weights were assigned, expert opinion for local environmental aspects were also incorporated in the normalised weight assignment.

Thematic layers of Depth to water level, Net recharge, Aquifer Media, Soil, Topography, Impact of vadose zone and Hydraulic conductivity (DRASTIC) which together influences the solute transport and combining these layers derives the vulnerability characteristics of the study area, the study area is categorized into very high, high, moderate and low vulnerable zones and relative weights were assigned.

The Analytic Network Process of super decisions software was used for the decision making and relative weight assignment for the problems of suitability and vulnerability in this study. The Analytic Network Process (ANP) for groundwater suitability is illustrated in Figure 5.1, where the goal for the problem is Ground Water Suitablity Index (GWSI) and the major 10 hydrochemical parameters formulates the criteria and 53 hydrochemical ranges as sub criteria ascertained by BIS and WHO standards respectively. Similar categorization is illustrated in Figure 5.2 for DRASTIC with goal as vulnerability and 7 layers as criteria and 28 sub criteria.

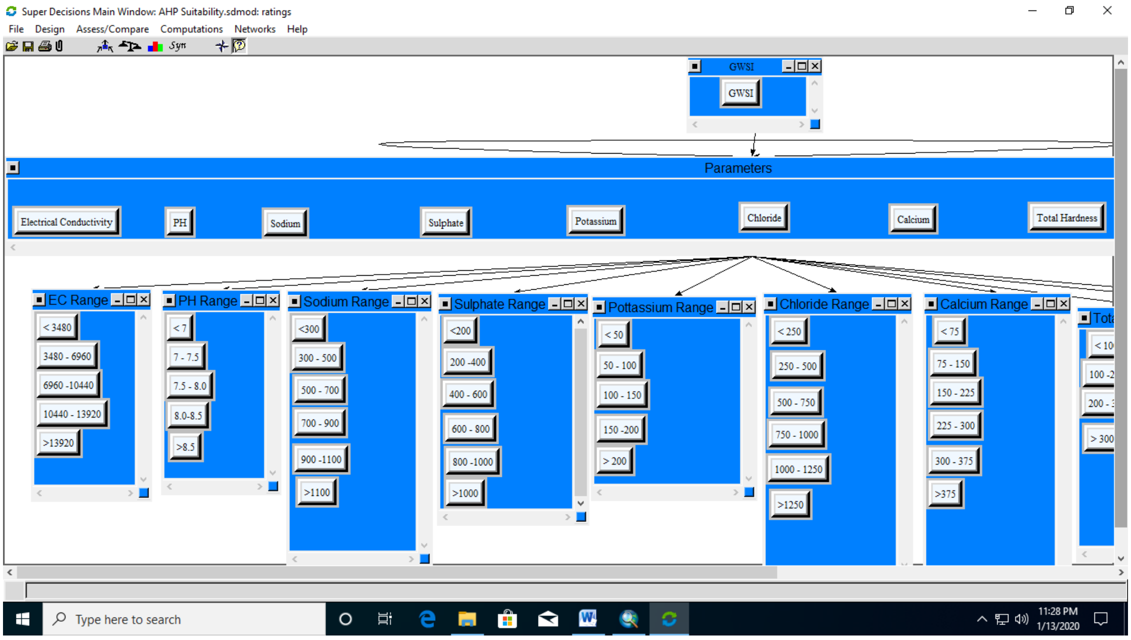


Fig. 5.1: ANP model for groundwater suitability zonation using super decision software

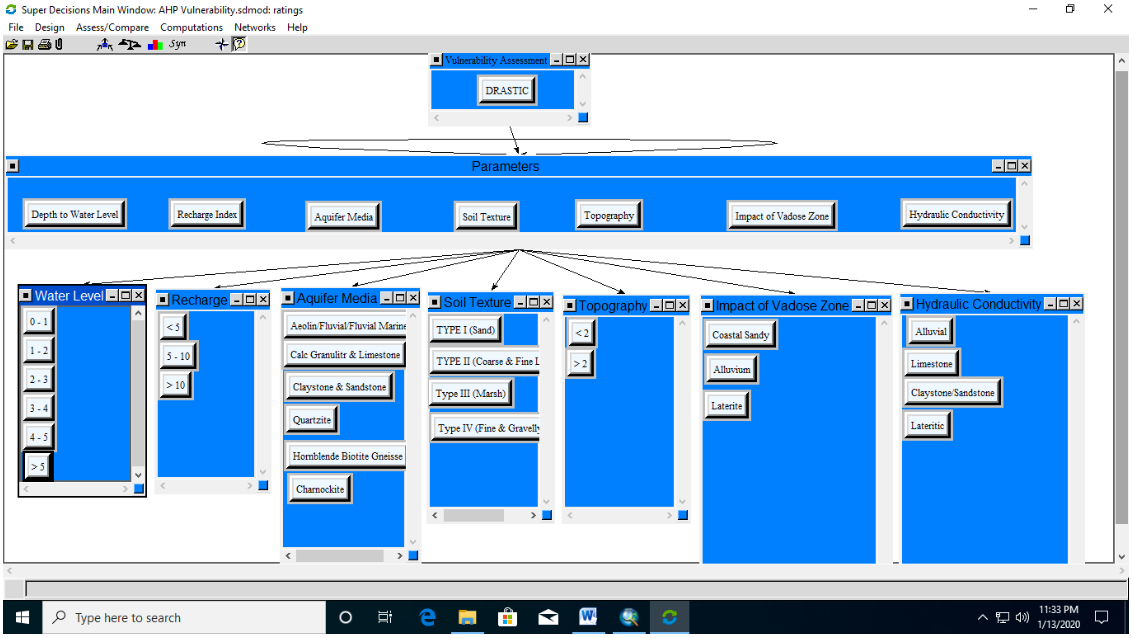


Fig 5.2: ANP model for vulnerability assessment using super decision software

5.2.2 Pairwise comparison and corresponding priorities

The normalised weight (W*i*) for GWSI and DRASTIC was derived by the pairwise-comparison matrix in ANP by combining the pairwise comparison of major criteria (parameters for GWSI & layers for DRASTIC) along with the experts judgement information, the ratings for (Q*i*) was derived using the pairwise-comparison matrix of ANP by pairwise comparison of sub criteria (hydrochemical ratings for GWSI and geological and hydrogeological factors for DRASTIC. Consistency ratio value for all criteria and sub criteria was < 0.1 which is the recommended value for the consistency of pairwise-comparison.

5.3 Integrating geospatial techniques with MCDM for groundwater suitability analysis

The hydrochemical spatial variation layers were reclassified using the reclassification method of ArcGIS with normalised weightages (W*i*) and ratings (Q*i*) derived from ANP, followed by integration of all these factors using the weighted sum overlay analysis using the spatial analyst extension of ArcGIS 10.6. The weighted sum overlay analysis derives a new raster categorized based on normalised weightages (W*i*) and ratings (Q*i*), the resultant raster was classified into good, moderate, poor and very poor zone. The groundwater suitability map so derived corroborates areas having good drinking water quality as well as the areas that require remedial measures to be adopted for immediate management.

Table 5.1: Normalised Weight and ratings derived using ANP for groundwater suitability

Chemical Parameter	ANP Weight (Wi)	Sub Criteria	ANP Ratings (Qi)
Electrical Conductivity	**0.299**	< 3480	0.5933
		3480 - 6960	0.2212
		6960 - 10440	0.0918
		10440 - 13920	0.0575
		> 13920	0.0362
P^H	**0.09**	< 7	0.666
		7.0 - 7.5	0.1182
		7.5 - 8.0	0.0992
		8.0 - 8.5	0.0755
		> 8.5	0.0411
Sodium	**0.095**	< 300	0.5933
		300 - 500	0.2212
		500 - 700	0.0918
		700 - 900	0.0433

		900 - 1100	0.0252
		> 1100	0.0252
Sulphate	**0.085**	< 200	0.6612
		200 - 400	0.2032
		400 - 600	0.0734
		600 - 800	0.0336
		800 - 1000	0.0143
		>1000	0.0143
Potassium	**0.052**	< 50	0.7669
		50 - 100	0.1072
		100 -150	0.0594
		150 - 200	0.0367
		> 200	0.0298
Chloride	**0.095**	< 250	0.5563
		250 - 500	0.2769
		500 - 750	0.0695
		750 - 1000	0.0501
		1000 - 1250	0.0236
		> 1250	0.0236
Carbonate + Bicarbonate	**0.052**	< 300	0.7002
		300 -400	0.2005
		> 400	0.0962
Calcium	**0.085**	< 75	0.5933
		75 - 150	0.2212
		150 - 225	0.0918
		225 - 300	0.0433
		300 - 375	0.0252
		> 375	0.0252
Total Hardness	**0.052**	<100	0.7002
		100 - 200	0.2005
		200 -300	0.0681
		> 300	0.0312
Magnesium	**0.085**	< 30	0.5933
		30 -60	0.2212
		60 -90	0.0918
		90 - 120	0.0433
		120 - 150	0.0252
		>150	0.0252

The water quality parameter percentage weightage and priority for electrical conductivity, followed by sodium and chloride were given the highest weightage (Table 5.2) as the area is prone to high dissolved ionic concentration and saline water ingress, other chemical parameters were assigned with respective weightage.

Table 5.2: Factor weight and priority index derived from ANP

Criterion	Weight in %	Priority
Electrical Conductivity	29.9	1
P^H	9	3
Sodium	9.5	2
Sulphate	8.5	4
Potassium	5.2	5
Chloride	9.5	2
Carbonate + Bicarbonate	5.2	5
Calcium	8.5	4
Total Hardnes	5.2	5
Magnesium	8.5	4

Table 5.3 illustrates the areal extend of groundwater suitability zone statistics derived from the GIS-MCDM technique. Groundwater suitability zonation map derived by integrating GIS-MCDM is shown in Figure 5.3. The suitability map derived from the study deciphers the fact 235 Km^2 (24%) of the total study area comprises of poor and very poor quality of groundwater, 409.44 Km^2 (41.75%) of the study area has good quality of drinking water and the remaining 34.29 % (336.36 Km^2) area is having moderate drinking water quality ascertained on the basis of BIS and WHO standards. Very poor water quality was observed in the coastal alluvial region towards north starting below from Tuticorin port and it extends all the way towards northern end of the study area, this area comprises of the major urbanized area and most of the salt pans of the study area are also vested in here. The inland areas over the charnockite formation and hard lateritic formation also recorded very poor and poor water quality. Good water quality is observed along the alluvial regions of Thamirabarani. Planners and researchers should adopt sustainable management of water quality in the urban areas and coastal stretch to mitigate this poor water quality prevailing in this area.

Table 5.3: Areal statistics of groundwater suitability zonation derived from GIS-MCDM technique

SL No.	Suitability Zonation	Area in Km^2	Area in %
1	**Very Poor**	118.8	**12.11**
2	**Poor**	116.2	**11.85**
3	**Moderate**	336.36	**34.29**
4	**Good**	409.44	**41.75**

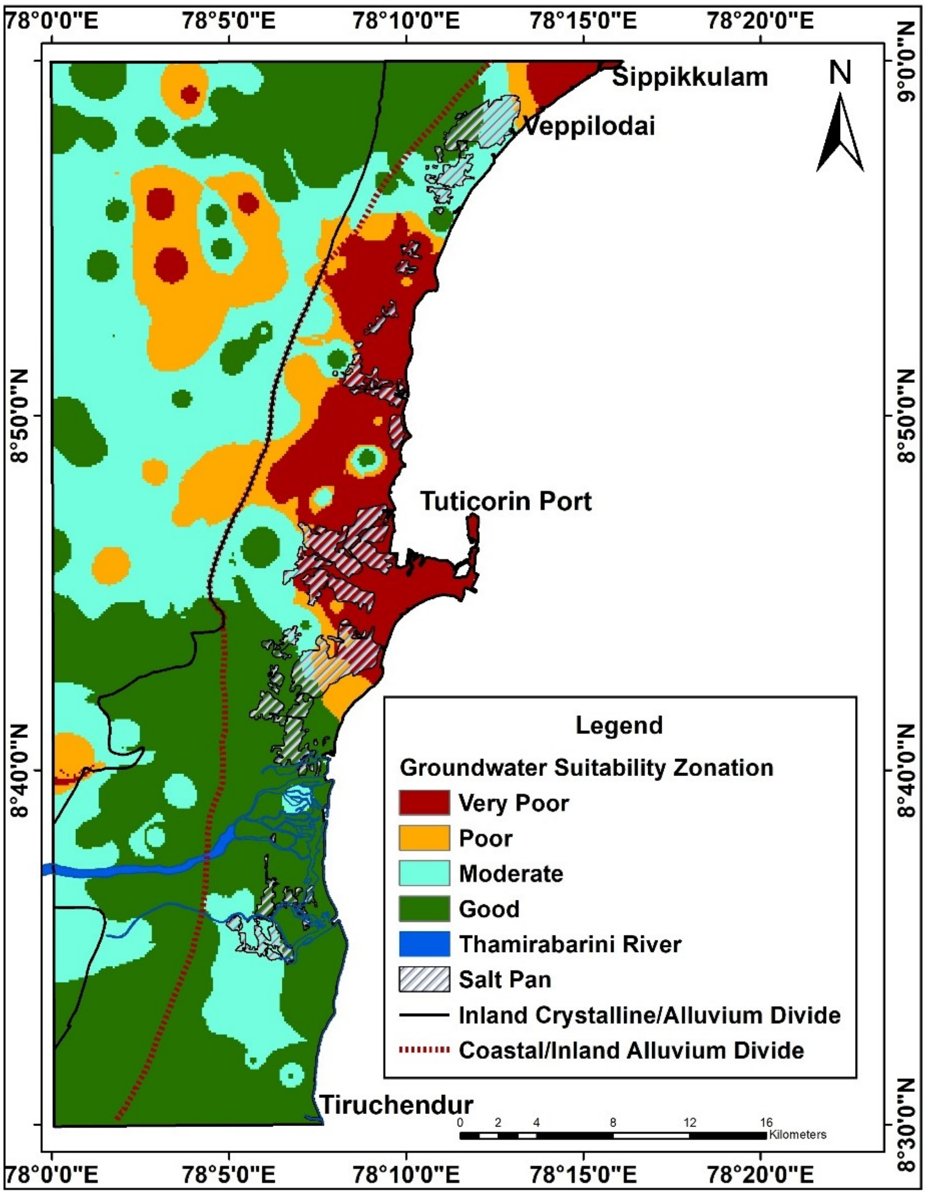


Figure 5.3: Groundwater suitability zonation for drinking water purpose in the study area

5.4 Groundwater vulnerability analysis

Contamination of groundwater is persistent and prohibitively difficult to remediate which leads to over extraction of this resource making it vulnerable to further contamination. The results from the groundwater suitability analysis decipher the fact that the area is having poor water quality in most of the urbanized areas making the situation more detrimental. Mitigation of polluted aquifers is cost intrusive procedure; therefore developing an aquifer vulnerability to assess the most vulnerable zones of the study area will help in sustainable management of this resource. The most widely used overlay and index method for groundwater vulnerability assessment technique DRASTIC was used in this study; this method was developed by USEPA (Aller et.al. 1987; USEPA, 1994). Groundwater vulnerability mapping helps in identifying the regions which are more vulnerable to contamination based on hydrogeological factors that controls the movement of groundwater.

In this study GIS-MCDM technique was adopted to assimilate normalized weight for hydrogeological parameters involved in the DRASTIC model for vulnerability assessment. The hydrogeological parameters which influence the movement of contaminant were assigned ratings based on their priority; higher weights were given to parameters having significant priority and less rating for others. MCDM technique was used to derive the normalized weight for criteria parameters (W_i) and sub criteria ratings (Q_i), pairwise comparison for the seven parameter criteria used in the DRASTIC model was derived as shown in Table 5.4. The resultant values were then induced in the reclassification and weighted sum overlay procedure to derive the vulnerability map of the study area.

Table 5.4: Normalised weight and ratings derived using ANP for groundwater vulnerability

Chemical Parameter	ANP Weight (Wi)	Sub Criteria	ANP Ratings (Qi)
Depth to water level	**0.165**	0 -1	0.343
		1 -2	0.201
		2 -3	0.135
		3 -4	0.122
		4 -5	0.11
		> 5	0.089
Recharge index	**0.224**	< 5	0.292
		5 - 10	0.332
		>10	0.376
Aquifer media	**0.118**	Aeolin/Fluvial/Fluvial Marine	0.347
		Calc Granulite & Limestone	0.201
		claystone & Sandstone	0.122
		Quartzite	0.118
		Hornblende Biotite Gneisse	0.118
		Charnockite	0.093
Soil texture	**0.087**	Type I (Sand)	0.354
		Type II (Coarse & Fine Loamy)	0.243
		Type III (Marsh)	0.201
		Type IV (Fine & Gravelly Clay)	0.206
Topography	**0.066**	< 2	0.631
		> 2	0.369
Impact of vadose zone	**0.119**	Coastal Sandy	0.397
		Coastal Alluvium	0.372
Hydraulic conductivity	**0.224**	Alluvial	0.395
		Limestone	0.305
		Claystone/Sandstone	0.15
		Laterite	0.15

5.4.1 Analysis of DRASTIC parameters

5.4.1.1 Depth to water level (D)

The time and depth of material through which the infiltrating water travels to reach the aquifer media can be determined using depth to water level data, it also helps in determining the time of contact with the surrounding media (Aller et.al. 1987). Depth to water level has significant influence on the extent and time of contaminant attenuation and transport. Considering these factors depth to water level was given a significant weightage. The coastal regions of the study area towards the north have a water level depth of 3- 4 m bgl and between 2-3 m bgl. The alluvial plains of Thamirabarani and its deltaic plain has a water level depth of 1-2 m bgl, while the inland crystalline zone has the highest water level depth ranging 4 -5 m bgl and certain areas with greater than 5 mbgl were also observed. Aquifers having the least water level data was given the highest normalized weight as they are much prone to contamination. Fluctuation in water level in the study area is due to the cumulative effect of southwest and north east monsoon, fall in water level in the area is partly due to inadequate recharge and local overdraft (CGWB, 2009). The Depth to water level layer is shown in Figure 5.4.

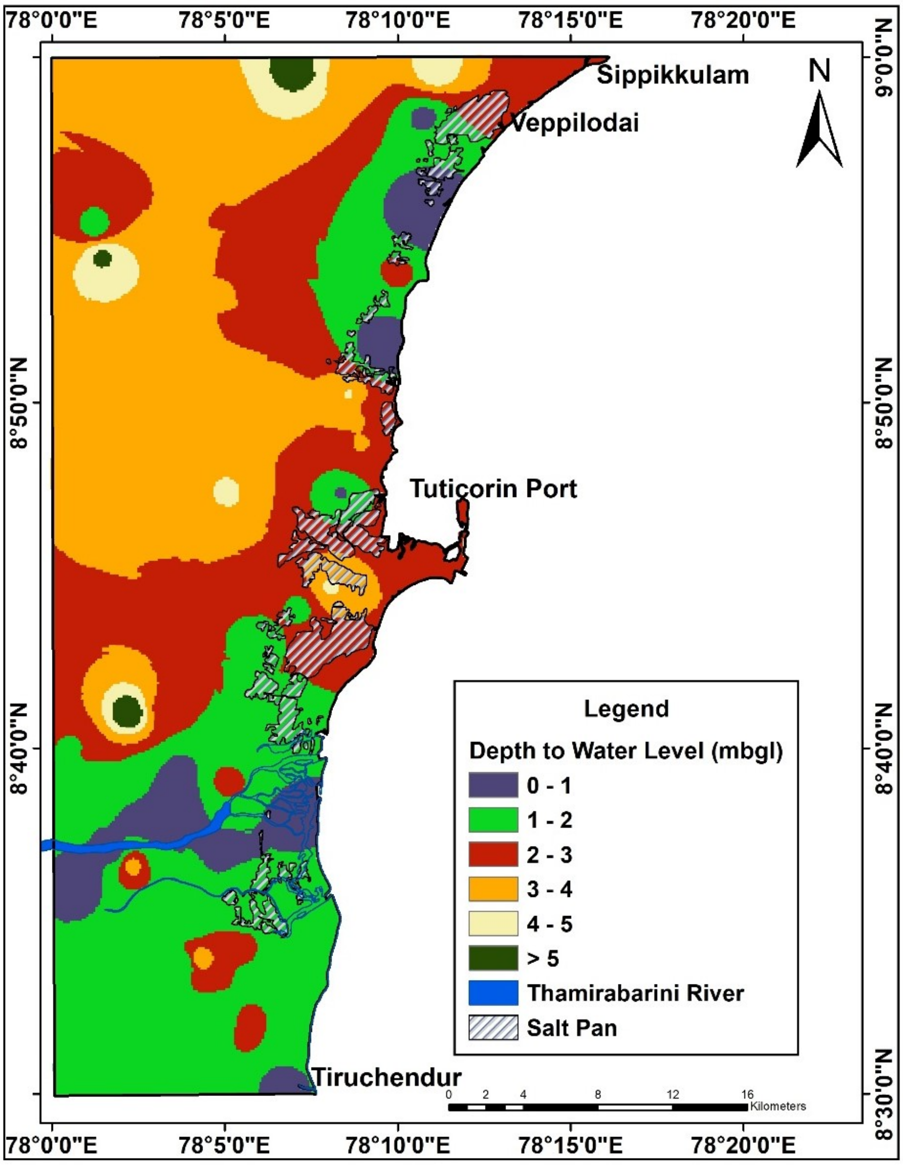


Fig 5.4: Spatial distribution of depth to the water level

5.4.1.2 Net Recharge (R)

The amount of that travels and percolates into the ground surface and reaches the aquifer media is known as net recharge. The travel and percolation of water into the aquifer media is controlled and affected by slope percentage, soil permeability and rainfall factors, net recharge act as a carrier for vertical and horizontal contaminant transport (Aller et.al. 1987).The net recharge of the study area was derived by the weighted sum overlay analysis of slope percentage, soil permeability and rainfall factors, weightage was given to these factors based on 1-5 Saaty's scale (Saaty, 2005). The equation for calculating the net recharge was formulated by Piscopo, 2001 and is:

Net Recharge Index = Slope % + Rainfall + Soil permeability

The slope % of the study area was derived from the SRTM DEM (30m).The slope percentage ranged between 0-9% which deciphered the fact that the area is having very gentle slope and the areas having gentle slope facilitates high recharge, higher slope percentage was observed in the inland area. The slope percent was categorized into two (< 2% and > 2%) and high priority ratings were given to low slope percentage area.

The study area comprises of four types of soil categories (Table 5.5), they were assigned ratings based on their permeability with highest rating assigned to the most permeable soil category. Sand soil category was given the highest rating as the permeability of this soil texture is the highest followed by fine and coarse loamy, marsh and fine gravelly clay.

The southwest and northeast monsoon contributes to the rainfall in the study area, while the significant contribution to rainfall in the area is from northeast monsoon (CGWB, 2009). The precipitation received in the study area is predominantly in the form of cyclonic storms formed due to the depression in Bay of Bengal, northeast monsoon is erratic and summer rains is negligible in the area (CGWB, 2009). The normal average rainfall in the study area is between 570mm to 740 mm (CGWB, 2009). The annual rainfall was categorized into two ranging from 520 – 600 mm and 600 -736 mm, the higher rainfall value was assigned the higher rating (Table 5.5). The rating values were assigned to the thematic layers by reclassification method of GIS and the resultant thematic layers were used for weighted sum overlay analysis in GIS. This resultant map derived is the net recharge index value for the study area. The net recharge index value were categorized as <5, 5-10, >10 (Table 5.5) and the Figure for net recharge is shown in Figure 5.5. The area with highest net recharge index (> 15) was given the highest weight and the regions with lowest recharge index (< 5) were given the least weightage.

Table 5.5: Rating for the calculation of net recharge index of the study area

Slope (%)	Rating	Soil Permeability	Rating	Rainfall, mm	Rating
< 2	5	Type I (Sand)	5	520 – 600	5
> 2	1	Type II (Coarse & Fine Loamy)	3	600 -736	1
		Type III (Marsh)	2		
		Type IV (Fine & Gravelly Clay)	1		

The areal extend of net recharge of < 5 covers an area of 28.46 Km^2, 5-10 net recharge area was accounted for 487.44 Km^2 and area with highest net recharge of >10 spreads to an area of 464.54 Km^2. Highest contamination transport and infiltration occurs in the area having highest net recharge as it promotes the vertical and horizontal movement of water into the aquifer media, coastal area with alluvium formations in the study area has the highest recharge index value of >10

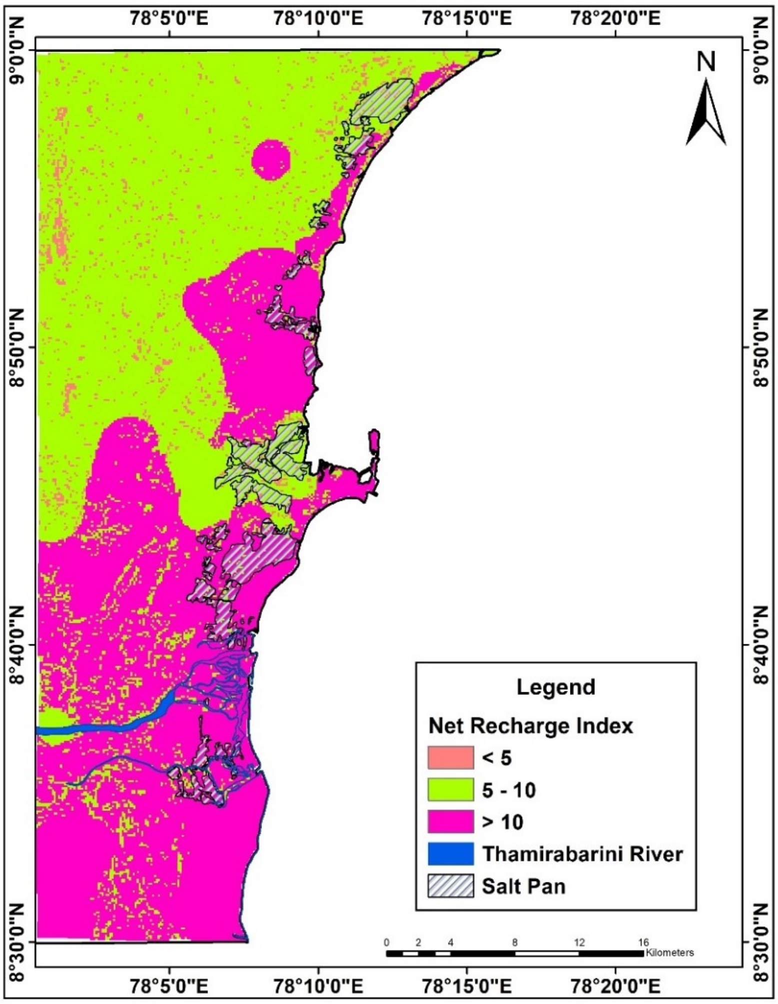


Fig 5.5: Spatial distribution of net recharge index in the study area

5.4.1.3 Aquifer media (A)

The unconsolidated and consolidated rock types which forms an aquifer is termed as aquifer media. The contaminant attenuation and flow is controlled by this saturated zone. The predominant aquifer formation in the study area are i) unconsolidated and semi consolidated formations ii) weathered and fractured crystalline rocks (CGWB, 2009). Sandstones and clay of recent to subrecent and quaternery age formulates the porous formation in the study area. The movement and occurrence of groundwater in the inland crystalline formations are controlled by the joints, fissures and extend of pores and interconnection of fractured zones (CGWB, 2009). Unconfined aquifers in aeolin/fluvial/fluvial marine are significantly influenced by the transport and attenuation of contamination and due to this higher weightage was assigned for this while the hard rock crystalline formations of hornblende biotite gneisse and charnockite found in the inland region is assigned with the least weightage Table 5.4.

5.4.1.4 Soil texture (S)

The weathered region of the surface of the ground characterized by biological activity is generally referred to as, soil texture; soil texture plays a crucial role in the vulnerability analysis as this has a significant impact on recharge which induce the vertical contaminant transport into the vadose zone (Aller et.al. 1987). The grain size, type of clay, porositivity of soil texture influences the rate of pollution in groundwater (Aller, 1985; Brindha and Elango, 2012 & 2015). The soil texture of the study area is classified into four categories i) Type I (Sand) ii) Type II (Coarse & Fine Loamy) iii) Type III (Marsh) iv) Type IV (Fine & Gravelly Clay) and is shown in Fig 5.6. Sandy and alkaline sandy soils are observed along the coastal tract of the study area (CGWB, 2009). Higher weightages were assigned to the Type I soil type as sand has the highest capability for tansporting contaminants to the vadose zone and the least ratings were assigned to fine and gravelly clay which being the least permeable inhibits the infiltration rate.

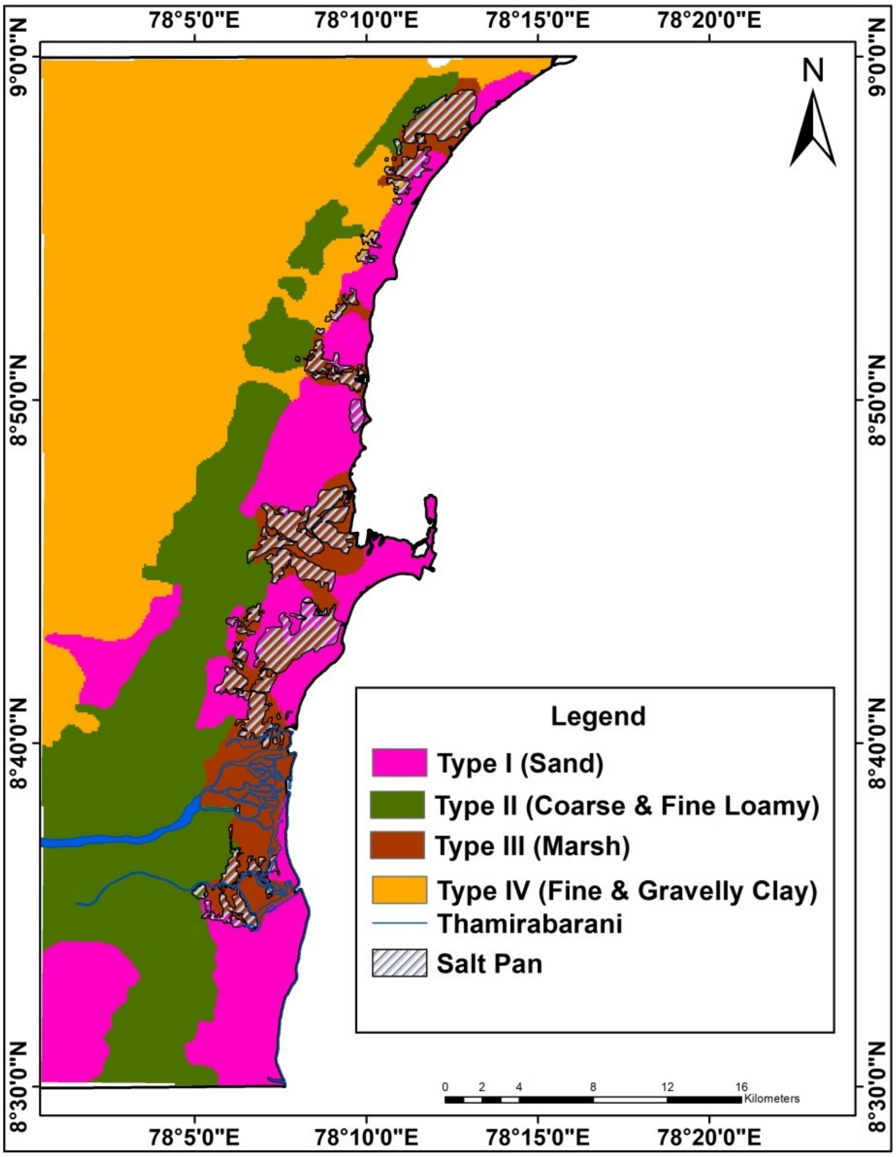


Fig 5.6: Spatial distribution of topography in the study area

5.4.1.5 Topography (T)

Topography generally refers to the slope of the study area (Aller et.al. 1987)., increased run off occurs in regions with higher slope leading to less contaminant attenuation. The study area has slope range between 0-9 percent and is classified into two < 2% and > 2% based on the inland and coastal region. Lower slope values were observed in the coastal region Fig 5.7 and higher weights were assigned for this.

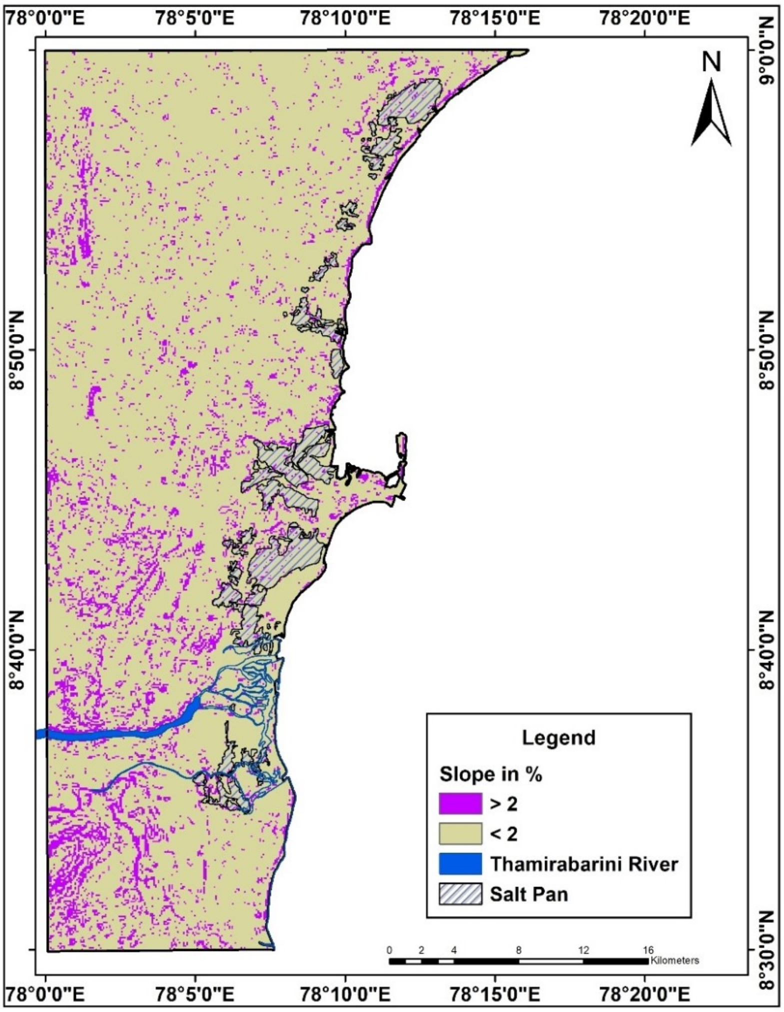


Fig 5.7: Spatial distribution of topography in the study area

5.4.1.6 Impact of vadose zone (I)

The area below the soil surface and above the water table is refered to as the vadose zone (Aller et.al. 1987). This plays a significant role in contamination attenuation. The Vadose zone of the study area was delineated from the lithology and hydrogeology maps of CGWB and Geological Survey of India maps. Coastal tracts of the study area were predominant in coastal alluvium and riverine alluvium was observed in the Thamrabarani drainage area, laterite formations were observed in the inland regions. The maximum thickness of alluvium is 45.0 m bgl and on an average thickness is 25 m (CGWB, 2009). The Figure 5.8 shown represents the spatial distribution of vadose zone along the study area. Higher weightage was assigned to the alluvium as it enhances the permeability of contaminants and lower weight was assigned to the laterite formations.

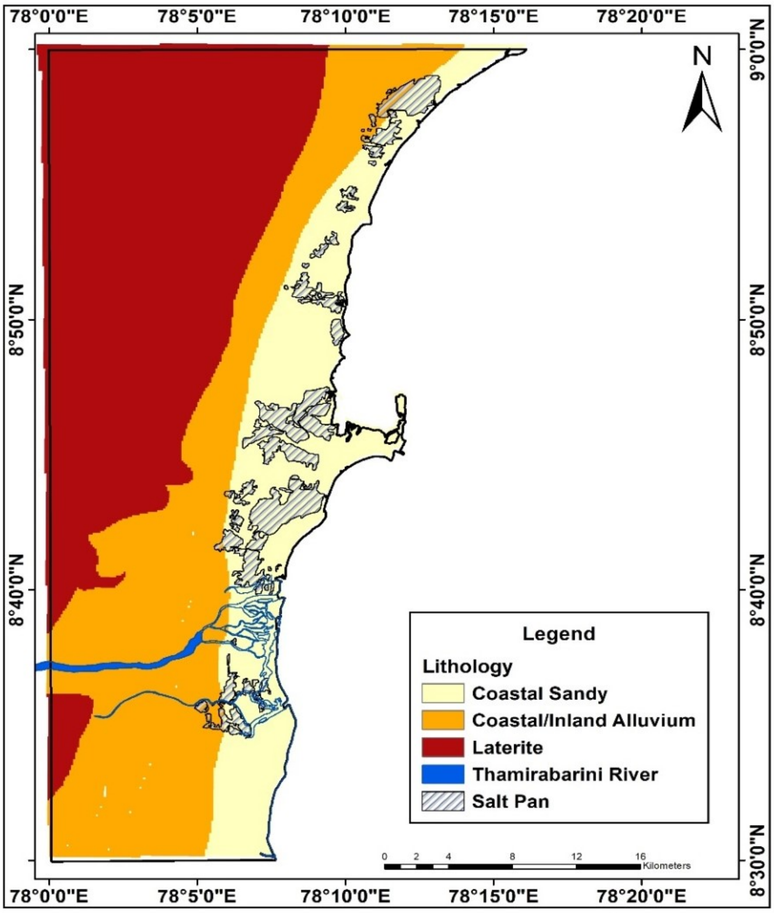


Fig 5.8: Spatial distribution of vadose zone in the study area

5.4.1.7 Hydraulic Conductivity (C)

The characteristics of an aquifer to transmit water under a hydraulic gradient is referred to as hydraulic conductivity (Aller et.al. 1987)., porosity fracture and void spaces controls the movement of contaminant through aquifers. The distance travelled by groundwater can be assessed by hydraulic conductivity hence the contaminant movement. When the hydraulic conductivity is low then the resistance towards contamination is high (Rahman, 2008).

The coastal alluvial aquifer of the study area has a hydraulic conductivity ranging between 1-5 m/day, while that of laterite was 14 m/day. Sandstone in the inland region observed a hydraulic conductivity of 3.1 m/day and limestone recorded 0.94 m/day. The regions of coastal alluvium with least hydraulic conductivity was assigned higher weightage as they are more prone to contaminant transport while laterite in the inland areas were assigned the least weightage which has higher hydraulic conductivity. Figure 5.9 shows the hydraulic conductivity pattern along the study area.

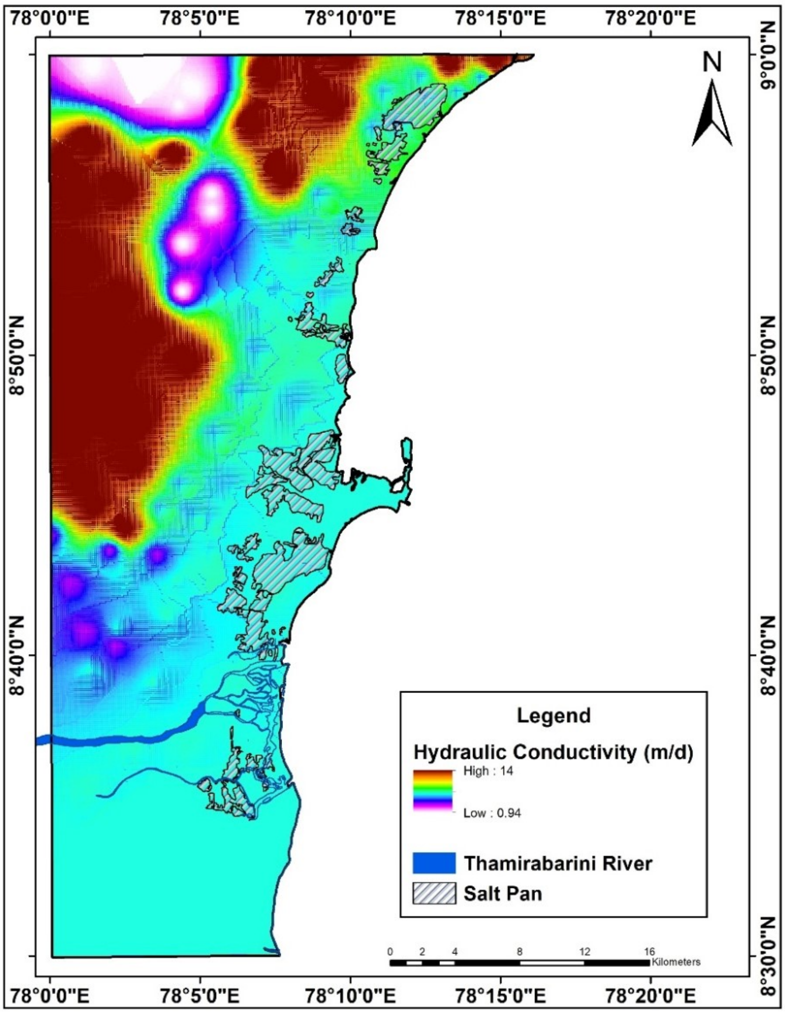


Fig 5.9: Spatial distribution of hydraulic conductivity in the study area

5.4.2 Groundwater vulnerability assessment

The study area was categorized into four vulnerability zones i) Very High Vulnerable ii) High Vulnerable iii)Moderate Vulnerable and iv) Low vulnerable zones from the DRASTIC and GIS-MCDM technique (Table 5.6). The vulnerability zonation map derived is shown in Figure 5.10.

Table 5.6: Areal distribution of aquifer vulnerability class

SL No.	Vulnerability Zonation	Area in Km^2	Area in %
1	Very High	220.94	22.54
2	High	176.48	18.01
3	Medium	220.5	22.5
4	Low	363.07	37.05

The areal statistics in Table 5.6 elucidates the fact that 40.55% (397.42 Km^2) of the total study area falls under the high and very high vulnerability zone. Groundwater vulnarability zonation map derived by integrating GIS-MCDM is shown in Figure 5.10.Very high vulnerable zones were identified on the coastal/inland alluvium where the transport of contaminants will be predominantly high, high vulnerability zones were surrounded to the very high vulnerability zone with fluvial, fluvial marine and aeolin formations. Majority of the urbanized area and industrial area sustaining in the study area falls under this zone making the situation critical. Low vulnerable zones were accounted for 37.05% (363.07 Km^2) of the total study area. This comprises of the inland regions having crystalline formations of hornblende biotite gneisse, charnockite and other hardrock formation making the aquifer least vulnerable to contamination. The vulnerable zones identified through DRASTIC and GIS-MCDM technique will lend a hand for the planners and researchers for sustainable management of this solitary water resource of the study area.

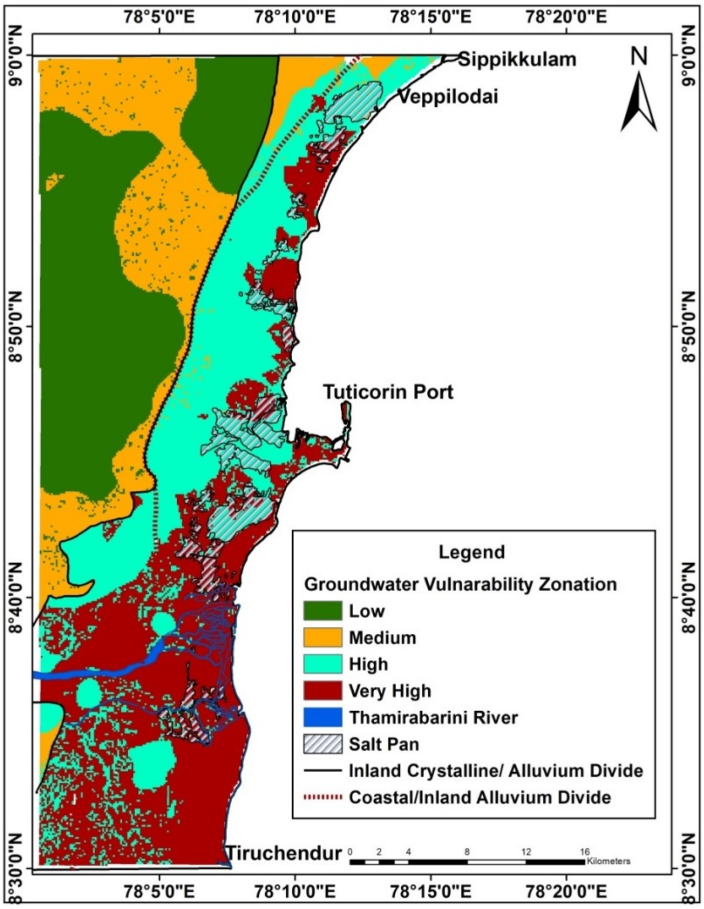


Fig 5.10: Groundwater vulnerability map for the study area

******

Chapter 6

SUMMARY AND CONCLUSIONS

Summary

An integrated approach has been taken in this study to understand the hydrochemistry of coastal aquifers of Tuticorin, Tamil Nadu using hydrogeochemical, stable isotopic and geospatial techniques. Based on the geological characteristics, the study area were classified in to coastal and inland areas. Physicochemical and bacteriological characteristics of 40 dug wells and 27 tube wells in the coastal/inland alluvium region, 8 dug wells and 43 bore wells in the inland crystalline regions during two different seasons, pre and post monsoon and their spatial distribution of ionic concentration were carried out. Hydrochemical processes were deciphered from ionic abundance, Hill piper diagram, Chadhas plot, Gibbs diagram and multi variate statistical analysis. Irrigation water quality assessment was also carried out.

The salinization mechanism of the study area was evaluated from environmental isotopes ($\delta^{18}O$ and δD). The local meteoric water line (LMWL) was established by using stable isotopes of precipitation. A GIS based Multi Criteria Decision Making (MCDM) technique was conducted to evaluate spatiotemporal variations of groundwater quality aspects and groundwater suitability zonation based on the BIS and WHO drinking water quality standards. Combination of DRASTIC and AHP methods was carried out for assessing ground water vulnerability to contamination.

Conclusions

- The alkaline nature of ground water in coastal and inland aquifers for pre and post monsoon season is due to the reduced precipitation in the area and proximity of coastal aquifers towards sea.

- Majority of the study area showed higher TDS value, it can be caused by the distribution of sparse rainfall.
- The majority of the groundwater in the area was hard. The geologic formation along the source of groundwater plays an inevitable role in making it hard.
- Higher ionic concentration are observed in north eastern coastal region during pre and post monsoon seasons.
- The predominant cation were sodium in all wells in the study area for both pre and post monsoon seasons. Chloride was the major anion found in coastal wells and sulphate was the predominant in inland wells. Highest sodium and chloride ion concentration were observed in aquifers lying near coast which indicates the saline water ingression.
- Hydrochemical facies of ground water evaluated by using Hill-Piper Trilinear diagrams and were

  In coastal/inland alluvial aquifers (dug well and tube well) –

  $Na\text{-}K\text{-}Cl\text{-}SO_4 > Na\text{-}K\text{-}HCO_3$ and $Na\text{-}K\text{-}HCO_3 > Na\text{-}K\text{-}Cl\text{-}SO_4$

  In inland crystalline aquifers (bore and dug well) –

  $Na\text{-}K\text{-}HCO_3 > Na\text{-}K\text{-}Cl\text{-}SO_4$ and $Na\text{-}K\text{-}Cl\text{-}SO_4 > Na\text{-}K\text{-}HCO_3$
- Bacteriological contamination was observed in areas near to Tuticorin port and north-west part of inland areas. This is due to lack of proper sanitation facilities in rural/urban areas.
- Using USSL diagram irrigation water quality was assessed and coastal aquifers showed salinity hazards.
- The ratio between the dissolved ionic species in groundwater were studied and the occurrence of leaching from aquifer material into the groundwater was confirmed.
- Gibb's analysis indicated that no precipitation dominance was found in coastal and inland groundwater for all the season. Multi-variate statistical analysis confirmed the influence of rock-water interaction in hydrochemistry of groundwater.

- The local meteoric water line (LMWL) was established for the entire study area using stable isotopic ratios (δD and $\delta^{18}O$) of rainwater and found that the local trend of stable isotopic signatures of the study area almost follows the global trend. Equation derived for LMWL in the study area is $\delta D = 6.9\ \delta^{18}O + 3.5$.
- $\delta^{18}O$ of the groundwater samples from the dug wells ranged between -3 to -5‰ and samples from tube wells ranged from -4 to -5‰ and bore well samples in the range -5 to -6‰. There is depletion in heavier isotopes in groundwater of the order of 1‰ as we go deeper in the Tuticorin area. After monsoon, depletion in $\delta^{18}O$ values is observed in the shallow and deeper aquifers in varied extents.
- The groundwater from coastal aquifers in the sedimentary formation is more depleted than those of the inland aquifer by ~2‰ in the premonsoon, and in the postmonsoon, it is reduced to ~1‰ between the coastal and inland samples. The tube well samples showed similar isotopic composition irrespective of the distance from the shore/lithology in the two seasons.
- Seasonal variation in isotopic composition in the hard rock aquifer is random compared to the other aquifers.
- The northeast monsoon rains are found to be the major recharge source to the groundwater of the region. Due to evaporation from the rain drops during its fall the resultant rain is highly enriched in heavier isotopes as the season progresses. Contribution from the recycled vapour to the precipitation is not significant enough to impart any isotopic modification of rain water.
- The regression analysis of $\delta^{18}O$ and δD of groundwater drawn from tube wells showed that during the non-rainy period of June to September, the groundwater is mixed probably with seawater. The groundwater in the alluvial aquifers in the study area is assumed to be recharged by the northeast monsoon rains after a time lag of approximately six months. The shallow groundwater from dug wells even though showed evaporative enrichment, is being recharged rapidly by the infiltrating rainwater.

- The shallow groundwater of Tuticorin district is affected by salinity due to direct ingress of seawater in the non rainy period, and also due to concentration of ions by evaporation. The results of the present investigation provide an outline of the geochemical processes controlling the groundwater chemistry of the fragile aquifer system of Tuticorin coast.
- With respect to drinking water suitability, the study area has been classified into four zones such as very poor, poor, moderate and good using GIS based MCDM technique. About 24% and 34% of entire study area were categorized as very poor to poor and moderate groundwater suitable zone for drinking purpose. The main reason for the poor groundwater suitability zone in coastal area are high urbanization, presence of salt pan, extraction of water for industrial use and so on.
- The groundwater vulnerability assessment by integrating GIS based DRASTIC-AHP techniques classified the study are into very high, high, medium and low groundwater vulnerable zones. An area of 40% and 23% of coastal region with a very high to high groundwater vulnerability which are characterized by porous & permeable vadose media with shallow groundwater table.
- Inland region of the study area is characterised with low vulnerability index value indicated that the groundwater in the zone is protected from contaminants leaching due to its inherent hydrogeology. This region is characterised with Charnockite/ Hornblende Gneiss of low porous vadose media and the presence of steep slope terrain favour this low vulnerability.

Future research fields suggested are:-

- The effect of industries on hydrological characteristics both qualitatively and quantitatively on shallow and deep aquifers in the study area.
- Mitigation measures for saline water ingress to ensure sustainable development of groundwater in the area.
- The residence time/recirculation of groundwater incorporating the tidal oscillations to be assessed for better planning measures.

******

REFERENCES

Abdul, A. H., Vanum, G., & Amare, G. M. N. (2017). Evaluation of ground water potential using geospatial technique. *Applied Water Science,* 7, 2447–2461.

Abtahi, M., Golchinpour, N., Yaghmaeian, K., Rafiee, M., Jahangiri-rad, M., Keyani, A., & Saeedi, R. (2015). A modified drinking water quality index (DWQI) for assessing drinking source water quality in rural communities of Khuzestan Province, Iran. *Ecological Indicators*, *53*, 283-291.

Aggarwal, P.K., Romatschke, U., Araguas Araguas, L., Belachew, D., Longstaffe, F.J., Berg, P., Schumacher, C., & Funk, A. (2016). Proportions of convective and stratiform precipitation revealed in water isotope ratios. *Nature Geoscience*, 9, 624-629.

Agriculture statistics, Statistical Year Book India. (2011). Ministry of Statistics and Programme Implimentation.

Ahmed, S. S., Mazhumder, Q. H., Jahen, C. S., & Islam, A. (2002). Hydrochemistry and classification of groundwater, Rajshahi city corporation area, Bengladesh. *Journal of Geological Society of India*, 60(4), 411-418.

Aller, L. (1985). DRASTIC: *A standardized system for evaluating ground water pollution potential using hydrogeologic setting*s. Robert S. Kerr Environmental Research Laboratory, Office of Research and Development, US Environmental Protection Agency, Oklahoma. Report No. 600/2-85/018, 163.

Aller, L., Bennett, T., Lehr, J. H., Petty, R. J., & Hackett, G. (1987). *DRASTIC:* A standardized system for evaluating ground water pollution potential using hydrogeologic settings. *Report No. 600/2-87/035, US Environmental Protection Agency, Washington, D.C.*

Allison, G. B., Gee, G. W., & Tyler, S. W. (1994). Vadose-zone techniques for estimating groundwater recharge in arid and semiarid regions. *Soil Science Society of America Journal*, 58(1), 6-14.

Ambiga, K., & Anna Durai, R. (2013). Use of geographical information system and water quality index to assess groundwater quality in and around Ranipet area, Vellore district, Tamil Nadu. *International Journal of Advanced Engineering Research and Studies*, 2, 73-80.

Amer, A.M., (1995). Salt water intrusion in coastal aquifers. *Proceedings of the international conference on water resources management in arid countries, Muscat, Sultanate of Oman,* 2, 521–529.

American Public Health Association (A.P.H.A A W) American Water Works for the Association & Water Environment Federation. (2012). *Standard Methods Examination of Water and Wastewater*. 22nd ed. Washington.

Andersen, M.S., Nyvang, V., Jakobsen, R., & Postma, D. (2005). Geochemical processes and solute transport at the seawater/freshwater interface of a sandy aquifer. *Geochimica et Cosmochimica Acta*, 69, 3979-3994.

Andreasen, D., & Fleck, W. (1997). Use of bromide: chloride ratios to differentiate potential sources of chloride in a shallow, unconfined aquifer affected by brackish water intrusion. *Hydrogeology Journal*, 5 (2), 17–26.

Apello, C. A. J., & Geinard, W. (1991). Processes accompanying the intrusion of saltwater. *In: Hydrogeology of Saltwater Intrusion*, 2, 291–304.

Aquilina, L., Ladouche, B., Doerfliger, N., Seidel, J.L., Bakalowicz, M., & Dupuy, C. (2002). Origin, evolution and residence time of saline thermal fluids (Balaruc springs, southern France): implications for fluid transfer across the continental shelf. *Chemical Geology,* 192, 1-21.

Aquilina, L., Landes, A.A. L., Ayraud-Vergnaud, V., Labasque, T., Roques, C., & Davy, P. (2013). Evidence for a Saline Component at Shallow Depth in the Crystalline Armorican Basement (W France). *Procedia Earth and Planetary Science*, 7, 19-22.

Aravindan, S. (1999). *Integrated hydrogeological studies in hard rocks aquifer system of Gadilam river basin, Tamil Nadu, India*. Ph.D thesis submitted to Bharathidasan University, 110.

Aris, A.Z., Abdullah, M.H., Ahmed, A., & Woong, K.K. (2007). Controlling factors of groundwater hydrochemistry in a small Island's aquifer. *International Journal of Environmental Science and Technology*, 4, 441-450.

Armandine Les Landes, A., Aquilina, L., Davy, P., Vergnaud, V., & Le Carlier C. (2014) Time scales of regional circulation of saline fluids in continental aquifers (Armorican Massif, Western France) *Hydrology and Earth System Sciences Discuss*ions, 19, 1413–1426.

Arnfield, A.J. (2003). Two decades of urban climate research: a review of turbulence, exchanges of energy and water, and the urban heat island. *International Journal of Climatology*, 23, 1-26.

Asa Rani, L., & Suresh Babu, D.S. (2008). A Statistical evaluation of ground water chemistry from the west coast of Tamil Nadu, India. *Indian Journal of Marine sciences*, 37 (2), 186-192.

Asaad, M.A., Abdelazim, N., & Valeriano, O.C.S. (2016). Groundwater quality investigation using multivariate analysis-case study: Western Nile Delta aquifer, Egypt. *International Journal of Environmental Science and Development*, 7, 1-9.

Ashley, R. P., & Lloyd, J. W. (1978). An example of the use of factor analysis and cluster analysis in groundwater chemistry interpretation. *Journal of Hydrology*, 39(3-4), 355-364.

Aunay, B., Dorfliger, N., Duvail, C., Grelot, F., Le Strat, P., Montginoul, M., & Rinaudo, J. D. (2006). Hydro-socio-economic implications for water management strategies: the case of Roussillon coastal aquifer. *In: International Symposium-DARCY. Aquifer Systems Management, Dijon.* 102.

Bastiaanssen, W.G.M., Menenti, M., Feddes, R.A., & Holtslag, A.A.M. (1998). A remote sensing surface energy balance algorithm for land (SEBAL). *Formulation Journal of Hydrology,* 212, 198-212.

Bennetts, D.A., Webb, J.A., Stone, D.J.M., & Hill, D.M. (2006). Understanding the salinization process for groundwater in an area of south-eastern Australia, using hydrochemical and isotopic evidence. *Journal of Hydrology.* 323, 178–192.

Bhattacharya, S. K., Froehlich, K., Aggrawal, P. K., & Kulkarni, K. M. (2003). Isotope variation in Indian monsoon precipitation; records from Bombay and New Delhi. *Journal of Geophysical research*, 30.

Bianchini, G., Pennisi, M., Cioni, R., Muti, A., Cerbai, N., & Kloppmann, W. (2005). Hydrochemistry of the high-boron groundwaters of the Cornia aquifer (Tuscany, Italy). *Geothermics*, 34, 297-319.

Biondic, B., Biondic, R., & Kapelj, S. (2006). Karst groundwater protection in the Kupa River catchment area and sustainable development. *Environmental Geology,* 49, 828-839.

Bouchaou, L., Michelot, J.L., Vengosh, A., Hsissou, Y., Qurtobi, M.,Gaye, C.B., Bullen, T.D., & Zuppi, G.M. (2008). Application of multiple isotopic and geochemical tracers for investigation of recharge, salinization, and residence time of water in the South-Massa aquifer, Southwest of Morocco. *Journal of Hydrolology*, 352, 267-287.

Brindha, K., & Elango, L. (2012). Impact of tanning industries on groundwater quality near a metropolitan city in India. *Water Resources Management*, 26 (6), 1747-1761.

Brindha, K., & Elango, L. (2015). Cross comparison of five popular groundwater pollution vulnerability index approaches. *Journal of Hydrology*, *524*, 597-613.

Brown, R. M., McClelland, N. I., Deininger, R. A., & O Connor, M. F. (1972). A water quality index—crashing the psychological barrier. *Indicators of environmental quality*, 173-182.

Bureau of Indian Standards (BIS). 2012. IS10500 *Indian Standard Drinking Water Specification IInd Rev*. New Delhi, India: BIS.

Buyadi, S., Mohd, W., & Misni, A. (2013). Impact of land use changes on the surface temperature distribution of area surrounding the National Botanic Garden, Shah Alam. *Procedia-Social and Behavioral Science*, 101,516-525.

Capaccioni, B., Didero, M., Paletta, C., & Didero, L. (2005). Saline intrusion and refreshening in a multilayer coastal aquifer in the Catania Plain (Sicily, Southern Italy): dynamics of degradation processes according to the hydrochemical characteristics of groundwaters. *Journal of Hydrology*, 307(1–4), 1–16.

Carrera, J., Hidalgo, J. J., Slooten, L. J., & Vazquez Sune, E. (2010). Computational and conceptual issues in the calibration of seawater intrusion models. *Hydrogeology Journal*, 18(1), 131–145.

Cary, L., Casanova, J., Gaaloul, N., & Guerrot, C. (2013). Combining boron isotopes and carbamazepine to trace sewage in salinized groundwater: a case study in Cap Bon, Tunisia. *Applied Geochemistry*, 34,126-139.

Cendon D. I., Larsen, J. R., Jones, B. G., Nanson, G. C., Rickleman, D., Hankin, S. I.,Pueyo, J. J., & Maroulis, J. (2011). Freshwater recharge into a shallow saline groundwater system, Cooper Creek flood plain, Queensland, Australia. *Journal of Hydrology,* 392 (2-4), 150-163.

Cendon, D.I., Ayora, C., Pueyo, J.J., Taberner, C., & Blanc Valleron, M.M. (2008). The chemical and hydrological evolution of the Mulhouse potash basin (France): Are "marine" ancient evaporites always representative of synchronous seawater chemistry. *Chemical Geology,* 252, 109-124.

Central Ground Water Board (CGWB). (2007). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2009). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2010). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2011). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2013). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2014). *A Concept Note on Geogenic Contamination of Ground Water in India With Special Reference to Nitrate.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2014). *Groundwater Year Book.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2017). *Dynamic Ground Water Resources of India.* Ministry of Water Resources, Govt.of India

Central Ground Water Board (CGWB). (2018). *Groundwater Year Book 2017–18.* Ministry of Water Resources, Govt.of India.

Central Ground Water Board (CGWB). (2019). *Groundwater Quality Scenario.* Ministry of Water Resources, Govt.of India.

Chadha, D.K. (1999). A proposed new diagram for geochemical classification of natural waters and interpretation of chemical data. *Hydrogeology Journal*, 7, 431-439.

Chidambaram, S., Sumar, G.S., Prasanna, M.V., Peter, A.J., Ramanthan, A.L., & Srinivasamoorthy, K. (2008). A study on the hydrogeology and hydrogeochemisty of groundwater from different depths in a coastal aquifer: Annamalai Nagar, Tamil Nadu, India. *Environmental Geology*, 57(1), 59–73.

Chockalingam, M. (1993). Coastal geomorphological studies of the region subtended between Mandapam and Devipattinam, Tamil Nadu, Thesis report, Tamil University, Tanjavur, 117.

Craig, H., (1961). Isotopic variations in meteoric waters. *Science*. 133, 1702-1703.

Custodio, E. (1997). Seawater Intrusion in Coastal Aquifers, Guidelines for Study, Monitoring and Control. Food and Agriculture Organization of the United Nation. *Water Report 11, Rome*.

Dalai, T.K., Bhattacharya, S.K., & Krishnaswami, S. (2002). Stable isotopes in the source waters of the Yamuna and its tributaries: seasonal and altitudinal variations and relation to major cations. *Hydrology Proceedings*, 16, 3345-3364.

Dar, M.A., Sankar, K., & Dar, I.A. (2010). Fluorine contamination in groundwater: a major challenge. *Environmental Monitoring and Assessment*, 173(1–4), 955–968.

Demlie, M., Wohnlich, S., Wisotzky, F., & Gizaw, B. (2007). Groundwater recharge, flow and hydrogeochemical evolution in a complex volcanic aquifer system, Central Ethiopia. *Hydro geology Journal*, 15, 1169-1181.

Deshpande, R. D. (2006). Groundwater in and around Cambay basin Gujarat some geochemical and isotopic investigations, Ph.d thesis submitted to Maharaja Sayajirao University of Baroda, 29.

Deshpande, R.D., Bhattacharya, S.K., Jani, R.A., & Gupta, S.K. (2003). Distribution of oxygen and Hydrogen isotopes in shallow groundwaters from southern India: influence of a dual monsoon system. *Journal of Hydrology*, 271, 226-239.

District Statistical Hand Book of Thoothukudi, Dept. of Economics & Statistics, (2014-15).

Dunning, D. J., Ross, Q. E., & Merkhofer, M. W. (2000). Multiattribute utility analysis for addressing Section 316 (b) of the Clean Water Act. *Environmental Science & Policy*, *3*, 7-14.

Duriez, A., Marlin, C., Dotsika, E., Massault, M., Noret, A., & Morel, J.L. (2008). Geochemical evidence of seawater intrusion into a coastal geothermal field of central Greece: example of the Thermopylae system. *Environmental Geology*, 54, 551-564.

Edmunds, W.M., & Milne, C.J. (2001). Palaeowaters in coastal Europe: Evolution of groundwater since the late Pleistocene. *Special Publications. Geological society, London*, 189.

Elango, L., Ramachandran, S., & Chowdary, Y.S.N. (1992). Groundwater quality in coastal regions of South Madras. *Indian Journal of Environmental Health*, 34,318– 325.

Epstein, S., & Mayeda, T K, (1953). Variation of the $^{18}O/^{16}O$ ratio in natural waters. *Geochim. Cosmochim. Acta,* 4, 213, 1953.

Escolero, O., Marin, L.E., Domínguez Mariani, E., & Torres Onofre, S. (2007). Dynamic of the freshwater–saltwater interface in a karstic aquifer under extraordinary recharge action: the Merida Yucatan case study. *Environmental Geology*, 51, 719–723.

Fischer, B.M., Van Meerveld, H.I., & Seibert, J., (2017). Spatial variability in the isotopic composition of rainfall in a small headwater catchment and its effect on hydrograph separation. *Journal of Hydrology*. 547, 755-769.

Flug, M., Seitz, H. L., & Scott, J. F. (2000). Multicriteria decision analysis applied to Glen Canyon Dam. *Journal of Water Resources Planning and Management*, *126*(5), 270-276.

Foster, S. (1998). Groundwater assessing vulnerability and promoting protection of a threatened resource. *In: Proceedings of the 8th Stockholm water symposium, Sweden*, 79-90.

Foster, S.S.D; & Chilton, P.J. (2003). Groundwater: the processes and global significance of aquifer degradation. *Philosophical Transactions of the Royal Society Biological Sciences*, 1957-1972.

Freeze, R. A., & Cherry, J. A. (1979). Groundwater. Englewood Cliffs. *New Jersey*, 604.

Gaaloul, N., Pliakas, F., Kallioras, A., Schuth, C., & Marinos, P. (2012). Simulation of seawater intrusion in coastal aquifers: forty five'years exploitation in an eastern coast aquifer in NE Tunisia. *Open Hydrology Journal*, 6(1), 31–44.

Ghabayen, M.S., McKee, Mac., & Kemblowski, M. (2006). Ionic and isotopic ratios for identification of salinity sources and missing data in the Gaza aquifer. *Journal of Hydrology*. 318, 360-373.

Ghosh, A., Tiwari, A. K., & Das, S. (2015). A GIS based DRASTIC model for assessing groundwater vulnerability of Katri Watershed, Dhanbad, India. *Modeling Earth Systems and Environment*, *1*(3), 1-14.

Giambastiani B., Antonellini, M., Oude Essink, G., & Stuurman, R. (2007) Saltwater intrusion in the unconfined coastal aquifer of Ravenna (Italy): a numerical model. *Journal of Hydrology*, 340(1–2), 91–104.

Gibbs, R.J. (1970). Mechanism controlling world's water chemistry. *Science*, 170, 1088-1090.

Gimenez, E., & Morell, I. (1997). Hydrogeochemical analysis of salinization processes in the coastal aquifer of Oropesa (Castellon, Spain). *Environmental Geology*, 29, 118–131.

Gopinath, S., Srinivasamoorthy, K., Vasanthavigar, M., Saravanan, K., Prakash, R., Suma, C. S., & Senthilnathan, D. (2018). Hydrochemical characteristics and salinity of groundwater in parts of Nagapattinam district of Tamil Nadu and the Union Territory of Puducherry, India. *Carbonates and Evaporites*, 33(1), 1-13.

Greenwood, N.N., & Earnshaw, A. (1984) Chemistry of the elements. *Oxford, Pergamon Press*.

Gupta, S.K. (2004). An insight in to the dynamics of Lake Nainital (Kumaun Himalaya, India) using stable isotope data. *Hydrolologival Science Journal*, 49, 1099-1113.

Gupta, S.K., Deshpande, R.D., Bhattacharya, S.K., & Jani, R.A. (2005). Groundwater $\delta 1^{8}0$ and δD from central Indian peninsula: influence of Arabian Sea and the Bay of Bengal branches of summer monsoon. *Journal of Hydrolology*, 303, 38-55.

Gupta, M., & Srivastava, P.K. (2010). Integrating GIS and remote sensing for identification of groundwater potential zones in the hilly terrain of Pavagarh, Gujarat, India. *Water International*, 35, 233-245.

Hameed, A. S., & Resmi, T. R. (2016). Application of Natural and Artificial Isotopes in Groundwater Recharge Estimation. *Groundwater Assessment, Modeling, and Management*, 455.

Hameed, A. S., Resmi, T. R., Suraj, S., Warrier, C. U., Sudheesh, M., & Deshpande, R. D. (2015). Isotopic characterization and mass balance reveals groundwater recharge pattern in Chaliyar river basin, Kerala, India. *Journal of Hydrology. Regional Studies*, 4, 48-58.

Han, D., Kohfahl, C., Song, X., Xiao, G., & Yang, J. (2011). Geochemical and isotopic evidence for palaeo seawater intrusion into the south coast aquifer of Laizhou Bay, China. Applied Geochemistry, 26, 863-883.

Hansen, J., Ruedy, R., Sato, M., & Lo, K. (2010). Global surface temperature change. *Reviews of Geophysics*, 48, 4.

Hayashi, M. (2004). Environmental Monitoring and Assessment, 96(1-3), 119.

Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water. *U.S. Geological Survey, Water Supply Paper*, 2254, 264.

Hem, J. D. (1992). Study and interpretation of the chemical characteristics of natural water. *Washington DC; U.S. Govt.*

Herczeg, A.L, and Edmunds, W.M., (1999). Environmental Tracers in Subsurface Hydrology. *Boston, Kluwer Academic Publishers*, 31-77.

Hill, R.A. (1940). Geochemical patterns in the Coachella valley, California. *Transactions American Geophysical Union*, 21, 46-49.

Horita, J. (1988) Hydrogen isotope analysis of natural waters using an H^2-water equilibration method. A special implication to brines. *Chemical Geol*ogy (*Isot. Geosci. Section*), 72, 89-94.

Horton, R.K. (1965). An index number system for rating water quality. *Journal of Water Pollution Control Federation*. 37, 300–305.

Houk, I.E. (1951). Irrigation Engineering Vo1.1. Agricultural and hydrological phases. John Wiley and Sons Inc.

Indu, S. Nair., Rajaveni, S.P., Schneider, M., & Elango, L. (2015). Geochemical and isotopic signatures for the identification of seawater intrusion in an alluvial aquifer. *Journal of Earth System Science*, 124, 1281-1291.

IPCC. (2007). Fourth assessment report of the intergovernmental panel on climate change. Cambridge: *Cambridge University Press*.

Jalali, M. (2007). Hydrochemical identification of groundwater resources and their changes under the impacts of human activity in the Chah basin in Western Iran. *Environmental Monitoring and Assessment*, 130(1–3), 347–364.

Jat, M. K., Khare, D., & Garg, P. K. (2009). Urbanization and its impact on groundwater: a remote sensing and GIS-based assessment approach. *The Environmentalist*, 29(1), 17.

Jesiya, N.P., & Gopinath, G. (2019 a). Groundwater suitability zonation with synchronized GIS and MCDM approach for urban and peri-urban phreatic aquifer ensemble of southern India. *Urban Water Journal*. *15*(8), 801-811.

Jesiya, N. P., & Gopinath, G. (2019 b). A Customized Fuzzy AHP-GIS based DRASTIC-L model for intrinsic groundwater vulnerability assessment of urban and peri urban phreatic aquifer clusters. *Groundwater for Sustainable Development*, *8*, 654-666.

Joubert, A., Stewart, T.J., & Eberhard, R. (2003). Evaluation of Water Supply Augmentation and Water Demand Management Options for the City of Cape Town. *Journal of Multi-Criteria Decision Analysis*, 121, 17-25.

Kafri, U., Goldman, M., Lyakhovsky, V., Scholl, C., Helwig, S., & Tezkan, B. (2007). The configuration of the fresh–saline groundwater interface within the regional Judea Group carbonate aquifer in northern Israel between the mediterranean and the Dead Sea base levels as delineated by deep geoelectromagnetic soundings. *Journal of Hydrology*, 344, 123–134.

Kalma, J.D., McVicar, T.R., & McCabe, M.F. (2008). Estimating land surface evaporation: A review of methods using remotely sensed surface temperature data. *Surveys in Geophysics*, 29, 421-469.

Karanth, K.R. (1987). Groundwater assessment, development and management. *Tata McGraw-Hill publishing Company Limited, New Delhi*, 720.

Khalid, S. (2019). An assessment of groundwater quality for irrigation and drinking purposes around brick kilns in three districts of Balochistan province, Pakistan, through water quality index and multivariate statistical approaches. *Journal of Geochemical Exploration.* 197, 14-26.

Khaska, M., La Salle, C.L.G., Lancelot, J., Mohamad, A., Verdoux, P., & Noret, A. (2013). Origin of groundwater salinity (current seawater vs. saline deep water) in a coastal Karst aquifer based on Sr and Cl isotopes. Case study of the La Clape Massif (southern France). *Applied Geochemistry*, 37, 212-227.

Kim, Y., Lee, K.S., Koh, D.C., Lee, D.H., Lee, S.G., Park,W.B., Koh, G. W., & Woo, N.C. (2003). Hydrogeochemical and isotopic evidence of groundwater salinization in coastal aquifer: a case study in Jeju volcanic island, Korea. *Journal of Hydrology*, 270, 282-294.

Kloppmann, W., Van Houtte, E., Picot, G., Vandenbohede, A., Lebbe, L., Guerrot, C., Millot, R., & Wintgens, T. (2008). Monitoring reverse osmosis treated wastewater recharge into a coastal aquifer by environmental isotopes (B, Li, O, H). *Environmental Science & Technology*, 42, 8759-8765.

Kogan, F.N. (2001).Operational space technology for global vegetation assessment. *Bulletin of the American Meteorological Society*, 82, 1949-1964.

Krishnamurthy, R.V., & Bhattacharya, S.K. (1991). Stable oxygen and hydrogen isotope ratios in shallow groundwater's from India and a study of the role of evapotranspiration in the Indian monsoon. *The Geochemical Society, special publication No.3*, 187-193.

Krishnan, G., Singh, S., Singh, R. P., Ghosh, N. C., & Khanna, A. (2016). Water quality index of groundwater of Haridwar District, Uttarakhand, India. *Water Energy International*, *58*(10), 55-58.

Kumar, K. S., Bhaskar, P. U., & Padmakumari, K. (2012). Estimation of Land Surface Temperature to study urban heat island effect using Landsat ETM + IMAGE. *International Journal of Engineering Science and Technology,* 4(02), 771–778.

Kumar, M.E.S., & Venugopal, K. (2003). Environmental modelling of ground water vulnerability migration of pollutants. *International Conference on water and environment.* 437.

Laluraj, C. M., Gopinath, G., & Dineshkumar, P. K. (2005). Groundwater chemistry of shallow aquifers in the coastal zones of Cochin, India. *Applied Ecology and Environmental Research 3*(1), 133-139.

Langelier, W. F. (1946). Chemical equilibria in water treatment. *Journal of the American Water Works Association*, 38(2), 169-178.

Lawrence, A.R., Gooddy, D.C., Kanatharana, P., Meesilp, M., & Ramnarong, V. (2000). Groundwater evolution beneath Hat Yai, a rapidly developing city in Thailand. *Hydrology Journal*, 8, 564–575.

Li, P., He, S., He, X., & Tian, R. (2018). Seasonal hydrochemical characterization and groundwater quality delineation based on matter element extension analysis in a paper wastewater irrigation area, northwest China. *Exposure and Health,* 10, 241–258.

Lloyd, J.W., & Heathcote, J.A. (1985). Natural inorganic hydrochemistry in relation to ground water -An Introduction, *Clarendon Press Oxford*, 296.

Lucas, Y., Schmitt, A.D., Chabaux, F., Clement, A., Fritz, B., Elsass, P., & Durand, S (2010). Geochemical tracing and hydrogeochemical modelling of water–rock interactions during salinization of alluvial groundwater (Upper Rhine Valley, France). *Applied Geochemistry*, 25, 1644-1663.

Machiwal, D., Jha, M. K., & Mal, B. C. (2011). Assessment of groundwater potential in a semi-arid region of India using remote sensing, GIS and MCDM techniques. *Water resources management*, *25*(5), 1359-1386.

Manjusree,T.M., Sabu joseph., & Jobin Thomas. (2009). Hydrogeochemistry and groundwater quality in the coastal sandy clay aquifers of Alappuzha district, Kerala. *Journal Geological Society of India*, 74, 459-468.

Masciopinto, C. (2006). Simulation of coastal groundwater remediation: The case of Nardò fractured aquifer in Southern Italy. *Environmental Modelling and Software,* 21, 85–97.

McClanahan, M.A., & Mancy, K.H. (1974). Effect of pH on the quality of calcium carbonate film deposited from moderately hard and hard water. *Journal of the American Water Works Association*, 66(1), 49-53.

Merchan, D., Auque, L.F., Acero, P., Gimeno, M.J., & Causape, J. (2015). Geochemical processes controlling water salinization in an irrigated basin in Spain: Identification of natural and anthropogenic influence. *Science of the Total Environment*, 502, 330-343.

Mogaji, K. A. (2018). Application of vulnerability modeling techniques in groundwater resources management: a comparative study. *Applied Water Science,* 8, 127.

Mondal, N. C., Singh, V. P., Singh, V. S., & Saxena, V. K. (2010). Determining the interaction between groundwater and saline water through groundwater major ions chemistry. *Journal of Hydrology*, 388, 100-111.

Mongelli, G., Monni, S., Oggiano, G., Paternoster, M., & Sinisi, R. (2013).Tracing groundwater salinization processes in coastal aquifers: a hydrogeochemical and isotopic approach in the NaCl brackish waters of northwestern Sardinia, Italy. *Hydrology and Earth System Sciences*, 17, 2917-2928.

Mukherjee, A., Fryar, A.E., & Rowe, H.D. (2007). Regional scale stable isotopic signatures of recharge and deep groundwater in the arsenic affected areas of West Bengal, India. *Journal of Hydrology*, 334, 151-161.

Murrel, N.E. (1987). Impact of metal solders on water quality. *Proceedings of the annual conference of the American Water Works Association, Part 1. Denver, CO, American Water Works Association*, 39-43.

Navada, S. V., & Rao, S. M. (1991). Study of Ganga river–groundwater interaction using environmental oxygen-18. *Isotopenpraxis Isotopes in Environmental and Health Studies*, 27(8), 380-384.

Navada, S.V., Nair, A.R., Rao, S.M., Paliwall, B.L., & Dashy, C.S. (1993). Groundwater Recharge Studies in Arid Region of Jalore, Rajasthan Using Isotope Techniques. *Journal of Arid Environments*, 24, 125-133.

Nawal Alfarrah., & Kristine Walraevens. (2018). Groundwater overexploitation and seawater intrusion in coastal areas of arid and semi-arid regions. *Water 10*(2), 143.

Negrel, P., Casanova, J., & Aranyossy, J.F. (2001). Strontium isotope systematics used to decipher the origin of groundwaters sampled from Granitoids: the Vienne Case (France). *Chemical Geology*, 177, 287-308.

Nordberg, G. F., Goyer, R.A., & Clarkson, T.W. (1985). Impact of effects of acid precipitation on toxicity of metals. *Environmental Health Perspectives*, 68,169-180.

Palmer, P.C., Gannett, M.W., & Hinkle, S.R. 2007. Isotopic characterization of three groundwater recharge sources and inferences for selected aquifers in the upper Klamath Basin of Oregon and California, USA. *Journal of Hydrology.* 338, 17-29.

Panagopoulos, G. (2008). Application of major and trace elements as well as boron isotopes for tracing hydrochemical processes: the case of Trifilia coastal karst aquifer, Greece. *Environmental Geology,* 58, 1067–1082.

Pande, K., Padia, J.T., Ramesh, R., & Sharma, K.K. (2000). Stable isotope systematic of surface water bodies in the Himalayan and Trans-Himalayaan (Kashmir) region. *Journal of Earth System Science,* 109, 109-115.

Parul Maurya., Rina Kumari., & Saumitra Mukherjee. (2019). Hydrochemistry in integration with stable isotopes ($\delta^{18}O$ and δD) to assess seawater intrusion in coastal aquifers of Kachchh district, Gujarat, India. *Journal of Geochemical Exploration*, 196, 42-56.

Pauleit, S., & Duhme, F. (2000). Assessing the environmental performance of landcover types for urban planning. *Landscape and Urban Planning,* 52, 1–20.

Peres, L.F., Dacamara, C.C., Trigo, I.F., & Freitas, S.C. (2010). Synergistic use of the two-temperature and split-window methods for Land Surface Temperature retrieval. *International Journal of Remote Sensing*, 31, 4387-4409.

Phan, T. N., Kappas, M., & Tran, T. P. (2018). Land Surface Temperature variation earth due to changes in elevation in Northwest Vietnam. *Climate*, 6, 28.

Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water analysis. *Eos, Transactions American Geophysical Union*, *25*(6), 914-928.

Piscopo, G. (2001). Groundwater vulnerability map, explanatory notes, Castlereagh Catchment, NSW. Department of Land and Water Conservation, Australia, Found at: http://www.dlwc.nsw.gov.au/care/water/groundwater/reports/pdfs/castlereagh_map_notes.pdf.

Post, V.E.A. (2005). Fresh and saline groundwater interaction in coastal aquifers: is our technology ready for the problems ahead. *Hydrogeology Journal*, 13, 120-123.

Prasad, K., & Shukla, J.P. (2014). Assessment of groundwater vulnerability using GIS based DRASTIC technology for the basaltic aquifer of Burhner watershed, Mohgaon block,Mandla, India. *Current Science.* 107 (10), 1649-1656.

Prasad, R.K., Singh, V.S., Krishnamacharyulu, S.K., & Banerjee, P. (2011). Application of drastic model and GIS for assessing vulnerability in hard rock granitic aquifer. *Environmental Monitoring and Assessment*. 176 (1–4), 143-155.

Prasanna, M.V., Chidambaram, S., Senthil Kumar, G., Ramanathan, A.L., & Nainwal, H.C. (2011). Hydrogeochemical assessment of groundwater in Neyveli Basin, Cuddalore District, South India. *Arabian Journal of Geosciences*, 4, 319-330.

Pulido Bosch, A., Tahiri, A., & Vallejos, A. (1999). Hydrogeochemical characteristics of processes in the Temara aquifer in northwestern Morocco. *Water Air and Soil Pollution*. 114, 323–337.

Pulido Leboeuf, P. (2004). Seawater intrusion and associated processes in a small coastal complex aquifer (Castell de Ferro, Spain). *Applied Geochemistry*, 19, 1517-1527.

Rahman, A. (2008). A GIS based DRASTIC model for assessing groundwater vulnerability in shallow aquifer in Aligarh, India. *Applied geography*, *28*(1), 32-53.

Rajesh, R., & Murthy, T. R. S. (2004). Groundwater quality and its change over a decade; An analysis of a coastal urban environment from the west coast of India. *Environmental Geology*, 45, 978-981.

Rajesh, R., Sreedhara, M.T.R., & Raghavan, B.R. (2001).Spatial distribution of pH, EC and *total* dissolved solids of Nethravathi river basin, Karnataka state, India. *Pollution Research*, 20 (3), 413 - 418.

Rajmohan, N., & Elango, L. (2004) Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar river basins, southern India. *Environmental Geology*, 46(1), 47-61.

Rajmohan, N., Elango, L., Ramachandran, S., & Natarajan, M. (2000). Major ion correlation in groundwater of Kancheepuram region, South India. *Indian Journal of Environmental Protection,* 20 (3), 188–193.

Ramesh, K., & Elango, L. (2011). Groundwater quality and its suitability for domestic and agricultural use in Tondiar river basin, Tamil Nadu, India. *Environmental Monitoring and Assessment,* 184(6), 3887-3899.

Rangarajan, R., & Balasubramanian, A. (1990). Corrosion and scale formation characteristic of ground water in and around Nangavalli, Salem district, Tamilnadu. *Journal of Applied Hydrology*, 2, 15-22.

Rekha, P.N., Ravichandran, P., Gangadharan, R., Bhatt, J. H., Panigrahi, A., Pillai, S.M., & Jayanthi, M. (2013). Assessment of hydrogeochemical characteristics of groundwater in shrimp farming areas in coastal Tamil Nadu, India. *Aquaculture International*, 21(5), 1137-1153.

Ribeiro, L., Pindo, J.C., & Dominguez Granda, L. (2017). Assessment of groundwater vulnerability in the Daule aquifer, Ecuador, using the susceptibility index method. *The Science of the Total Environment*. 574, 1674-1683.

Richey, G. D., McDonnell, J. J., Erbe, W. M., & Hurd, M. T. (1998). Hydrograph separation based on chemical and isotopic concentrations: a critical appraisal of published studies from New Zealand, North America and Europe. *Journal of Hydrology (NZ)*, 37(2), 95–111.

Runnells, D.D. (1993). Inorganic Chemical Processes and Reactions, in Alley, W.M.,ed. *Regional Groundwater Quality : New York, Van Nostrand Reinhold*, 131-153.

Saaty, T. L. (1980). The Analytical Hierarchy Process, Planning, Priority. Resource Allocation. USA. *RWS Publications*.

Saaty, T. L. (2005). Theory and applications of the analytic network process: decision making with benefits, opportunities, costs, and risks. *RWS publications*.

Sandeep Goyal., Bharadwaj, R.S., and Jugran, D.K. (1999). Multi criteria analysis using GIS for ground water resource evaluation in Rawasen and Pili Watershed, U.P. *Groundwater assessment, Proceedings of Map India*, 1-3.

Sankaran, S., Sonkamble, S., Krishnakumar, K., & Mondal, N.C. (2012), Integrated approach for demarcating subsurface pollution and saline water intrusion zones in SIPCOT area: a case study from Cuddalore in Southern India. *Environmental Monitoring Assessment,* 184(8), 5121-5138.

Saravana Kumar, U., Suman, S., Navada, S. V., Deodhar, A. S. (2009). Environmental isotopes investigation on recharge processes and hydrodynamics of the coastal sedimentary aquifers of Tiruvadanai, Tamil Nadu State, India. *Journal of Hydrolology*, 364, 23-39.

Sarwade, D., Nandakumar, M., Kesari, M., Mondal, N., Singh, V., & Singh, B. (2007) Evaluation of sea water ingress into an Indian Atoll. *Environmental Geology*, 52, 1475–1483.

Sastri, J.C.V. (1975). Hydrogeochemistry of Charnockites of Karnataka State: Studies in Precambrians of (ed. C. Naganna). *Bangalore University Press*, 243-249.

Sathish, S., Elango, L., Rajesh, R., & Sarma, V.S. (2011). Assessment of seawater mixing in a coastal aquifer by high resolution electrical resistivity tomography. *International Journal of Environmental Science & Technology,* 8, 483-492.

Sawyer, C.N., & McCarty, P.L. (1967). Chemistry for sanitary engineers. 2nd Edition. *McGraw-Hill, New York*, 518.

Sener, E., & Sener, S. (2015). Evaluation of groundwater vulnerability to pollution using fuzzy analytic hierarchy process method. *Environmental Earth Sciences*, 73 (12), 8405-8424.

Sexana, V.K., Singh, V.S., Mondal, N.C., & Jain, S.C. (2003). Use of chemical parameters to delineation fresh groundwater resources in Potharlanka Island, India. *Environmental Geology*, 44(5), 516–521.

Shankar, K., Aravindan, S., Rajendran, S. (2011). Hydrochemical profile for assessing the groundwater quality of paravanar river sub-basin, Cuddalore district, Tamil Nadu, India. *Current World Environment*, 6(1), 45-52.

Shivanna, K., Kulkarni,U.P., Joseph, T.B., & Navada, S.V. (2004). Contribution of storm to groundwater in semi-arid regions of Karnataka, India. *Hydrological Process*, 18, 473-485.

Sola, F., Vallejos, A., Daniele, L., & Pulido-Bosch, A. (2014). Identification of a Holocene aquifer–lagoon system using hydrogeochemical data. *Quaternary Research*, 82, 121-131.

Sprenger, M., Leistert, H., Gimbel, K., & Weiler, M. (2016). Illuminating hydrological processes at the soil-vegetation-atmosphere interface with water stable isotopes. *Reviews of Geophysics*, 54, 674-704.

Srinivasamoorthy, K., Gopinath, M., Chidambaram, S., Vasanthavigar,M., & Sarma, V.S. (2014). Hydrochemical characterization and quality appraisal of groundwater from Pungar sub basin, Tamilnadu, India. *Journal of King Saud University -Science*, 26(1), 37-52.

Stambuk Giljanovic, N. (1999). Water quality evaluation by index in Dalmatia. *Water Research*, *33*(16), 3423-3440.

Stigter, T. Y., Ribeiro, L., & Dill, A. C. (2006). Application of a groundwater quality index as an assessment and communication tool in agro-environmental policies–Two Portuguese case studies. *Journal of Hydrology*, *327*(3-4), 578-591.

Stone, A., Spyridakis, D., Benjamin, M., Ferguson, J., Reiber, S., & Osterhus, S. (1987) The effects of short-term changes in water quality on copper and zinc corrosion rates. *Journal of the American Water Works Association*, 79(2), 75-82.

Sukhija, B.S., Varma, V.N., Nagabhushanam, P., & Reddy, D.V. (1996). Differentiation of paleomarine and modern seawater intruded salinities in coastal groundwaters (of Karaikal and Tanjavur, India) based on inorganic chemistry, organic biomarker fingerprints and radiocarbon dating. *Journal of Hydrology*, 174 (1–2), 173-201.

SundaraKumari, K., Udayabhaskar, P., & Padmakumari, K. (2012). Estimation of Land Surface Temperature to study urban heat island effect using Landsat ETM+ Image. *International Journal of Engineering Science and Technology,* 4, 771-778.

Swetha, T. V., Gopinath, G., Thrivikramji, K. P., & Jesiya, N. P. (2017). Geospatial and MCDM tool mix for identification of potential groundwater prospects in a tropical river basin, Kerala. *Environmental Earth Sciences*, *76*(12), 428.

Tahmasebi, P., Mahmudy Gharaie, M.H., Ghassemzadeh, F., & Karouyeh, A.K. (2018). Assessment of groundwater suitability for irrigation in a gold mine surrounding area, NE Iran. *Environmental Earth Sciences* , 77, 766.

Taylor, R. G., & Howard, K.W.F. (1994). Groundwater quality in rural Uganda: Hydrochemical consideration for the development of aquifers within the basement complex of Africa. *Groundwater Quality, special report, eds. H. Nash and G.J.H. McCall, Chapman and Hall publication.* 31-43.

Thilagavathi, R., Chidambaram, S., Prasanna, M. V., Thivya, C., & Singaraja C. (2012). A study on groundwater geochemistry and water quality in layered aquifers system of Pondicherry region, southeast India. *Applied Water Science*, 2, 253-269.

Thirumalaivasan, D. 2002. Specific aquifer vulnerability assessment using geographic information system and modified drastic model. Ph. D thesis submitted to Anna University.

Todd, D.K. (1980). Groundwater Hydrology, *2nd edition, Wiley,* New York.

Todd, D.K., Mays, L.W., (2005). *Groundwater hydrology*, *3rd edition. Wiley,* New York.

Tziritis, E., Skordas, K., & Kelepertsis, K. (2016).The use of hydrogeochemical analyses and multivariate statistics for the characterization of groundwater resources in a complex aquifer system. A case study in Amyros river basin, Thessaly, Central Greece. *Environmental Earth Science*, 75,339. .

Umar, R., & Sami Ahmed, M. (2000). Groundwater quality in parts of central Ganges basin. *Environmental Geology,* 170, 1080-1090.

Unsal, B., Yagbasan, O., & Yazicigil, H. (2014). Assessing the impacts of climate change on sustainable management of coastal aquifers. *Environmental Earth Sciences*, 72, 2183-2193.

Vengosh, A. (2003). Salinization and Saline Environments, in Environmental geochemistry. Treatise in Geochemistry. *Elsevier Science,* 9, 333-365.

Vengosh, A., Chivas, A.R., Starinsky, A., Kolodny, Y., Baozhen, Z., & Pengxi, Z. (1995). Chemical and boron isotope compositions of nonmarine brines from the Qaidam Basin, Qinghai, China, *Chemical Geology*, 120, 135-154.

Vengosh, A., Gill, J., Davisson, M.L., & Hudson, G.B. (2002). A multi-isotope (B, Sr, O, H, and C) and age dating study of groundwater from Salinas Valley, California. Hydrochemistry, dynamics, and contamination process. *Water Resources Research*. 38 (1), 1-17.

Venugopal, T.N. (1998). *Hydrogeological investigation in the Arkavathi river basin - A tributary of Cauvery river, Karnataka*. Ph.D Thesis submitted to Mysore University, 224.

Vetrimurugan, E., & Elango, L. (2015). Groundwater chemistry and quality in an intensively cultivated river delta. *Water Quality Exposure and Health*, 7, 125-141.

Viswanathiah, M.N., & Sastri, J.C.V. (1973). Hydrogeochemistry of the Precambrian graywackes and chlorite schists of certain areas of Mysore State. *Proce. Sem. Vol. Water well drilling in hard rock areas of India, Bangalore*, 155-169.

Voudouris, K. (2009) Assessing groundwater pollution risk in Sarigkiol basin, NW Greece. In: Gallo M, Herrari M (eds) River Pollution Research Progress. *Nova Science Publishers Inc.*, 7, 265-281.

Wang, S., Zhang, M., Catherine, E. H., Crawford, J., Wang, G., Chen, F., Du, M., Qiu, X., & Zhou, S. (2018). Meteoric water lines in arid Central Asia using event based and monthly data. *Journal of Hydrology*, 562, 435-445.

Webber, J.S., Covey, J.R., & King, M.V. (1989). Asbestos in drinking water supplied through grossly deteriorated A-C pipe. *Journal of the American Water Works Association*, 81(2), 80-85.

Wedepohl, K. H. (1978) Handbook of Geochemistry. *Springer, Berlin*.

Weng, Q., Lu, D., & Schubring, J. (2004). Estimation of land surface temperature-vegetation abundance relationship for urban heat island studies. *Remote Sensing of Environment,* 89(4), 467-483.

Werner, A.D., Bakker, M., Post, V.E.A., Vandenbohede, A., Lu, C., Ataie-Ashtiani B, Simmons, C.T., & Barry, D.A. (2013). Seawater intrusion processes, investigation and management: Recent advances and future challenges. *Advances in Water Resources*, 51, 3-26.

Wilcox, L.V. (1955). Classification and use of irrigation waters, US Department of Agriculture. Circ. Washington, DC. 969.

World Bank Report. (2010). Deep wells and prudence: towards pragmatic action for addressing ground water over exploitation in India, *The World Bank, Washington* Report, 51676.

World Health Organization, WHO, (1984). Guidelines to drinking water quality. World Health Organisation, Geneva.

World Health Organization, WHO. (2011). *Guidelines for Drinking-Water Quality*. 4th ed. WHO, Geneva.

Zahedi, S. (2017). Modification of expected conflicts between drinking water quality index and irrigation water quality index in water quality ranking of shared extraction wells using multi criteria decision making techniques. *Ecological Indicators*, *83*, 368-379.

Zaporozec, A. (1972). Graphical interpretation of water quality data. *Groundwater*, 10 (2), 32-43.

Zektser, I.S., & Everett, L.G., (2004). Groundwater resources of the world and their use. *IHP-VI Series on Groundwater, Paris, UNESCO*, 6, 342.

Zhu, C. (2000). Estimate of recharge from radiocarbon dating of groundwater and numerical flow and transport modelling. *Water Resources Research*, 36(9), 2607-2613.

Zhu, G.F., Li, Z.Z., Su, Y.H., Ma, J.Z., & Zhang, Y.Y., (2007). Hydrogeochemical and isotope evidence of groundwater evolution and recharge in Minqin Basin, Northwest China. *Journal of Hydrology*, 333, 239-251.

Web sites

http://tnenvis.nic.in/

http://unesdoc.unesco.org/

https://bhuvan.nrsc.gov.in/

https://chrsdata.eng.uci.edu/

******