HYDROGEOCHEMISTRY AND GROUNDWATER QUALITY OF COASTAL AQUIFERS OF ALAPPAD REGION, KOLLAM, KERALA, INDIA

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By

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Certificate

Certified that the work presented in the thesis entitled **“Hydrogeochemistry and Groundwater Quality of Coastal Aquifers of Alappad Region, Kollam, Kerala, India”** is an authentic record of research work carried out by **Ms. Ambili M. S.** under my supervision and guidance in the School of Environmental Studies, Cochin University of Science and Technology, Kochi-682 022 and that this work has not been included in any other thesis submitted previously for the award of any degree. All the relevant corrections and modifications suggested by the audience and recommended by the doctoral committee of the candidate during the pre-synopsis seminar have been incorporated in the thesis.

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Declaration

I hereby declared that the work presented in this thesis entitled **“Hydrogeochemistry and Groundwater Quality of Coastal Aquifers of Alappad Region, Kollam, Kerala, India”** is based on the original work done by me under the supervision of **Dr. V. Sivanandan Achari**, Director, Associate Professor, Co-ordinator, UGC-SAP-DRS (II) Programme [2015-2020], School of Environmental Studies, Cochin University of Science and Technology, Kochi-682 022 and has not been included in any other thesis submitted previously for the award of any degree.

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Dedicated to
My Beloved Father
M. K. Sivaraman
&
Mother Vimala K. K.

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Preface

The present research study is focused on the hydrogeochemical nature of one of the ecologically prominent region, Alappad coast ($9^0$2'57''N to $9^0$7'15''N latitude and $76^0$28'19''E to $76^0$30'13''E longitude) in the south west coast in Kollam district of Kerala state. Geologically, this is a narrow strip of barrier island on the shoreline of Arabian sea in the west and the Thiruvananthapuram-Shoranur canal (T-S canal) running north-south along the east side, separating from the mainland. There are sea walls along the entire coastal stretch, for protection and control of erosion. This fragile coastal land has very valuable heavy black mineral sand deposit making this region economically and geologically important. Rainfall is the major groundwater recharge source in the dense study area and due to special features of this coastal islets water directly flows towards the sea. This selected study area is under continuous research investigations on groundwater quality from the year 2005 - the post tsunami period after 26th December, 2004 Indian Ocean Tsunami. This village was completely inundated by tsunami waves of average height 5.0 meters causing wide spread damages.

Groundwater from eighteen sources (15 dug wells & 3 bore wells) are collected and analyzed for every month (January-December) in the year 2012. This study afterwards continued for every year in the month of December 2013, 2014, 2015, 2016 and 2017. Sampling and analysis are done following the standard analytical procedures (APHA; 2005, 2012) and methods (IS 10500:2012).The primary data obtained are compared with the post-tsunamic data available for the year 2005 and December 2008, also with the reported pre-tsunamic data of April 2001. Physico-chemical parameters analysed are compared with the water quality standards recommended by WHO (2011) and BIS (2012). Hill-Piper trilinear plots, Gibb's plot and various ionic ratios are used to find the hydrogeochemistry of the study area. Irrigation water quality parameters such as sodium adsorption ratio (SAR), sodium percentage (Na%), permeability index (PI), Kelley's index (KI), magnesium adsorption ratio (MAR) and residual sodium carbonate (RSC) are used to determine the suitability of water for irrigation purposes. Corrosive nature of the groundwater is evaluated using indices such as Langelier saturation index (LSI), Ryznar stability index (RSI), aggressiveness index (AI) and Larson-Skold index. The results of this study are statistically interpreted using Pearson's correlation matrix, t-test and ANOVA.

The major hydrochemical facies of the study area during the year 2001, 2005 & 2008 are Na^+-K^+-Cl^- -SO_4^{2-} for dug wells and during year 2005 in bore wells as well. It is also confirmed that in the year 2005, the chloride and sulphate has been enough to promote corrosion activities, where as in all other periods, these ions does not appears to have a major role in the corrosive behaviour of groundwater.

In the year 2012, the prominent physico-chemical parameters analysed are under permissible limits prescribed by WHO; 2011 and BIS; 2012. The overall hydrochemical facies of the groundwater sources during the year 2012 is Ca^{2+}-Mg^{2+}- HCO_3^- type followed by Ca^{2+}- Na^+- HCO_3^- (mixed type). Water type in the study area falls under *temporary hardness water type* with non-dominant cation and bicarbonate anion type water. The hydrogeochemistry of the study area is controlled by ion-exchange process and weathering of silicate minerals of rocks. Gibb's plot signifies the rock dominance in controlling the chemistry of groundwater for dug wells, whereas the bore wells in July 2012 shifts to evaporation dominance due to high TDS content. The WQI indicates groundwater is suitable for drinking purposes only after conventional treatments and disinfection. Water is suitable for irrigation purposes and corrosion indices shows water is moderately aggressive where the rate of calcium carbonate scale formation is not sufficient to inhibit corrosion. ANOVA test proves that there is significant difference between groundwater from different sources ($p<0.05$). Bore wells showed significantly higher values followed by dug wells and control well ($p<0.001$).

Groundwater (from dug well sources) of Alappad during April 2001, year 2005 (annual mean) and December 2008 have hydrochemical facies Na^+-K^+-Cl^- - SO_4^{2-}. The water type during these periods is found to be *saline water type* with Na^++ K^+ as dominate cations and Cl^- dominate anion water due to the impact of tsunami inundation. This clearly indicates the occurrence of contamination in shallow fresh water aquifers. From the year 2012 to December 2016 water maintained *temporary hardness water* having non–dominant cation and bicarbonate dominant water. The hydrochemical facies of groundwater during this period is Ca^{2+}-Mg^{2+}-HCO_3^{2-}. In December 2017 water exhibited a mixed behavior. Eventhough no prominent hydrochemical facies can be identified here the dominant cation and anion in groundwater are Na^+-K^+ and Cl^- . However over the years (for shallow and deep groundwater) there is no significant difference in the quality of groundwater but the variability is visible among the prominent physicochemical parameters.

Contents

Chapter 1

Chapter 2

Chapter 3

Chapter 5

List of Tables

List of Figures

List of Abbreviations

CW	-	Control well
BW	-	Bore well
DW	-	Dug well
MSL	-	Mean Sea Level
amsl	-	Above Mean Sea Level
bgl	-	Below Ground Level
BIS	-	Bureau of Indian Standards
WHO	-	World Health Organisation
DBU	-	Designated Best Use
CPCB	-	Central Pollution Control Board
WQI	-	Water Quality Index
CI	-	Confidence Interval
DO	-	Dissolved Oxygen
BOD	-	Biochemical Oxygen Demand
EC	-	Electrical Conductivity
TH	-	Total Hardness
TDS	-	Total Dissolved Solids
Alk	-	Alkalinity
t Fe	-	Total Iron
TC	-	Total Carbon
TIC	-	Total Inorganic Carbon
TOC	-	Total Organic Carbon
KI	-	Kelley’s Index
MAR	-	Magnesium Adsorption Ratio
PI	-	Permeability Index
SAR	-	Sodium Adsorption Ratio
USSL	-	United States Salinity Laboratory
RSC	-	Residual Sodium Carbonate
LSI	-	Langelier Saturation Index
RSI	-	Ryznar Stability index
AI	-	Aggressiveness Index
L-S	-	Larson-Skold Index
p value	-	Significance level
ms	-	Mean square
ANOVA	-	Analysis of variance

……

Chapter 1

INTRODUCTION

1.1 Groundwater

Groundwater, an unseen ocean of fresh water beneath the surface of the earth contained in the aquifers is serving the man kind for their ever ending water requirements[1]. Groundwater plays significant role in the global water balance being a long term reservoir of fresh water[2]. Hydrosphere covers about 71% of the Earth's surface. Out of the total percentage of water on our planet 96.5% is contained in oceans, 1.7% in glaciers and ice cap, 1.7% of water forms the part of groundwater and the remaining small fraction is present in surface water bodies [3].

Solar radiation evaporates this salt water and forms clouds, which later condense and precipitate to become the part of the long path way of global hydrological cycle. When precipitation reaches the surface of the crust, a part will join the surface water body as a result of surface run-off. The water that succeeds to infiltrate and percolate through the soil layers under the force of gravity, crossing the vadose zone (unsaturated zone) and saturates all pore spaces of soil to form groundwater (zone of saturation). Approximately 30% of fresh water resource of our planet is contained in this saturated zone, which accounts about 96% of the liquid fresh water [4].

Fresh water is very essential for the upkeep and wellbeing of human society, as about 80% of diseases affecting human beings are caused through water[5]. Contaminated drinking water and poor sanitation results in health problems[6]. According to UN report in the international year of fresh water (2003), 20% of the world's population lacks clean drinking water whereas 40% of the total population is not having sufficient sanitation facilities[7]. Global climate changes have direct impact on water resources, surface water as well as groundwater. Previously, scientists were interested to study the effect of global change on surface water due to its easily observable nature. But now recognising the role of groundwater in meeting the global demand for fresh water for drinking, irrigation and industrial purposes, research is done exclusively on the impact of climate changes along with human activities on groundwater resources[8]. It was found that groundwater throughout the world is facing three main challenges: groundwater depletion through overdraft, water logging problems and salinization issues. In most of the thickly populated areas, groundwater withdrawal exceeds the annual recharge of aquifers. In coastal areas, over pumping of groundwater leads to salt water intrusion due to up coning of sea water into the freshwater regime[9].

The quality and quantity of groundwater is determined by the sub surface geology of the region. In India 65% of the overall aquifer surface area consist of hard-rock aquifers. It is found in peninsular region. According to water and related statistics, central water commission, the annual water availability in our country is reported as of April 2015 is 1,869 BCM/year (Billion Cubic Meter), out of which 433 BCM is found as groundwater. It is assumed as 35 BCM of groundwater is lost as natural discharge. So the net available annual groundwater is estimated has 98 BCM/year. The government of India in the year 2011 issued a Model Bill for Groundwater Management. According to this laws can be enacted by states itself to protect groundwater resources. Kerala is one among 11 states and 4 Union territories that have adopted and implemented groundwater legislation. In India groundwater is a resource under the public trust doctrine as addressed by Model Bills and National Water Policy. Right to safe drinking water has evolved as a fundamental right in our country after Supreme Court as well as various High Courts delivered verdicts as part of ‘Right to Life’ under Article 21 of the constitution[10]. Kerala depends up on groundwater for a great extent for its social and economic needs. About 80% of water requirements for domestic purposes in rural sector and 50% of water needs in the urban and industrial sectors are covered by groundwater resources. In this context, awareness about the protection and management of groundwater as well as the significance of hydrological cycle for supporting the economic, social and environmental values is very essential to conserve these valuable resources[11].

1.2 Hydrology: A Holistic Approach

The science of water is not a separate entity but includes many atmospheric as well as lithological factors. Hydrometeorology, that deals with atmospheric processes which affect water resources[12] and hydrogeology have significant role in the formation and development of specific chemical characteristics of water. The major hydrometeorological factors affecting water are solar radiation, evaporation, precipitation, temperature, humidity and wind. Solar radiation, the ultimate source of energy influences the global atmospheric processes. Water balance of a region is primarily influenced by the amount of precipitation received which eventually contributes to the usable quantity of surface water and groundwater resources. Temperature and humidity of atmosphere have direct effect on the type (rain, hail, snow and mist) and amount of precipitation as well as the rate of evaporation and condensation. Atmospheric temperature controls phase change of water from gaseous state to liquid state and also solid phase. The amount of water vapour contained in the atmosphere is measured in terms of humidity[13].

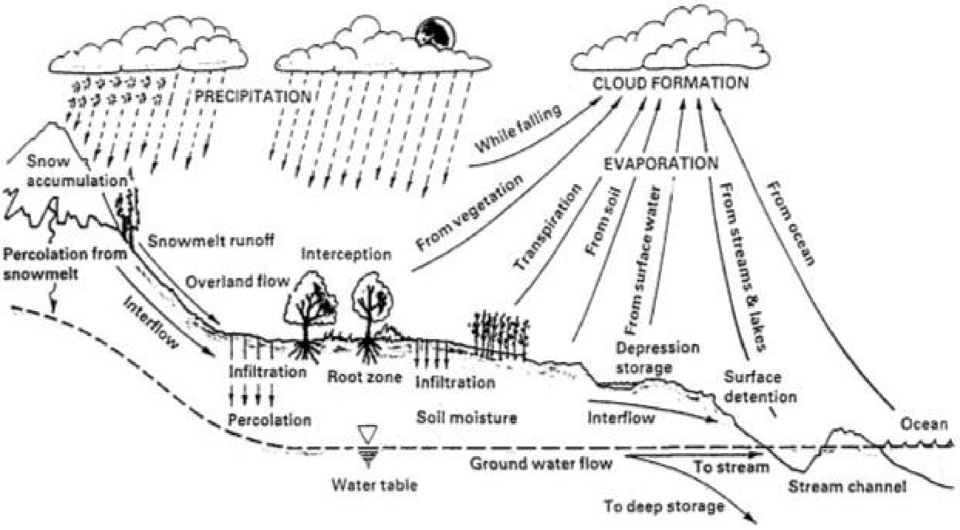

Figure 1.1: Hydrological cycle and its major components (from Rango and Usachev[14], 1990 and NASA[15], 1984).

1.3 Groundwater Aquifers

Groundwater resources are broadly classified into four categories based on their recharge possibilities[16] their effect on climate change.

1. *Confined aquifers*: Aquifers that have a layer of impermeable or confined layer of rocks on upper portion of a permeable water containing formation.
2. *Unconfined aquifers*: aquifers that have confined or impervious layer of rocks only at the bottom and open on the top are known as unconfined or phreatic aquifers. Its upper portion is the water table. This is found where precipitation exceeds evapotranspiration and they are highly promising.
3. *Unconfined aquifers in semiarid and arid regions*: Another type of aquifer is unconfined aquifers in semiarid and arid regions where shifting annual balances between precipitation and evapotranspiration occurs. They are usually dry most of the period as recharge is very less.
4. *Coastal aquifers*: These fresh water aquifers are vulnerable to rising sea levels [17] and salt-water intrusion. They may loss water due to subsurface discharge.

Studies on the depletion of groundwater across the globe suggested that during the past 50 years, the exploitation of groundwater by human activities such as over pumping of groundwater for domestic and irrigation purposes along with climate change have created a prolonged effect, so that it expands from local issues of water scarcity to a prolonged effect on larger areas throughout the world[18]. This depletion of groundwater resources leads to rise in sea-level, again contributed to the destruction of remaining coastal aquifers. Threat to groundwater can be broadly classified in to two categories: 1) *Threats to quantity* and 2) *Threats to quality*. Threats to quantity are associated with over extraction of groundwater which includes overdraft, drawdown and subsidence. Overdraft is the result of faster rate of extraction than the recharge rate leading to permanent loss in storage capacity of aquifers. This leads to saline water intrusion in coastal region. Drawdown is the outcome of over pumping from groundwater sources that leads to temporarily lowering of water table in the localized area which later recovers and flourish after a short interval. Extreme case of over pumping results in subsidence of land as a result of decline in water table and reduced water pressure. Threats to quality include contamination of groundwater due to various pollutants, salt water intrusion, inland salinity etc.[19]

1.4 Groundwater Chemistry

Water chemistry plays an important role in the research activities related to fresh water as several chemical constituents of water have to be tested and treated in order to determine whether the water is suitable for consumption or not. Water contains many inorganic and organic matters. The inorganic substances are mineral in origin whereas organic being chemical substances of plant and animal origins made up of carbon structure. Usually subsurface geology determines the quality and composition of groundwater, as soil plays as a buffering agent also. The quality of groundwater is affected from climate, topology of watershed and geology. In addition to these factors, coastal aquifers are very much affected by salt water intrusion[20]. The phenomenon that governs chemistry of water includes acid-base reactions, solubility, oxidation-reduction reaction and complexation reactions[21].

Chemically water molecule consists of one atom of oxygen is bonded to two atoms of hydrogen at an angle of approximately 104.5^0. But in natural environment, water molecules does not occur in this purest form but also present hydrogen, hydroxyl, various ions and elements including carbonates, silicates etc.

Acid-Base Reaction

Acid-base reaction involves loss and acceptance of H^+ ions, water molecules itself act as both. In addition to this, natural water system have many chemical species act as acids by releasing H^+ ions where as others acts as bases by accepting H^+ ions. In natural water CO_2 is present in sufficient amount and it reacts with water to form carbonic acid (H_2CO_3).

$$CO_{2\,(g)} + H_2O \rightarrow H_2CO_{3\,(aq)} \ldots\ldots (1.1)$$

The first and the second dissociations of carbonic acid as follows

$$H_2CO_{3\,(aq)} \leftrightarrow HCO_3^- + H^+ \ldots\ldots (1.2)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \ldots\ldots (1.3)$$

The reaction (1.3) is less likely to occur in natural water. The CO_3^{2-} content in water is evolved from the weathering of carbonate bearing rocks such as limestone ($CaCO_{3\,(s)}$).

$$CaCO_{3\,(s)} \leftrightarrow Ca^{2+} + CO_3^{2-} \ldots\ldots (1.4)$$

Solubility

Solubility of a solute is its ability to dissolve in the solvent. It is the number of moles of a solute dissolves in one litre of solution. A salt can dissolve in a solvent until the solvent reach saturation or equilibrium. It is influenced by solubility product, the equilibrium constant. The chemical equation representing the dissolution of gypsum is

$CaSO_4\ 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$ ....(1.5)

and the corresponding solubility product expression is ,

$[Ca^{2+}]\ [SO_4^{2-}] = Ksp$ ....(1.6)

In water chemistry, determination of solubility and solubility products has a vital role in inorganic water chemistry [22].

Oxidation-Reduction Reaction

Oxidation-reduction or redox reaction plays significant role in water chemistry as it affects the mobility and availability of certain species including contaminants [23]. It is very important water quality parameter as biogeochemical processes of many major and trace elements are influenced by the redox reactions[24]. Redox reaction involves gaining or loosing of electrons. In oxidation reaction, oxidizing agent gains one electron and become reduced where as in a reduction reaction, reducing agent gets oxidized by losing one electron. Dissolved oxygen is the major oxidizing agent found in natural water. The redox reaction of iron is a best example of redox process in water.

Oxidation-reduction reaction of iron occur as follows

$Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ ....(1.7)

Complexation Reaction

All species in fresh water is considered as hydrated form where water molecules forms co-ordination sphere with metal ions (insoluble or soluble ligand formation). For example, in $M^{III}(H_2O)_6^{3+}$ the six water molecules form the first co-ordination sphere of the metal ion, M^{III}. Here, hydrated form is often represented as, $M^{3+}_{(aq)}$. There are mainly five types of complexation reaction involved in water chemistry- outer and inner sphere complexes, hydrolyis, inorganic complexes, surface complex formation and organic complexes.

Outer sphere complexation involves initial step in the formation of ion pairs where interactions between metal ions and other solute species in the co-ordinated water of the metal ion. Other solute species are maintained by forces of attraction such as coulombic that are held together by two opposite charged particles when they reach within a critical distance. This ion paring is depending up on factors like the nature of the oppositely charged ions, the ionic strength of the solution and ion charge. In inner sphere complexation reaction, interaction occurs between metal ions and other species in solution in which lone pairs of electrons are present. Here, there is transfer of at least one lone pair of electron is involved and they are termed as ligands. The hydrolysis of hydrated metal ions possesses the interaction between the hydrated metal ion and the hydroxyl ligand. Inorganic complexes are formed with inorganic ligands. The inorganic ligands in oxygenated freshwaters are OH^-, HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-} and F^-. HS^- and S^{2-} are seen under anoxic conditions. The properties of ligand and the nature of the metal ion involved are the factors that determine the stability of the complexes formed. Surface complex formation includes metal ions that form outer and inner sphere complexes with solid surfaces such as hydrous oxides of iron and manganese. Depending up on the strength of the ions, metal ions may be held in a diffused layer on the charged surface. Complexation reaction involving organic ligands forms organic complexes. Dissolved organic matters with humic substances provide more than one functional group for complex formation with a hydrated metal ion [25].

1.5 Natural Disasters and Groundwater Chemistry

Natural disasters like flood, drought, land slide, earthquake and tsunami have direct and wide range of impacts on the available quality and quantity of groundwater. They completely alter the chemical composition of water depending on the extend and intensity of the disaster. Climate change contributes to more extreme weather conditions that trigger these natural disasters. The immediate results of these disasters are environmental degradation, loss of life, disease, poverty etc. Another important matter of concern is sea-level rise as a result of global climate change. In the flood affected areas, flood water infiltrated to the groundwater aquifers and leads to high nutrient content in shallow groundwater sources than the deep aquifers. This may leads to retention on colloidal particles and phosphate precipitation in calcareous soils [26]. Highly soluble minerals gets dissolved resulting in increased concentration of sulphate, iron, manganese, calcium and magnesium.

Drought conditions drastically decreases the groundwater recharge, bring down the water table level[27]. This leads to concentrate the chemical pollutants in groundwater. The impact of earthquake on groundwater includes, change in the concentration of dissolved elements, increase in organic matter content and water level fluctuations. Coastal groundwater system is severely threatened by Tsunami waves occur as a result of displacement of large volume of water due to earth quake or volcanic eruption. Indian Ocean Tsunami took place in 26th December 2004 got shaken the coastal aquifers of south Asia. The related calamities include mass environmental destruction of coastal ecosystem including deterioration of groundwater quality. Seawater infiltrated through the shallow unsaturated zone entered to the shallow aquifers leading to vertical mixing both by forced and free convection. Extensive pumping of wells to remove seawater led to upcoming of the saltwater interface[28].

1.6 Tsunami and Coastal Groundwater Quality

The groundwater quality was severely deteriorated after the 26 December 2004 Indian Ocean Tsunami with respect to the pre-tsunamic situation of regions of Kerala. Water quality variation along the most severely affected Kollam, Alappuzha, Ernakulam coast of Kerala were carried out to determine the regional groundwater chemistry of the region. The study comprises of the critical analysis of the 42 groundwater resources, for a period of 12 months starting from the month of January - December 2005 and December 2008 from Alappad, Arattupuzha, Andhakaranazhy and Cherai coasts of Kerala with respect to the pre and post-tsunami situations [29]. The long term variation of water quality parameters of shallow and deep groundwater sources of the Arattupuzha coast over a period of time (2012 - 2016) is a commendable work in this region. The study found that dug well strata showed poor quality compared to deep bore wells [22]. Groundwater quality evaluation of Andhakaranazhy and Cherai coasts of Kerala, India was done over the period of time (2012 - 2017) on a temporal & spatial basis and the data obtained from the study were compared with available pre-tsunami (2001) and post-tsunami data [6]. Saline intrusion was most striking feature of the region but most of the groundwater sources were temporary hard in nature. Groundwater was slightly contaminated by iron, originated from the recent coastal alluvium deposits[6]. In this context, as a part of continuous monitoring of Alappad coastal segment water samples were collected from 15 dug wells and 3 bore wells from 2012 onwards and compared with the previous data[29] (Year 2001, 2005 and December 2008).

1.7 Review of Literature

There are a lot of literatures related to study of various aspects of groundwater quality and hydrogeochemistry from all around the world as the quality of water is of primary importance for the sustenance of life.
Study on hydrogeochemistry of groundwater is very important for ascertaining the evolutionary course and reason for deterioration of water quality in many parts of the world[30].

Hydrochemistry of Small Island is affected by seawater intrusion due over extraction of freshwater from the groundwater aquifer. From the analysis it is found that seawater intrusion, pH mediated leaching process from underlying rocks, minerals weathering process and dissolution of carbonate minerals are the controlling factors together with anthropogenic activities[31]. GIS is an effective tool for monitoring and mapping groundwater. Researchers attempted of mapping spatial distribution of various prominent water quality parameters[32,33].

Hitherto a comparative study reported on hydrogeochemistry of groundwater and sand pit lake waters indicates the sand extraction process is the major factor that altered the hydrochemistry of this system. Water collected from sand pit lakes show low pH and low content of dissolved substances. It is found that even though Al^{3+} and SO_4^{2-} are high compared natural waters, the sand pit lakes present lower concentrations of most chemical species than contained in mining pit lakes. This peculiar environment of sand pits is attributed to local geological features[34].

Hydrogeochemistry of groundwater and its suitability for water supply and irrigation in Jilin City, China shows that the evolution of groundwater is mainly due to rock-water interaction[35]. Various ionic interactions such as Ca^{2+}/Mg^{2+} ratio, $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$, Na+ versus Cl^- signifies carbonate dissolution of minerals like gypsum and halite.

Higher concentrations of NO_3^-, Cl^-, PO_4^{3-} and Fe are found in the lower part of the Ponnaiyar River Basin, Cuddalore District, South India[36]. The hydrogeochemistry of the area have $Ca–Mg^{2+}–Cl^{2+}$, $Na^+–Cl^-$, $Ca^{2+}–HCO_3^-$ and $Na^+–HCO_3^-$ water type.

Geochemical assessment of surface sediments from mangroves, seagrasses, dead coral and sandy beaches of the Andaman islands, India is reported to find the spacial distribution of heavy metals[37]. It is assumed that the contamination by cadmium may be due to tsunamigenic sediment deposition along with sources of anthropogenic origin like off-shore oil based power generation, waste from ships and anticorrosive paints applied on the boats and ships.

The hydrogeochemical and groundwater quality variation during pre and post tsunami situation of Pumpuhar to Portnova coastal region in Tamil Nadu is reported[38]. It is observed that the subsurface water is contaminated due to seawater mixing with fresh water. The saline water entered to the inland areas through river mouth and drained back after causing stagnation in the inland region lead to salt enrichment of the sediments due to evaporation and subsequent salt water accumulation. During rainy season these salts get leached to the groundwater aquifers leading to more complex hydrochemical processes.

Groundwater major ions of the coastal aquifers in Sadras watershed, in south India, is having identified two distinct groundwater types- fresh water and saline water[39]. But it is observed from ionic ratios, Mg^{2+}/Ca^{2+}, Cl^-/HCO_3^-, Ca^{2+}/Na^+ and TDS that the salinity of freshwater is increasing over time and clearly differentiate groundwater affected by saline water intrusion. High concentration of Na^+ in fresh water sources are attributed to cation exchange process.

In one of the studies of groundwater in Varanasi[40], assessed to find the hydrogeochemistry by collecting 68 water samples and found that about 81% of water samples have calcium–bicarbonate type water. High values of $HCO_3^-/(HCO_3^- + SO_4^{2-})$ ratio indicates hydrogeochemistry of groundwater is controlled by rock dominance mechanism and weathering of carbonic acid weathering is prominent in the study area.

Geographical Information System (GIS) is used to find the relationship between groundwater flow patterns and the distribution of hydrochemival facies. Two distict hydrochemical facies Ca^{2+}-Mg^{2+}-SO_4^{2-} -

Cl^- and Na^+-SO_4^{2-} -Cl^- water types were delineated using Inverse Distance Weighted (IDW). It is inferred that Ca^{2+}-Mg^{2+}-SO_4^2 -Cl^- water is evolved from mixing of two prominent water types, Ca^{2+}-Mg^{2+}-HCO_3^- and Na^+-SO_4^{2-} -Cl^- facies along with reverse cation exchange. The modification of groundwater chemistry occurs due to rock water interaction and anthropogenic activities [41].

A study on groundwater geochemistry and water quality of aquifers in Pondicherry, South India[42] found the water falls fresh to brackish category with dominant hydreochemical facies Na^+ – Cl^- and few aquifers falls in Ca^{2+} - HCO_3^-. Results of chemical characteristics of groundwater in Varaha River Basin, Visakhapatnam District, Andhra Pradesh found that the groundwater contains high concentrations of TDS, TH, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, NO_3^- and F^- exceeding the prescribed limit. This make water unsuitable for drinking[43].

The groundwater quality study conducted in Nagarcoil town is known to evaluate the hydrogeochemistry and find suitability for drinking and irrigation purposes[44]. It is seen that the concentration of various chemical constituents of water varies spatially and temporarily. The most dominant cation is sodium and the dominant anions are chloride followed by bicarbonate. In spite of this, most of the water sources could be used for drinking and agricultural purposes. But some of the samples are unfit for consumption due to high total hardness and TDS concentrations.

Study of hydrochemistry of groundwater is essential to check the suitability of water for drinking, irrigation and industrial purposes[45].

To assess the hydrogeochemistry of groundwater in Kottur Block, Tiruvarur, Tamilnadu, India by Thirunavukkarasu Ramkumar[46] and others find that the groundwater is saline and alkaline in nature with hydrochemical facies Na^+ - Cl^- and Ca^{2+} - Mg^{2+} - SO_4^{2-}.

In a study conducted on hydrochemistry and groundwater quality in the coastal South Chennai region, results of physico-chemical analysis reveals water is alkaline in nature. The hydrochemical facies and dominant cation and anion suggest the incidence of contamination of groundwater sources with seawater. Origin of high chloride concentration is due to infiltration of seawater, marine aerosols transported through wind, industrial and domestic wastes. The rock–water interaction is the major process controlling water chemistry whereas cation exchange controls the source of Na^+ in groundwater [47].

Geostatistical Modeling Techniques based on GIS is used for the identification of groundwater contamination sources in a hard-rock aquifer in Udaipur district, Rajasthan. Groundwater resources in the southern, eastern and northeast portions of the study area are contaminated by anthropogenic factors. Ion exchange process and weathering of rock is the major factors contributing dissolved salts in groundwater[48].

Statistical analysis of water quality parameters is very significant in groundwater studies to interpret large number of variables. In a study conducted in two municipal waste sources in Jabalpur, Urdana Nala and Moti Nala suggested that the sources are severely contaminated by sodium. The correlation analysis revealed strong correlations among pH, NO_3^- and SO_4^{2-} in Urdana Nala and Cu, TA, pH and TH in Moti Nala [49].

Physico-chemical parameters of groundwater in Avinashi-Tirupur region of Tamil Nadu is assessed to find the hydrochemistry of the region. From the study, it is found that the chloride concentration exceeds the most desired limit prescribed by WHO and IS standards and groundwater belongs to brackish type with promonant hydrochemical facies Ca^{2+} - HCO_3^- - Cl^- type [50].

Assessment of hydrochemistry of tropical spring in south India, suggested use of chemical fertilizers should be replaced by biofertilizers in the near catchment areas [51].

Groundwater quality study related to its suitability for irrigation and domestic purposes were conducted in Rajnagar Block, Birbhum District in West Bengal, India[52]. The groundwater is found to be slightly acidic to basic range and hardness is found to be moderately hard to very hard with sulphate concentration above the maximum permissible limit in seven of the post-monsoon analysis. Hill-Piper trilinear plot reveals bicarbonate dominant water type. Water Quality Indices (WQI) shows 75% of pre-monsoon samples fall in excellent to good drinking water quality which is declined to 56% during post- monsoon. Gibb's diagram expressed rock dominance in groundwater chemistry. Prominent irrigation water quality parameters such as sodium adsorption ratio (SAR), residual sodium carbonate (RSC) and soluble sodium percentage (SSP) were within the permissible limit.

Sea water intrusion also plays a major role in the hydrochemical processes. Hydrogeochemistry of groundwater in West Nile Delta was evaluated using major ions and found that the main factors controlling water chemistry is soil salinity and mineral content that reaches the groundwater aquifers through infiltration and seepage from irrigation canals[53].

Vegetation cover has a positive effect on soil structure as well as the subsurface water resources[54]. Salt affected soils were assessed to find the morphological, physico-chemical and mineralogy in semi-arid land after irrigation and cultivation. After converting the salt affected soil to crop land, desalinization and desodification of soil is attempted. This is indicated by decreased values of soil pH, EC, SAR, exchangeable Na, and ESP and increase in soluble Ca^{2+} and Mg^{2+} in analysed soil samples.

Kerala is one of the most thickly populated states in our country and many people depend on homestead open wells for domestic purposes. The groundwater problems in Kerala are due to the presence of excess salinity, iron, fluoride, hardness and coli forms [55].

Hydrogeochemical characteristics of groundwater in phreatic aquifers of Alleppey district were studied by Shaji *et al.,* (2009)[56]. The hydrogeochemistry of groundwater is controlled by mineralogy and marine aerosol. The mineralogy of coastal aquifers and the marine aerosol are playing significant role in the hydrogeochemistry of groundwater in the phreatic aquifer system.

Over extraction of groundwater results in water logging, land subsidence, lowering of water table, sea water intrusion in coastal aquifers and deterioration in water quality[57].

Critical evaluation of pre-tsunami water quality of Alappad coast was done by Achari and Jaison, (2011) [58] as a reference standard to make evaluations and judgments in the post tsunami situations. Hill –Piper Trilinear plots indicate that slight contamination by sea water has been prevalent in this area and this may be due to the geographical features of the place. The present work is an extension of studies on variations in water quality started just after the 26th December 2004 tsunami along Alappad coast in Kollam district of Kerala.

Boominathan *et al.,* (2012) [59] studied the physico-chemical and biological quality of groundwater throughout Kerala to assess its suitability for drinking as per BIS standards and to see the type of hydrochemical and spatial distribution of major ions.

Remote sensing and GIS techniques is used to prepare tsunami vulnerability map for Kollam district, Kerala which have one of the worst effected coastal segment by December 26, 2004 Indian Ocean Tsunami using thematic maps such as geomorphology, elevation, slope, distance from shoreline, and land use/land cover[60].

Water quality of shallow aquifers of Western Flanks of Southern Western Ghats, south India is assessed based on hydrogeochemistry and weathering of silicate bearing rock controls the water chemistry[61]. Ionic ratios such as Na^+/Cl^-, Ca^{2+}/Mg^{2+} and ion exchange process prevailed are evidence for the silicate weathering. Hydrochemical facies identified in the study area are $Ca^{2+}+Mg^{2+}/Cl^- + SO_4^{2-}$, $Na^+ - Cl^-$, $Na^+ - Ca^{2+} - Mg^{2+} - Cl^- - CO_3^-$ and mixed type.

A study on hydrogeochemistry of groundwater in Arattupuzha Village, Alappuzha, India reveals the water quality of the region exceeded the permissible limit recommended by IS 2012, WHO 2011 and USEPA 2014.

The hydrochemistry of the region is dominated by mixed nature of hydrochemical facies. Some groundwater aquifers are affected by saline water in many instances[62]. A study of drinking, irrigation and corrosion water quality of Andhakaranazhy and Cherai Coastal Regions of Kerala showed that major physico-chemical parameters like pH, temperature, total dissolved solids, alkalinity and hardness were affecting the quality of the groundwater and exhibits both scaling and corrosion nature[63]. Detailed study on the groundwater quality of coastal aquifers in Arattupuzha revealed that according to water quality index the quality of water is improving[64]. Studies on hydrochemical facies of Tsunami affected Alappad coast is done from the year 2005 to find the evolution behaviour of shallow groundwater sources[65]. Assessment of groundwater quality of Andhakaranazhy Coast in Alappuzha, Kerala indicates the rock dominance and evaporation are the controlling factors of hydrochemistry of groundwater. The hydrochemical facies is characterized by Ca^{2+}- Mg $^{2+}$-HCO_3^- with temporary hardness water type[66]. An assessment of physico-chemical parameters of shallow dug wells of Alappad coast, Kollam district, Kerala, is done continuously for a period of five years from 2012 to 2016 for hydrogeochemistry of the groundwater resources[67].

1.8 Significance of the Study

Present research work is specifically focussed to evaluate the hydrogeochemistry of shallow and deep groundwater sources along coastal segment, Alappad village in Kollam district, Kerala, India. Sample collection and analysis from the selected water sources in the study area are started in 2012 January and continued in each month till December 2012. In the subsequent years, 2013, 2014, 2015, 2016 & 2017 groundwater samples are collected in December month of each year and analysed for variability with respect to post tsunami water quality. This work is conducted in a region which was severely inundated by the 26th December 2004 Indian Ocean Tsunami. Post-tsunamic studies of the region were conducted in the year 2005 and December 2008. These post tsunami data along with the 2012 to 2017 data are compared with the available pre-tsunami data from for the year 2001. This will help in generating a database for over 16 years along the study area that will serve as a reference data for all further studies related to groundwater chemistry of coastal Kerala for many future purposes.

From the beginning of the post tsunamic study, one dug well (temple well at cheriyazekal), is selected as the control well (CW), as it maintained good quality water throughout the period of study even immediate months after tsunami. The sampling stations are classified into two strata based on depth profile.

1) Dug well strata (DW) which consist of 15 shallow groundwater sources (2m-3m depth)
2) Bore well strata (BW) which consist of 3 deep groundwater sources (150 m depth on average)

The groundwater sources chosen for the present study have conspicuous and specific utility as a potential fresh water source. Each one has a definite water regime with a representative nature and some degree of specific economic utility. Standard methods were systematically followed during sampling, preservation and analysis.

1.9 Objectives

The main objective of groundwater monitoring programme is to get information on water quality on a regional scale as well as to create a primary data bank of different chemical constituents in groundwater. The various objectives may be listed as follows;

1) To determine the physico-chemical parameters and to evaluate the groundwater chemistry of groundwater sources during every month of the year 2012.
2) To identify the drinking water quality of groundwater sources with respect to BIS (Bureau of Indian Standards, IS 10500:2012) and WHO (World Health Organization) standards during the year 2012.
3) To characterize the hydrochemical facies of groundwater to identify and differentiate the water type using Hill-Piper Trilinear plots.
4) To study the hydrogeochemistry of groundwater of the study area by using Gibb's plot and ionic ratios during the year 2012.
5) To check the incidence of seawater intrusion using Revell's co-efficient for each month in the year 2012.
6) To compute the monthly water quality index (WQI) of the groundwater by giving adequate weightage to significant water quality parameters.
7) To assess the irrigation water quality of the groundwater to find the suitability for irrigation purposes.
8) To evaluate various corrosion indices for studying the industrial utility of shallow and deep groundwater.

9) To analyze the trace element content of shallow and deep groundwater sources.

10) To classify the groundwater using designated best use (DBU) suggested by CPCB (Central Pollution Control Board, Government of India).

11) To evaluate the temporal variations of groundwater quality of the dug well sources in Alappad coast intermittently for a period from the year 2001 to 2017.

12) To evaluate the temporal variations of groundwater quality of the bore well sources in Alappad coast intermittently for a period from the year 2001 to 2017.

Attempts are made to structure the thesis in respect of the systemic approach followed to achieve the outcomes, with suitable interpretations.

1.10 Hypothesis

In the bound thesis, the hypothesis are scientifically tested, verified and critical constants are evaluated. The prominent findings are systematically presented:

i. Whether there is any significant difference between mean values of various parameters of groundwater sampled from the control well (CW) stratum in different months of the year 2012.

ii. Whether there is any significant difference between mean values of various parameters of groundwater sampled from dug well (DW) strata in different months of the year 2012.

iii. Whether there is any significant difference between mean values of various parameters of groundwater sampled from bore well (BW) strata in different months of the year 2012.

iv. Whether there is any significant difference between mean values of various parameters of groundwater sampled from control well (CW), dug well (DW) and bore well (BW) strata in different months of the year 2012.

v. Whether there is any significant difference between water quality index of groundwater sampled from dug well (DW) and bore well (BW) strata in the year 2012.

vi. Whether there is any significant difference between water quality index of groundwater sampled from the control well (CW), dug wells (DW) and bore wells (BW) in different months of the year 2012.

vii. Whether there is any significant difference in the mean values of the parameters of groundwater sampled from dug well (DW) strata over the years.

viii. Whether there is any significant difference in the mean values of the parameters of groundwater sampled from bore well (BW) strata over the years.

1.11 Structure of the Thesis

Chapter 1 comprises a concise **introduction** of the thesis, with reference to hydrogeochemical aspects of the study discussed. It briefly introduces the topic hydrogeochemistry, which is an interdisciplinary subject and its significance in the study of groundwater. The various factors affecting groundwater quality with special reference to problems related to coastal aquifers and studies reported in literature forms a major part of this chapter. The objectives of the research work, scope of the study and hypothesis are followed by a description of the overall structure of the thesis and references.

Chapter 2 is **materials and methods**. It mainly describes methodology followed for this research study. Location map of the study area with clear representation of sampling sites with source types are presented in the initial part of the chapter. This includes description of the study area with different thematic maps and delineation of groundwater potential zones in the study area constructed using GIS. It is followed by materials and methods, instrumentation, sampling protocols, standard operating procedures. Analytical chemistry and hydroanalytical methods followed for the estimation of each parameter is briefly described. This is followed by a detailed description of analytical methods such as hydrochemical facies by Hill-Piper trilinear plots, Gibbs plots and major ionic ratios, water quality index (WQI), irrigation water quality parameters and corrosion and scaling indices. This is followed by trace elemental analysis, TOC analysis and designated best use (DBU). Statistical tools used for the interpretation of water quality data are briefly explained. This chapter ends with the references.

Chapter 3 explains **hydrogeochemistry** of shallow and deep groundwater sources of the study area. It comprises the results and discussions on the monthly variations in physico-chemical water quality parameters of shallow and deep groundwater sources of the study area during year 2012. Monthly variation of individual parameters with graphical representation is followed by hydrochemical facies and water type study using Hill-Piper Trilinear plot and Gibb's plot. Other studies includes various ionic ratios in order to find the hydrogeochemical processes, ion-exchange processes and incidence of sea water intrusion prevail in the study area. This is followed by statistical analysis of the various physico-chemical parameters. The chapter ends with a conclusion followed by references.

Chapter 4 explains the **groundwater quality** of (groundwater sampled from dug wells and bore wells) the Alappad coast during the year 2012. It comprises the results and discussion on the monthly variation of water quality index (WQI), irrigation water quality evaluation and corrosion indices to find the suitability of water sources for domestic, irrigation and industrial purposes. This is followed by total organic carbon analysis, trace element study and classification of water sources based on designated best use (DBU). This chapter ends with statistical interpretation of the results with a conclusion followed by references.

Chapter 5 discusses the **temporal variation of major groundwater quality parameters groundwater sampled from dug wells** of the study area intermittently for the last 16 years (2001-2017). Major water quality parameters are discussed with respect to impact of coastal hazard occurred in 26th December 2004 as Indian Ocean Tsunami. Other interpretation methods includes evaluation of hydrochemical facies and water types using Hill-Piper Trilinear plot which is followed by water quality index (WQI), ionic ratio, irrigation quality and corrosion indices in view of pre and post tsunami situations. The chapter ends with statistical interpretation of the results with a conclusion followed by references.

Chapter 6 discusses the **temporal variation of major groundwater quality parameters of groundwater sampled from bore wells** of the study area intermittently for the last 16 years (2001-2017). Major water quality parameters of groundwater (deep bore well stations) form major part of the chapter. Interpretation of Hill-Piper Trilinear plot for hydrochemical facies, water quality index, ionic ratio, irrigation quality and corrosion indices are presented in related to pre and post tsunami situations. This chapter ends with statistical interpretation of the results with conclusion followed by references.

Chapter *7* is the **summary** of the research based on the major findings. The hypotheses proposed in the introduction chapter are tested by statistical methods and the conclusions are presented in this chapter followed by **Future scope of the study**.

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Chapter 2

MATERIALS AND METHODS

2.1 Introduction

Kerala is having a very undulating terrain including coastline of approximately 590 km with Arabian Sea in the west. The Western Ghats in the east nourishes this land with monsoon rain fall. Freshwater availability is the vital factor for the survival and ecological sustenance[1]. Every developmental activities in the state are directly related to the availability of fresh water sources both surface and groundwater. Surface water elsewhere is more subjected to pollution due to its exposure to the open surroundings. But unscientific exploitation of groundwater to meet the ever increasing demand leads to depletion of subsurface sources[2,3]. In this regard, the global concern of groundwater resources with respect to quality status is a prominent area of research.

2.2 Study Area

Alappad coast is situated in south west part of Kerala state in Kollam district between $9^0 2'57''$N to $9^0 7'15''$N latitude and $76^0 28'19''$E to $76^0 30'13''$E longitude is the focus of this research study. It is one of the most seriously affected regions by 26th December Indian Ocean Tsunami[4].

Geologically, this is a narrow strip of barrier island with Arabian sea in the west and the Thiruvananthapuram-Shoranur cannal (T-S cannal) is running north-south along the east side, separating from main land. There are sea walls along the entire coastal stretch. The maximum width of the study area is 450 meters in Alappad region and minimum width is 60 meters (approximately) in Srayikadu area (Figure 2.2 & 2.3).

The Alappad village consist of a total area of 7.38 sq. km in Oachira block, Karunagapally Thaluk. According to 2011 census[5], 5229 families are residing in Alappad, with a total human population of 21,655. This fragile coastal land has heavy black mineral sand deposit making this region economically and geologically significant. Rainfall, is the major groundwater recharge source in the study area and due to special features, of this coastal islets water directly flows towards the sea. Thickly populated by local inhabitants, and being a renowned tourist destination, demand for fresh water to meet the requirements leads to more stress to groundwater sources[6,7]. The study area is under continuous monitoring from the year 2005 onwards - the post tsunami period after the occurrence of 26th December, 2004 Indian Ocean Tsunami[4] (Figure 2.5).

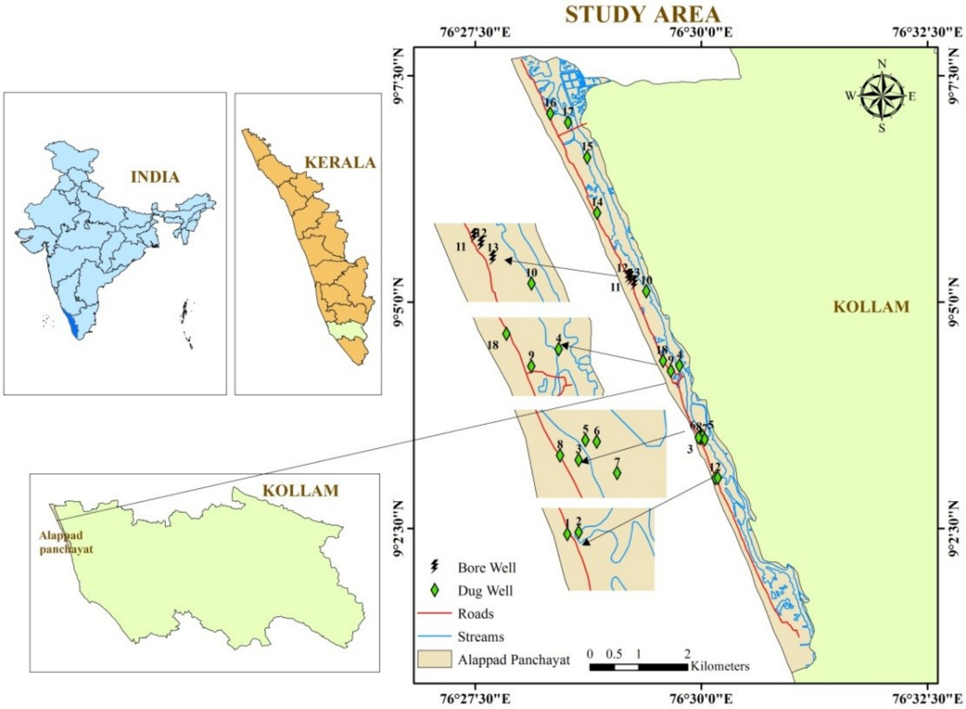


Figure 2.1: Location map of the study area with sampling sites

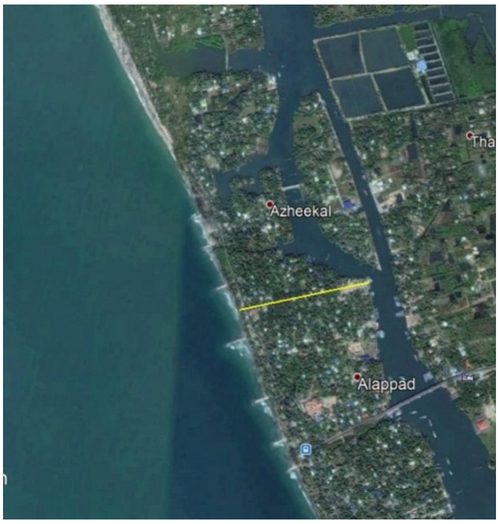


Figure 2.2: Satellite image of the widest region of the study area, Alappad coast, Kollam, Kerala, India

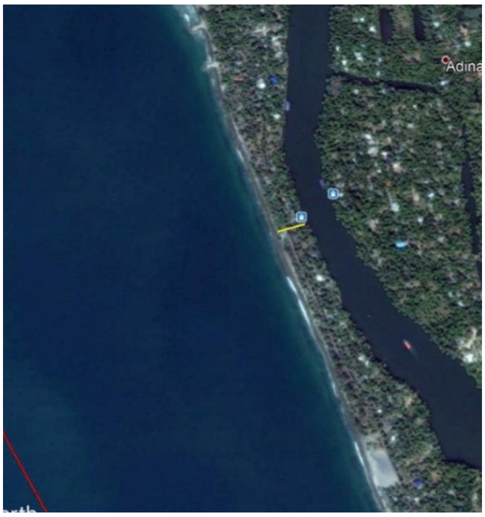
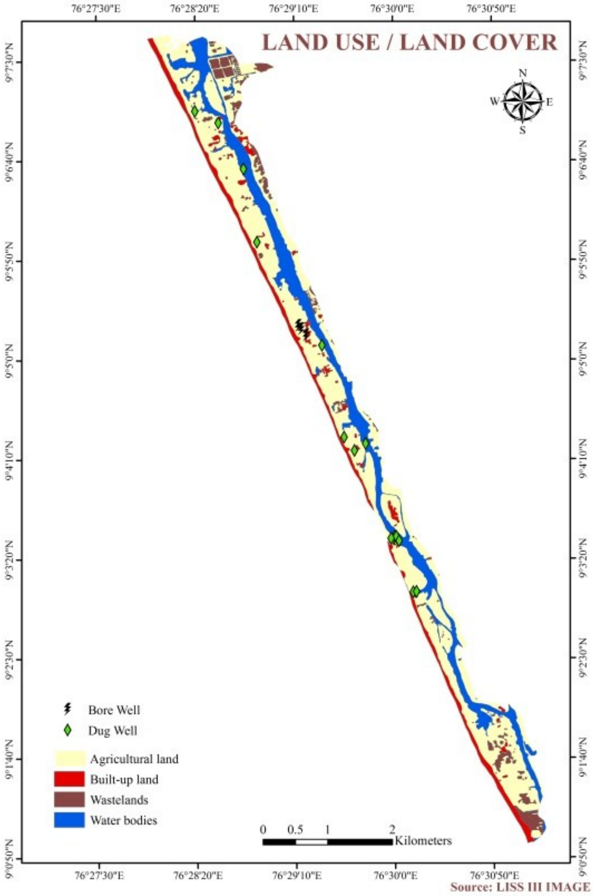


Figure 2.3: Satellite image of the narrow region of the study area, Alappad coast, Kollam, Kerala, India

2.2.1 Land Use-Land Cover

In order to plan, utilize and manage the land resources, the information about the available land cover and land use is very important. The land use – land cover maps gives complete and valuable evidence on spatial distribution of land cover[8].



Source: LISS III IMAGE

Figure 2.4: Land use-land cover of the study area, Alappad coast, Kollam, Kerala, India, during the year 2012

To find the land use pattern of the Alappad region during the study period, land use-land cover map have constructed using Geographic

Information System (GIS). This map is very useful in determining the land use pattern prevailing in the study area[2,3]. According to the land use-land cover map (Fig. 2.4) of the study area, about 53% of total area is agricultural land, 8.1% is built-up land, 34% of the study area comprises of water body and rest of 3.8% is considered as waste land (Table 2.1).

Table 2.1: Land use type of the study area, Alappad coast, Kollam, Kerala, India, during the year 2012.

No:	Land Use Type	Area (sq km)	Area (%)
1.	Agricultural land	16.24	53.5%
2.	Built-up land	2.46	8.1%
3.	Waste land	1.15	3.8%
4.	Water body	10.49	34.6%
	Total Area	30.34	100%

Figure 2.5: View of the entire coastal stretch of the study area, Alappad coast, Kollam, Kerala, India.

2.2.2 Geology and Geomorphology

The district is divided into three physiographical units: the coastal plains, the midlands and the eastern high land regions. The geology of the study area mainly consists of sand and silt (Figure 2.6). According to Department of Soil Survey and Soil Conservation, Kerala Bench mark soil in Alappad coast is identified as Neendakara. Mineral deposit consists of ilmenite and other placers and with the rich black sand deposit makes this region economically significant. The coastal region of the district is rich in mineral resources that mainly consists of bauxite, clay, chrysoberyl, graphite, heavy sand, mica and lime shell. The beach along Chavara-Neendakara is rich in ilmenite, rutile, zircon, monazite and garnet [9,10]. Exploration of these mineral resources is a matter of environmental concern.

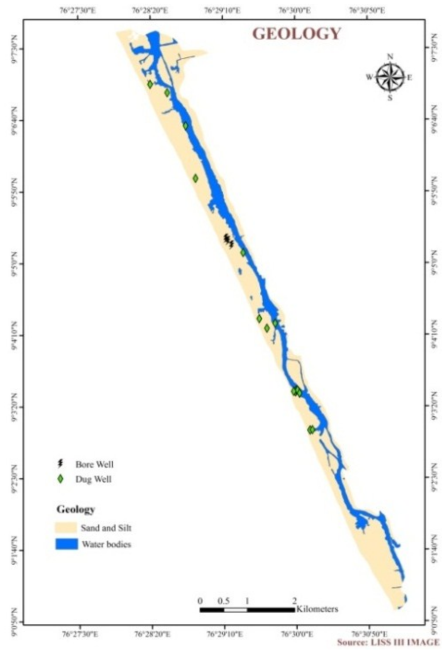


Figure 2.6: Geology of the study area, Alappad coast, Kollam, Kerala, India, during the period 2012.

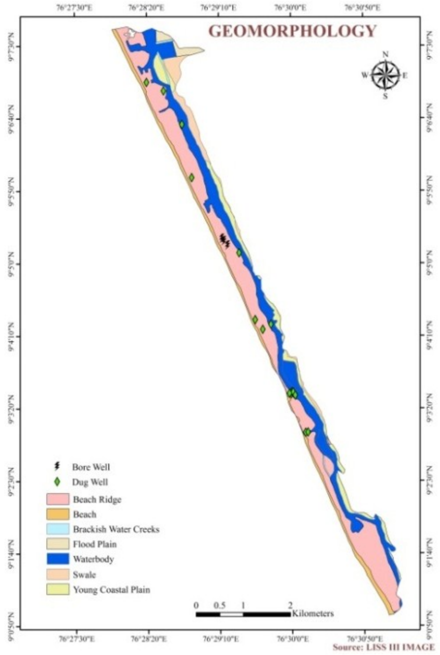


Figure 2.7: Geomorphology of the study area, Alappad coast, Kollam, Kerala, India, during the period 2012.

The geomorphology of the area includes beach, beach ridges, flood plains, swale and young coastal plains (Figure 2.7). In this region high grounds are all together absent. The elevation of narrow coastal plains range from 0 to 6 m, amsl [11]. This further confounds the fragile environment in this region (Figure 2.8 & 2.9). The land is at the sea level so even a small reflection of heavy wave can impose serious damage to this region. The soils of the coastal plains are very deep with sandy texture, with sand content ranging from 70-80% and clay up to 15%. The region possess high water table. But due to this sandy nature, water holding capacity is very low. The soil texture ranges from sand to loamy sand. The colour of the soil ranges from greyish brown to reddish brown and yellowish red colour.

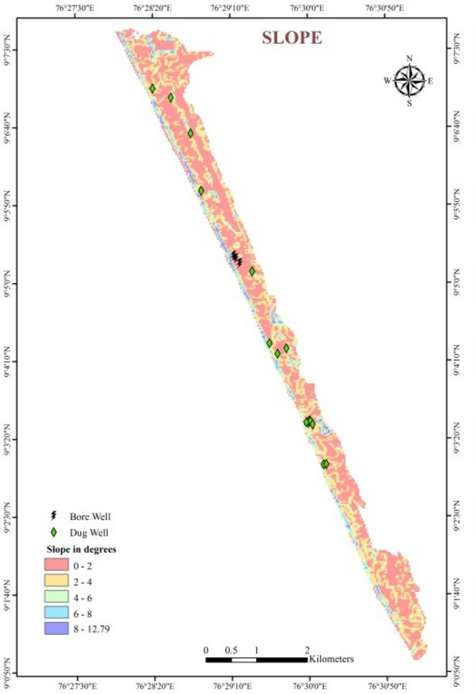


Figure 2.8: Slope of the study area, Alappad coast, Kollam, Kerala, India, during the period 2012.

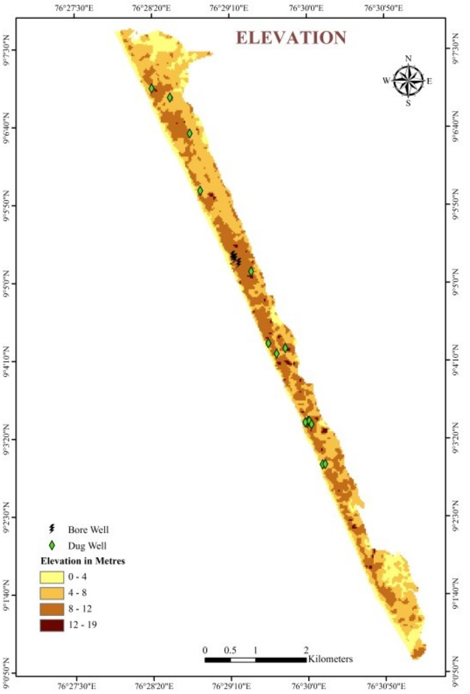
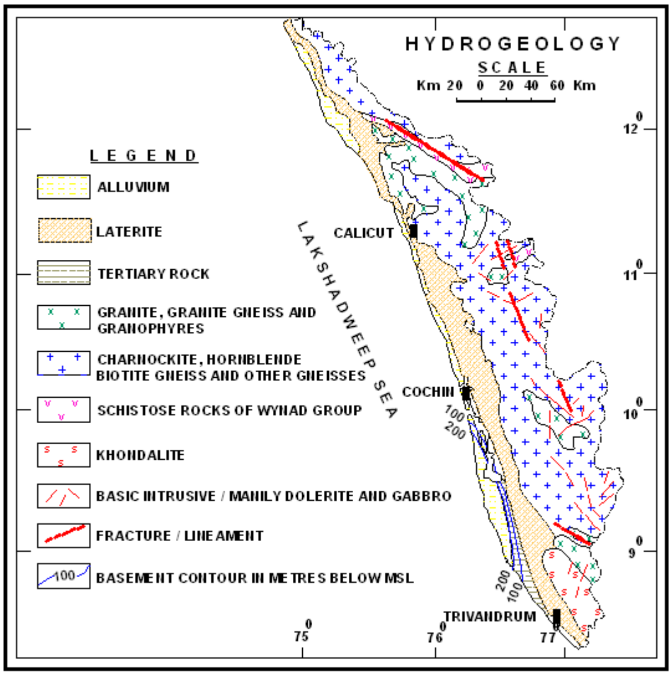


Figure 2.9: Elevation of the study area, Alappad coast, Kollam, Kerala, India, during the period 2012.

2.2.3 Hydrogeology

The hydrogeology of groundwater is controlled by physiographical as well as geological settings of the area (Figure 2.10). The Alappad region is a coastal plain, comprised of crystalline rock with coastal sand and alluvium[12]. The coastal alluvium has poor water holding capacity.



Source: CGWB Report, Faridabad

Figure 2.10: Hygrogeological map of Kerala

In Kerala, the landform features are evolved from Cenozoic belt. The basement of the geomorphology of the area is layed down by Precambrian crystalline (Khondalite, Charnockite & migmatite), then Neogene formation and Quaternary sediments (Padmalal, 2012). The subsurface geology of the coastal area of the district interpret that the Alappad region consists of three distinct tertiary sediment formations namely *Vaikom beds, Quilon beds* and *Warkali beds*[13]. *Vaikom bed* is the oldest and extensively developed aquifer and contains most of the potential groundwater zone. Above this, the *Quilon formation* is noticed. This is a thin and not continuous layer, occurred as a lower marine sequence of limestone which is fossiliferous in nature. It also represents sandy carbonaceous clays and is not very promising compared to other two formations. Above Vaikom bed is the youngest and most extensively developed aquifer known as *Warkali formation*. Generally this aquifer is fine to medium grained semi-consolidated unfossiliferous sediments.

2.2.4 Climate & Rainfall

The study area Alappad in the coastal plain of Kollam district, is having a tropical humid climate and is dominated by south-west monsoon. The annual average rainfall is 270 cm, received during south-west monsoon season starting from June to September and followed by north-east monsoon from October to December. In the year 2012, monsoon started in 1st June to 30th September and the rainfall is deficient compared to that expected during the first half of the rainy season. But in the second half, from August to September 2012, rainfall activity picked up and received excess rain of the year.

2.2.5 Depth to Water Level

Central Groundwater Board, in 2015[14] reported about the depth to water level of all the monitoring stations all over the country including Kerala based on the data obtained during the pre-monsoon period of the year 2013. It also gives the comparison the fluctuation in depth to water level in pre-monsoon 2012 and over a decade (2003 to 2013). From this report, it is found that the study area has a depth to water level of 2 to 5m during 2013. The analysis of fluctuation over the decade indicates that the change in water level is mostly restricted to rise or fall upto 2 m (Figure 2.11).

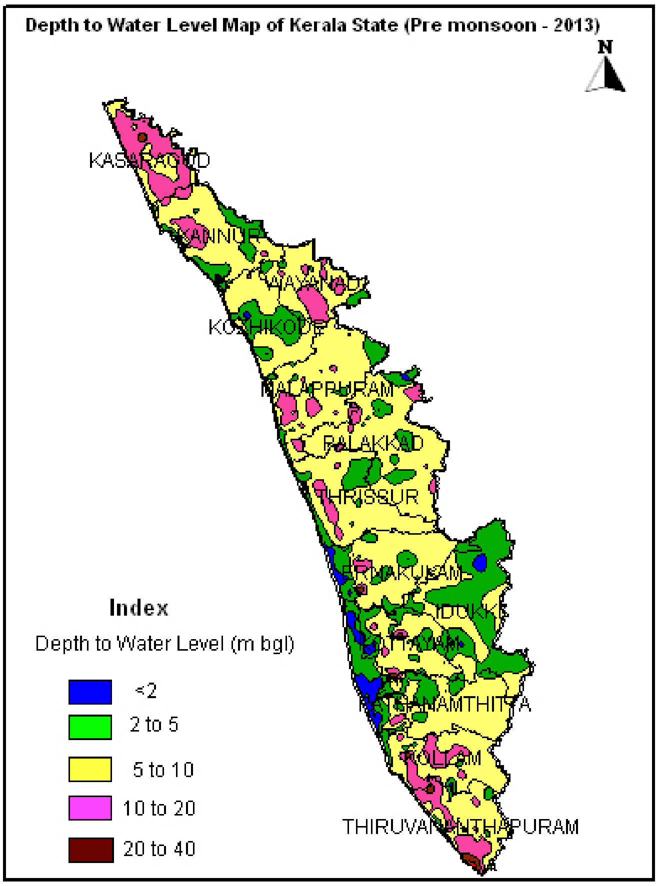


Figure 2.11: Depth to water level (m bgl) of Kerala, India during pre-monsoon 2013 (CGWB, Faridabad, 2015)

2.2.6 Groundwater potential zones

Groundwater potential zones for the study area are identified through the integration of various thematic maps such as slope, elevation, geomorphology, geology, land use-land cover using remote sensing and GIS techniques[15]. Groundwater potential zones are classified into very low, low, moderate, high and very high categories. Effective extraction of groundwater is possible based on the groundwater potential zones for the well-being of the settlers of Alappad. In the study area 84% of the wells (dug wells and bore wells) fall in moderate to high potential category (Figure 2.12).

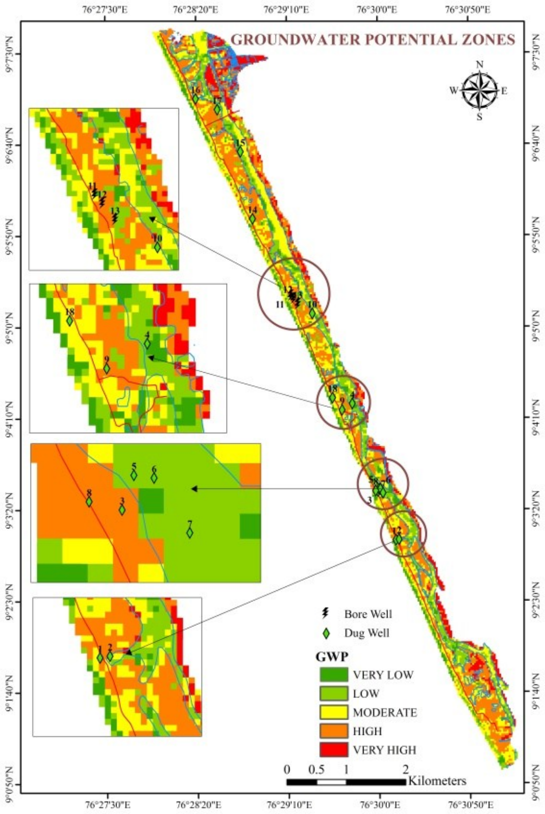


Figure 2.12: Groundwater potential zones of the Alappad coast, Kollam, Kerala, India, during the period 2012.

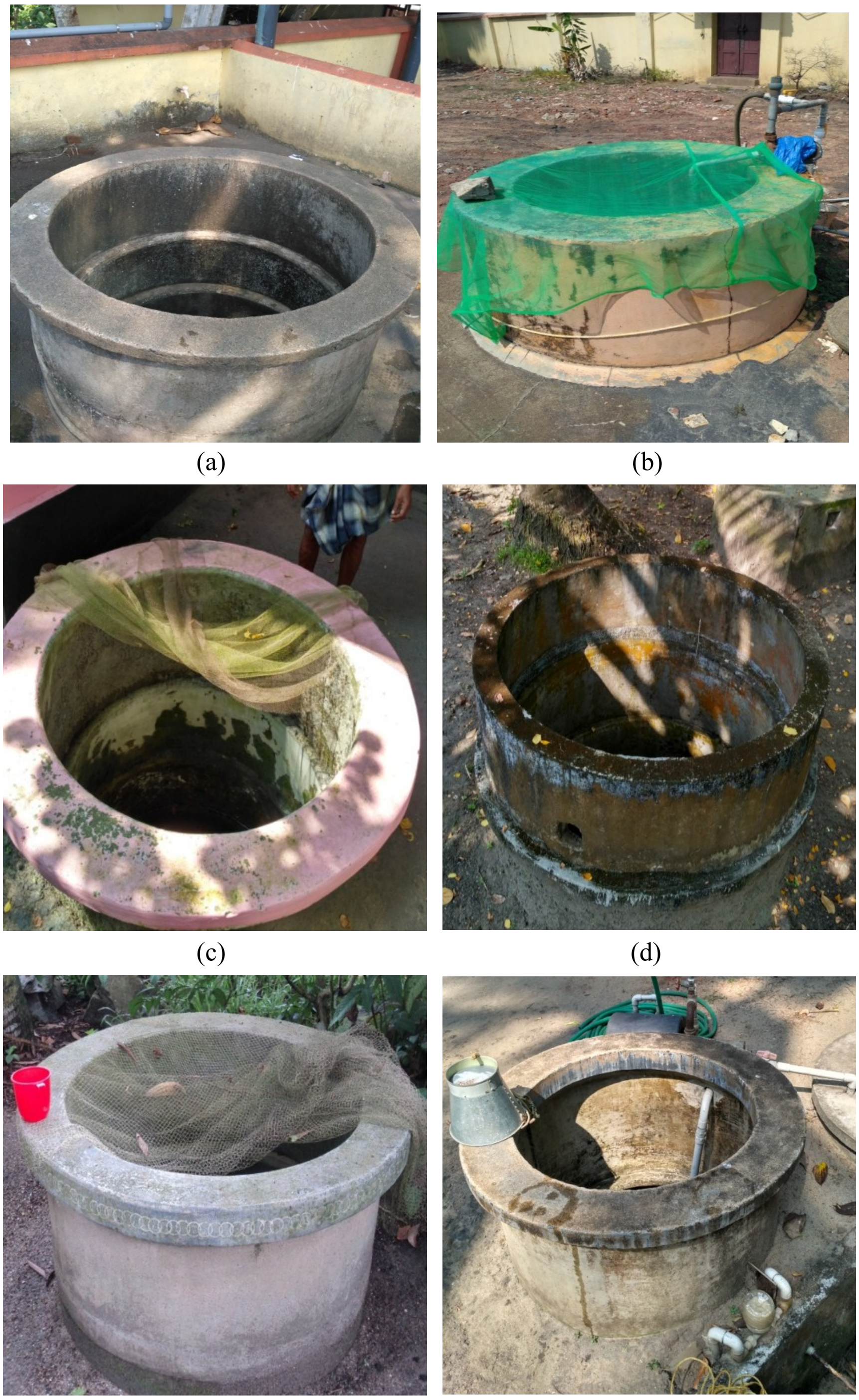
2.3 Sample Collection and Preservation

Groundwater samples are collected from 18 locations of Alappad coast consisting of fifteen (15) dug wells and three (3) bore wells (Figure 2.13). The samples were collected, preserved and analyzed as per the standard procedures recommended by APHA[16,17]. In addition to this a standard operating procedure (SOP) was prepared for the groundwater quality-monitoring program to avoid any deviation in analytical procedures.

Field trips were carried out towards the end of each month starting from January 2012. The parameters pH, Eh, alkalinity (AL), electrical conductivity (EC), dissolved oxygen (DO), biological oxygen demand (BOD), total dissolved solids (TDS), chloride (Cl^-), total hardness (TH), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium(Na^+), potassium (K^+), phosphate (PO_4^{3-}), sulphate(SO_4^{2-}), nitrate (NO_3^-) and total iron (t Fe) were chosen as regular parameters to be monitored because they are indicators of the degree of the saline water intrusion and evidence of hydrogeochemistry. Alkalinity, conductivity, chloride, hardness and sulphate are directly related to saline intrusion in the study area. Nitrate (NO_3^-) and phosphate (PO_4^{3-}) are the essential plant macro-nutrients and their ratio is indicative of sewage or external contamination. Solubility of iron is directly related to pH and DO and it is also significant in corrosion studies. DO and BOD are the most important parameters required to define the quality of a groundwater.

Plastic container of two liter (2 L) capacity are used to collect and store the groundwater samples. For analyzing dissolved oxygen (DO) and biological oxygen demand (BOD), standard BOD bottles were used after proper treatment. In order to collect water samples for the analysis of total iron, separate 100 mL borosil bottles are used. Samples are fixed with conc. HCl from the site itself and stored separately. Separate fresh plastic containers are used to collect water during each sampling and all the containers are washed thoroughly with fresh water and rinsed few times with distilled water prior to the water sample collection. For heavy metal analysis, 250 mL of water samples are collected in separate borosil bottles that are fixed with supra-pure nitric acid from the field itself.

Groundwater samples are collected in each month of year 2012, starting from January 2012 for 12 continuous months. Collected samples are labeled with station name and number. Time of the sampling and temperature of the water are recorded in situ in the field diary. The same collection strategy is followed in subsequent years with one sampling each year during December 2013, 2014, 2015, 2016 and 2017. These results were compared with previous data available for the period April 2001, year 2005 and December 2008. This has been done to evaluate temporal and spatial variation of the groundwater properties over a long period of time. Also to equate the pertinent findings being as the study is a part of a continuous research program initiated in the year 2005 as a post tsunami impact study with respect to groundwater quality of coastal region of Kerala [4,18].



(a) (b)

(c) (d)

(e) (f)


(g)


(h)


(i)


(j)


(k)


(l)

(m) (n)

(o)

Figure 2.13: Groundwater monitoring dug wells (a) DW1, (b)DW2, (c) DW3, (d) DW4, (e) DW5, (f) DW6, (g) DW7, (h) DW8, (i)DW9, (j) DW10, (k) DW14 (l) DW15, (m) DW16, (n) DW17, (o) DW18 in the Alappad coast, Kollam, Kerala, India.

2.4 Experimental Procedure

Analytical procedures followed for the groundwater analysis are done as per APHA precisely described as following:

2.4.1 pH (4500 H^+ B: APHA) : Electrometric Method

Apparatus: *pH meter*

Instrument used: SCIENTIFIC TECH; model ST2025 Digital pH meter.

Reagents and Solutions: 1) Buffer solution pH 4.60: 200mL acetic acid is mixed with 100 mL sodium hydroxide both of 1mol/L concentration and made up to 1000 mL with distilled water. 2) Buffer solution, pH 7.0 a) Potassium dihydrogen phosphate (9.078 g) is dissolved in water to make the volume up to 1L. b) Disodium hydrogen phosphate (11.88 g) is dissolved in water and made up to 1L. Buffer solution is made by mixing two parts of solution **a** and three parts of solution **b**. Buffer solution pH=9.0: Prepared by mixing 8.5 parts of 12.40g of boric acid and 100mL sodium hydroxide, (1 mol/L) dissolved in 1 L of distilled water and 1.5 parts of 0.1 mol/L of hydrochloric acid.

Calibration and measurement: The electrodes are allowed to stand in KCl solution of 3 mol/L, for several days before taking pH of water samples. For calibration of the instrument two standard buffer solutions are prepared. The pH reading is recorded after the value remained constant about 1 minute.

2.4.2 Eh (2580 B: APHA): Electrometric Method

Principle: Electrometric measurements are made by potentiometric determination of electron activity (or intensity) with an inert indicator electrode and a suitable reference electrode. Ideally, the indicator electrode will serve as either an electron donor or acceptor with respect to electroactive oxidized or reduced chemical species in solution. At redox equilibrium, the potential difference between the ideal indicator electrode and the reference electrode equals the redox potential of the system. However, inert indicator electrodes that behave ideally in all aqueous systems, particularly in natural waters, do not exist.

Apparatus: *pH or millivolt meter:* Use a pH meter or other type of high-impedance potentiometer capable of reading either pH or millivolts (mV).

Instrument used: SCIENTIFIC TECH; model ST2025 Digital pH meter.

Calibration and measurement: It is not possible to calibrate Eh electrodes over a range of redox potentials. Instead, standard solutions that exhibit both chemical stability and known redox potentials for specific indicator electrodes are used to check electrode response at the temperature of measurements.

2.4.3 Electrical conductivity (2510b: APHA): Conductivity method

Principle: Electrical conductivity of an aqueous solution is a measure of its ability to carry electric current depending up on the ions present in the solution, their total concentration, mobility and valence. It is also influenced by the temperature of solution at the time of measurement. Solutions containing most inorganic compounds are good conductors compared to organic compounds that fail to dissociate in aqueous solution resulting in conduct a current very poorly.

Apparatus: *Digital conductivity meter.*

Instrument Used: DELUX Conductivity Meter 601.

Reagents: Standard potassium chloride solution (0.0100M): 745.6 mg of anhydrous potassium chloride (AR) is dissolved in conductivity water and diluted to 1 litre at 25°C.

Calibration and measurement: The container and the cell are rinsed 2 to 3 times with the solution to be tested prior to record the measurement. Adjust the temperature of the samples to 25°C. To check the instrument, timely, the cell constant is measured using standard KCl solution.

2.4.4 Total Dissolved Solids (2540 C: APHA): Filtration Method

Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures. The results may not agree with the theoretical value for solids calculated from chemical analysis of sample. Approximate methods for correlating chemical analysis with dissolved solids are available. The filtrate from the total suspended solids determination is used for determination of total dissolved solids. Interferences: Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

Apparatus: a) Evaporating dishes: Dishes of 100-mL capacity made of porcelain materials, 90-mm diam. b) Desiccator: provided with a desiccant containing a color indicator of moisture concentration or an instrumental indicator. c) Drying oven: for operation at 180 ± 2°C. d) Analytical balance: capable of weighing to 0.1 mg. e) Magnetic stirrer with TFE stirring bar. f) Wide-bore pipets g) Suction flask: of sufficient capacity for sample size selected h) Filtration apparatus with reservoir and coarse (40- to 60-µm) fritted disk as filter support.

Instrument Used: LABLINE Laboraory Oven.

Procedure: *a.* Preparation of evaporating dish: The total dissolved solids were measured by heating clean dish to 180 ± 2°C in an oven for 1 hour. Store in desiccator until needed and weigh immediately before use. *b.* Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10 mL volume of reagent-grade water, allowing complete drainage between washings, and continued suction for about 3 minutes after filtration is completed. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness in a drying oven. Dry evaporated sample for at least 1 hour in an oven at 180 ± 2°C, cool in a desiccator to balance temperature and took the weight. Repeated drying cycle, cooling, desiccating, and weighing until a constant weight is obtained.

Calculation:

$$\text{total dissolved solids mg/L} = \frac{(\mathrm{A} - \mathrm{B}) \times 1000}{\text{sample volume (mL)}}$$

where, A = weight of dried residue + dish, mg, and B = weight of dish, mg.

2.4.5 Alkalinity (2320 B: APHA): Titration Method

Principle: Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points.

Apparatus: Pipettes- volumetric, Flasks-volumetric 250 mL, Burettes-borosilicate glass 50 mL.

Reagents: *a.* Sodium carbonate solution (approximately 0.05N)*:* Dry 3 to 5 g primary standard Na_2CO_3 at 250°C for 4 hours and kept in a desiccator to cool down to room temperature. Transfer 2.5 ± 0.2 g to a 1L standard flask and fill up to the mark with distilled water, and dissolve. Mix well to dissolve the reagent and this can be used no longer than a week. *b.* Standard hydrochloric acid (0.1N) *c.* Methyl Orange indicator solution.

Procedure: HCl solution is standardized using 0.05N Na_2CO_3 solution. 50 mL samples are taken in 250mL conical flask and two drops of methyl orange indicator solution is added. The sample is titrated against standard HCl, the end point was the color change from yellow to red.

Calculation:

$$\text{Alkalinity in mg } CaCO_3/L = \frac{\text{Volume of HCl} \times \text{Normality of HCl} \times 50{,}000}{\text{Volume of the sample}}$$

2.4.6 Total Hardness (2340 C: APHA): EDTA Titrimetric Method

Principle: Principle: Ethylenediaminetetraacetic acid and its sodium salts make a chelated soluble complex when added to a solution containing certain metal cations. If a small amount of a dye such as Eriochrome Black T is added to solution (aqueous) containing calcium and magnesium ions at a pH of 10.0 ± 0.1, the solution turns to wine red color. If titrant EDTA is added to this solution the calcium and magnesium will be complexed. When all of the magnesium and calcium get complexed the solution turns from wine red to blue color, marking the end point. To obtain a satisfactory end point sufficient magnesium ion must be present in solution. To ensure this a small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer to generate adequate magnesium. In order to minimise $CaCO_3$ precipitation a limit of 5 minutes is set for the duration of titration.

Apparatus: Pipettes- volumetric, Flasks-volumetric 250 mL, Burettes-borosilicate glass 50 mL.

Reagents: a) Buffer solution: Dissolve 16.9 g of ammonium chloride in 143 mL conc. Ammonium hydroxide, followed by 1.35 g of magnesium salt of EDTA. Dilute this mixture to 250 mL with distilled water. (If the magnesium salt of EDTA is not available, dissolve 1.179 g of disodium salt of EDTA and 780mg $MgSO_4 .7H_2O$ in 50mL distilled water and this solution is added to 16.9g NH_4Cl and 143 mL conc. NH_4OH. Dilute this solution to 250 mL with distilled water). b) Eriochrome Black-T indicator: 0.5 g dye and 100g NaCl are mixed to prepare a dry powder mixture. c) Standard EDTA titrant (0.01M): 3.723g disodium salt of EDTA (analytical grade) is weighed and dissolved in distilled water and made up to 1L.Store this solution in polyethylene or Pyrex bottles. Gradual deterioration of this solution is compensated by periodic re-standardization. d) Standard Calcium solution:

Weigh 1.000 g anhydrous CaCO3 powder of primary standard or special reagent low in heavy metals, alkalis, and magnesium into a 500-mL erlenmeyer flask. Place a funnel in the flask neck and add and carefully add 1:1 HCl (50%) little by little until all CaCO3 get dissolved. Add 200 mL distilled water and boiled to eject CO2. Allow the solution to cool and add a few drops of methyl red indicator. Adjust to the intermediate orange color by adding 3*N* NH4OH

Transfer it to standard flask (1 L) and dilute to 1000 mL with distilled water (1 mL = 1.00 mg CaCO3).

Procedure: Selected a sample volume that requires less than 15 mL of EDTA solution. Titration has to be completed within 5 minutes. Diluted lesser volumes of sample to 50 mL with distilled water. Added 1 to 2 mL buffer solution. Added a grain of the indicator powder and add the titrant slowly, with continuous stirring, until the last reddish tinge disappeared.

2.4.7 Calcium Hardness (3500 B: APHA): EDTA Titrimetric Method

Principle: When EDTA (ethylenediaminetetraacetic acid or its salts) is added to water containing both calcium and magnesium, it combines first with the calcium. Calcium can be determined directly, with EDTA, when the pH is made sufficiently high that the magnesium is largely precipitated as the hydroxide and an indicator is used that combines with calcium only. Several indicators give a color change when all of the calcium has been complexed by the EDTA at a pH of 12 to 13.

Apparatus: Pipettes- volumetric, Flasks-volumetric 250 mL, Burettes-borosilicate glass 50 mL.

Reagents: 1) Murexide indicator (ammonium purpurate) this indicator changes from pink to purple at the end point. Preparation: Mixing 200 mg murexide with 100g solid NaCl and grind it. After adding the indicator titrates immediately because murexide indicator is unstable under alkaline conditions. 2) Sodium hydroxide buffer (1N).

Procedure: 50 mL of the sample is pipetted out and added 2.0 mL of sodium hydroxide, mixed well to produce a pH of 12- 13. Add 0.1-0.2 g of the indicator and titrated immediately with EDTA. The end point is the color change from pink to purple.

Calculation:

$$\text{Hardness as mg } CaCO_3/L = \frac{\text{Strength of EDTA x Vol of EDTAx100x 1000}}{\text{mL of sample}}$$

2.4.8 Magnesium Hardness (3500 B: APHA): Calculation Method

Magnesium can be estimated as the difference between total hardness and calcium as $CaCO_3$. Mg/L = [total hardness (as mg $CaCO_3$/L) − calcium hardness (as mg $CaCO_3$/L)] × 0.243.

2.4.9 Sodium (3500 B: APHA): Flame Emission Photometric Method

Principle: Trace amounts of sodium can be determined by flame emission photometry at 589 nm. Sample is nebulized into a gas flame under carefully controlled, reproducible excitation conditions. The sodium resonant spectral line at 589 nm is isolated by interference filters or by light-dispersing devices such as prisms or gratings. Emission light intensity is measured by a phototube, photomultiplier, or photodiode. The light intensity at 589 nm is approximately proportional to the sodium concentration. Alignment of the wavelength dispersing device and wavelength readout may not be precise. The appropriate wavelength setting, which may be slightly more or less than 589 nm, can be determined from the maximum emission intensity when aspirating a sodium standard solution, and then used for emission measurements. The calibration curve may be linear but has a tendency to level off or even reverse at higher concentrations. Work in the linear to near-linear range.

Apparatus: a) Flame photometer or atomic absorption spectrometer operating in the flame emission mode. b) Glassware: Rinse all glassware with 1:15 HNO_3 followed by several portions of reagent water.

Instrument Used: ELICO CL378 Flame photometer

Reagents: All solutions are stored in plastic bottles to minimize sodium contamination. Small containers are used to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake all containers vigorously to wash accumulated salts from walls before pouring solution. *Reagent water:* All reagents and calibration standards are prepared using reagent water. Stock sodium solution: 2.542 g of NaCl dried at 140°C is dissolved and diluted to 1000 mL with water; 1.00 mL = 1.00 mg Na. Intermediate sodium solution: Dilute 10.00 mL stock sodium solution with water to 100.0 mL; 1.00 mL = 0.10 mg Na (1.00 mL = 100 µg Na). Used this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L. Standard sodium solution: Dilute 10.0 mL intermediate sodium solution with water to 100 mL; 1.00 mL = 10.0 µg Na. Use this solution to prepare calibration curve in sodium range of 0.1 to 1.0 mg/L.

Procedure: a) Instrument operation: Followed manufacturer's recommendations for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and oxidant gas pressures, correcting for interferences and flame background, rinsing of burner, igniting flame, and measuring emission intensity. b) Direct-intensity measurement: Prepared a blank and sodium calibration standards following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Determined emission intensity at 589 nm. Aspirated calibration standards and samples enough times to secure a reliable average reading for each. Constructed a calibration curve from the sodium standards. Determined sodium concentration of samples from the calibration curve.

Calculation:

For direct reference to the calibration curve: mg Na/L = (mg Na/L in portion) × D
Where, D = dilution ratio.

2.4.10 Potassium (3500 B: APHA): Flame Photometric Method

Principle: Trace amounts of potassium is determined in either a direct-reading or internal-standard type of flame photometer at a wavelength of 766.5 nm. Because much of the information pertaining to sodium applies equally to the potassium determination, carefully study the entire discussion dealing with the flame photometric determination of sodium before making a potassium determination. Interference: Interference in the internal-standard method may occur at sodium-to-potassium ratios of 5:1 or greater. Calcium may interfere if the calcium-to-potassium ratio is 10:1 or more. Magnesium begins to interfere when the magnesium-to-potassium ratio exceeds 100:1. Minimum detectable concentration: Potassium levels of approximately 0.1 mg/L can be determined.

Apparatus: a) Flame photometer (either direct-reading or internal-standard type) or atomic absorption spectrometer operating in the flame emission mode. b) Glassware: Rinse all glassware with 1:15 HNO_3 followed by several portions of reagent water.

Instrument Used: ELICO CL378 Flame photometer

Reagents: Stored all solutions in plastic bottles in order to minimize potassium pickup. Shaked each container thoroughly to dissolve accumulated salts from walls before pouring.

a) Reagent water: Used this water for preparing all reagents and calibration standards. b) Stock potassium solution: 1.907g of KCl dried at 110°C is dissolved and diluted to 1000 mL with reagent water (1 mL = 1.00 mg K). c) Intermediate potassium solution: Dilute 10.0 mL of stock potassium solution and make up to 100 mL (1.00 mL = 0.100 mg K). Calibration curve in potassium range of 1 to 10 mg/L is prepared using this solution. d) Standard potassium solution: Dilute 10.0 mL intermediate potassium solution with water to 100 mL (1.00 mL = 0.010 mg K). Use this solution to prepare calibration curve in potassium range of 0.1 to 1.0 mg/L.

Procedure: Instrument operation: Followed manufacturer's recommendation for selecting proper photocell and wavelength, adjusting slit width and sensitivity, appropriate fuel and oxidant gas pressures, and the steps for warm-up, correcting for interferences and flame background, rinsing of burner, igniting flame, and measuring emission intensity. Direct-intensity measurement: Prepared a blank and sodium calibration standards in stepped amounts. Determined emission intensity at 766.5 nm. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Construct calibration curve from the potassium standards. Determined potassium concentration of sample from the calibration curve.

Calculation:

For direct reference to the calibration curve: mg K/L = (mg K/L in portion) × D
Where, D = dilution ratio.

2.4.11 Chloride (4500 B: APHA): Argentometric method

Principle: In a neutral or slightly alkaline solution, potassium chromate can indicate the end point of the silver nitrate titration of chloride. Silver chloride is precipitated quantitatively before the red silver chromate is formed. Interference: Substances in amounts normally found in potable water will not interfere. Sulfide thiosulfate and sulfite interfere but can be removed by treatment with hydrogen peroxide, orthophosphate in excess of 25 mg/ L and iron in excess of 10 mg/ L interfere.

Apparatus: Pipettes- volumetric, Flasks-volumetric 250 mL, Burettes-borosilicate glass 50 mL. Reagents: 1) Potassium chromate indicator solution: 50 g of K_2CrO_4 is dissolved in a little distilled water. Added silver nitrate solution until a definite red precipitate is formed. After 12 hours, filtered and diluted to 1L with distilled water. 2) Standard silver nitrate solution, 0.0141N. Dissolved 2.395 g of $AgNO_3$ in distilled water and diluted to 1000 mL with distilled water. This is standardized against 0.0141 N NaCl. Stored in a brown bottle. 3) Standard sodium chloride (0.0141N): Dissolved 824.1 mg of NaCl dried at 140°C for 24 hours in chloride free water and dilute to 1000mL. 4) Special reagents for the removal of interference: a) Aluminiun hydroxide suspension: 125 g aluminium potassium sulfate is dissolved in 1L distilled water. Warmed to 60°C and slowly added 5 mL con. NH_4OH with stirring. Allowed to stand this solution for 1 hour. The precipitate is washed with through mixing and decantation of distilled water until free from chloride. b) Phenolphthalein indicator solution. c) Sodium hydroxide (1.0 N) d) Sulfuric acid (1N) e) Hydrogen peroxide (30%).

Procedure: Used a 100 mL sample or a suitable portion diluted to 100 mL for analysis. 3 mL $Al(OH)_2$ suspension is added to highly colored samples, mixed and let it settle. Filtered, washed and combined filtrate and washing. Added 1mL H_2O_2 and stirred for 1 minute if sulfide, thiosulfate or sulfite were present. The samples were titrated directly in the pH range 7 to 10 after adjusting pH range if necessary. 1mL K_2CrO_4 indicator solution is added and titrated with standard silver nitrate to a pinkish yellow end point. Standardize with silver nitrate titrant and used the reagent blank using distilled water.

Calculation:

Chloride, mg/L = strength of silver nitrate × mL of silver nitrate × 35,450/mL of sample.

2.4.12 Sulphate (4500 E: APHA): Turbidimetric method

Principle: Sulfate ion is precipitated in an acetic acid medium with barium chloride so as to form barium sulfate crystals. The sulfate concentration is determined by comparison of the reading with the standard curve.

Apparatus: a) Spectrophotometer, for use at 420 nm. b) Flasks, volumetric 250 mL. c) Magnetic stirrer.

Instrument Used: Varian model Cary 50 c UV

Reagents: 1) Buffer solution: Dissolved 30g magnesium chloride, sodium acetate, 1.0g potassium nitrate and 20 mL acetic acid in 500 mL distilled water and made up to 1L. 2) Barium chloride. 3) Standard sulfate solution: Dissolved 0.1479g anhydrous sodium sulfate in distilled water and diluted to 1000mL.

Procedure: 100 mL sample was taken in an Erlenmeyer flask. 20mL buffer solution is added and mixed by stirring apparatus. Add a pinch of barium chloride crystals and stirred for one minute. Readings are taken in a spectrophotometer at 420 nm.

2.4.13 Phosphate (4500 E: APHA): Ascorbic acid method

Principle: Ammonium molybdate and potassium antimonyl tartrate react in the acid medium with dilute solutions of orthophosphate to form a heteropoly acid- phosphomolybdic acid- that is reduced to intensely colored molybdenum blue by ascorbic acid. Interference: Arsenates react with the molybdate reagent to produce a blue color. Hexavalent chromium and nitrite interfere with the phosphate determination. Minimum detectable concentration is 10 μg/L.

Apparatus: Spectrophotometer with infra-red photo tube for use at 880 nm.

Instrument Used: Varian model Cary 50 c UV

Reagents: a) Sulfuric acid solution (5N): 70 mL conc. H_2SO_4 is diluted with distilled water to 500 mL. b) Potassium antimonyl tartrate solution:

Dissolved 1.3751g potassium antimonyl tartrate in 400 mL distilled water taken in a 500 mL volumetric flask and diluted to the volume. Store in a glass stoppered bottle. c) Ammonium molybdate solution: Dissolved 20 g ammonium molybdate tetra hydrate in 500 mL distilled water and stored in a plastic bottle at 4°C. d) Ascorbic acid (0.1M): 1.76 g ascorbic acid is dissolved in 100 mL distilled water. This solution is stable for about one week at 4°C. e) Combined reagent: 50 mL of 5N H_2SO_4, 5mL potassium antimonyl tartrate solution, 15mL ammonium molybdate solution and 30 mL ascorbic acid solution are mixed together to obtain 100 mL of combined reagent. After the addition each reagent mix the solution thoroughly. If turbidity is formed in the combined reagent, stirred it and let it stand for a few minutes until turbidity disappears. The reagent is stable for 4 hours. f) Stock phosphate solution: Dissolved 219.5g anhydrous potassium dihydrogen phosphate, KH_2PO_4 in distilled water and diluted to 1000 mL (1mL = 50micro gram PO_4-P). g) Standard phosphate solution: 50.0 mL stock phosphate solution is taken and diluted to 1000 mL with distilled water (1 mL= 2.50 micro gram).

Procedure: Treatment of the sample: Pipetted 50 mL of the water sample into an acid washed and oven dried 125 mL Erlenmeyer flask. Added one drop of phenolphthalein indicator and if color developmented, neutralize the pH with 5N H_2SO_4. 8 mL combined reagent is added and mixed well. Measured at wavelength 880 nm, 10 minutes after color development but not longer than 30 minutes. Used distilled water as blank with combined reagent.

2.4.14 Nitrate (4500 B: APHA): Ultraviolet Spectrophotometric Screening Method

Principle: Measurement of UV absorption at 220nm enables rapid determination of NO_3^-. Because dissolved organic matter also may absorb at 220 nm and NO_3^- does not absorb at 275 nm, a second measurement made at 275 nm may be used to correct the NO_3^- value. The extent of this empirical correction is related to the nature and concentration of organic matter and may vary from one water sample to another. The NO_3^- calibration curve follows Beer's law up to 11 mg N/L. Interference: Dissolved organic matter, surfactants, NO_2, and Cr^{6+} interfere. Various inorganic ions not normally found in natural water, such as chlorite and chlorate, may interfere. Inorganic substances can be compensated for by independent analysis of their concentrations and preparation of individual correction curves.

Apparatus: Spectrophotometer, used at 220 nm and 275 nm with matched silica cells of 1-cm or longer light path.

Instrument Used: Varian model Cary 50 c UV

Reagents: a) Nitrate-free water: Redistilled or distilled, deionized water of highest purity is used to prepare all solutions and dilutions. b) Stock nitrate solution: Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 hours and dissolved 0.7218 g in water, diluted to 1000 mL (1.00 mL 100 g NO_3^--N). Preserve with 2 mL $CHCl_3$/L. This solution is stable for at least 6 months. c) Intermediate nitrate solution: Diluted 100 mL stock nitrate solution to 1000 mL with water (1.00 mL 10.0 g NO_3^- -N). Preserved with 2 mL $CHCl_3$/L. This solution is stable for 6 months. d) Hydrochloric acid solution, (1N).

Procedure: Treatment of sample: To 50 mL clear sample (filtered if necessary), added 1 mL HCl solution and mixed thoroughly. Preparation of standard curve: Prepared NO_3^- calibration standards in the range 0 to 7 mg NO_3^- $^-$N/L by diluting to 50 mL the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, 7.00 . . . 35.0 mL. Treated NO_3^- standards in same manner as the samples.

Spectrophotometric measurement: Read absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Used a wavelength of 220 nm to obtain NO_3^- reading and a wavelength of 275 nm to determine interference due to dissolved organic matter.

Calculation: For samples and standards, subtract two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3^-. Construct a standard curve by plotting absorbance due to NO_3^- against NO_3^-- N concentration of standard. Using corrected sample absorbance, obtain sample concentrations directly from standard curve.

2.4.15 Total Iron (3500 B: APHA): Phenanthroline method

Principle: Iron is brought into solution, reduced to the ferrous state by boiling with acid and hydroxylamine, and treated with 1,10-phenanthroline at pH 3.2 to 3.3. Three molecules of phenanthroline chelate each atom of ferrous iron to form an orange-red complex. The colored solution obeys Beer's law at 510 nm; its intensity is independent of pH from 3 to 9. A pH between 2.9 and 3.5 insures rapid color development in the presence of an excess of phenanthroline. Interference: Strong oxidizing agents, cyanides nitrite, phosphates, chromium, zinc, cobalt, copper and other heavy metals precipitate phenanthroline. The initial boiling with acid converts poly phosphates to orthophosphates and removes cyanide and nitrite. Addition of excess hydroxylamine removes strong oxidizing agents. Addition of excess phenanthroline accounts for heavy metals. Minimum detectable concentration: 10 µg/L.

Apparatus: 1) Spectrophotometer, for use at 510nm providing a light path of 1 cm. 2) Acid washed glassware. Wash all glassware with concentrated HCl and rinse several times with distilled water. 3) Separating funnels 125 mL with ground glass or Teflon stopcocks and stoppers.

Instrument Used: Varian model Cary 50 c UV

Reagents: 1) Hydrochloric acid (concentrated); containing less than 0.00005% iron. 2) Hydroxylamine solution: Dissolved 10g NH_2OH HCl in 100 mL distilled water. 3) Ammonium acetate buffer solution: Dissolved 250 g ammonium acetate in 150 mL distilled water. Added 700mL conc. Glacial acetic acid. Prepared new reference standards for each buffer preparation. 4) Sodium acetate solution: Dissolved 200g $NaC_2H_3\,O_2.3H_2O$ in 800 mL distilled water. 5) Phenanthroline solution: Dissolved 100 mg 1, 10 phenanthroline monohydrate in 100 mL distilled water. Added 2 mL of conc. HCl. 6) Stock iron solution: Added slowly 20mL conc. H_2SO_4 to 50 mL distilled water and dissolve 1.404 g Fe $(NH_4)_2(SO_4)_2.6H_2O$. Added 0.1N $KMnO_4$ drop wise until a faint pink color persists and diluted to 1000 mL with iron free distilled water. Each 1mL of this solution contains 200 micro grams Fe. 7) Standard iron solution: Pipetted out 50 mL stock solution into a 1L volumetric flask and diluted to the mark with iron free distilled water. 1mL of this solution contains 10 micro grams Fe.

Procedure: Preparation of calibration curve: Pipetted out 10.0, 20.0, 30.0, 40.0 and 50.0 mL of standard iron solution into 100 mL volumetric flasks. The samples are mixed thoroughly and measured 50.0 mL of each into a 125 mL flask followed by addition of 2 mL conc. HCl and 1mL hydroxylamine solution. Added a few glass beads and heated to boiling until the volume was reduced to 15 to 20 mL. The solutions are allowed to cool down to room temperature and transferred to a100 mL standard flask. 10 mL ammonium acetate solution and 4mL phenanthroline solution were added and diluted to the mark with distilled water. Mixed and waited for 10 to 15 minutes for maximum color development before taking measurement.

2.4.16 Dissolved Oxygen (4500 C: APHA): Azide Modification Method

Level of dissolved oxygen in water body is depend upon the physical, chemical and biochemical activities in the water.

Principle: When divalent manganese solution is added to the water sample in a glass-stoppered bottle followed by strong alkali, an equivalent amount of the dispersed divalent manganous hydroxide precipitate is quickly oxidized by the dissolved oxygen to hydroxides of higher valency states. This oxidized manganese returns to the divalent state in the presence of iodide ions in an acidic solution, in the liberation of iodine equivalent to the original DO content. This iodine is titrated with a standard solution of thiosulfate. Azide modification of the iodometric method is used to remove the effect of interfering nitrite commonly found in biological effluents.

Sampling Procedure: Samples are collected very carefully in narrow-mouth glass-stoppered BOD bottles (300-mL capacity), without agitation. Let the water overflow three times the volume of the BOD bottle to avoid air bubbles. Add Winkler A followed by Winkler B and there after protect from sunlight.

Apparatus: 300 mL capacity of BOD bottles with ground glass stoppers.

Reagents: a) Winkler A- 480g $MnSO_4$.$4H_2O$ is dissolved in 1 L of distilled water. This solution must not give color in acidified KI. Winkler B-Dissolve 500 g NaOH or 700 g KOH and 135 g NaI or 150 g KI in 1L. Add 10 g NaN_3 in 40 mL distilled water and transfer to the alkaline KI solution. b) Conc. H_2SO_4. c) Starch solution: Add starch (2 g) to 100 mL of boiling distilled water and stir well to dissolve. Add 0.2 g salicylic acid. d) Sodium thiosulfate: Take 6.205 g $Na_2S_2O_3.5H_2O$ and dissolve in distilled water and add 0.4 g solid NaOH. Make this dilute solution to 1L and standardized against standard potassium dichromate solution. e) Standard potassium dichromate solution (0.025N): Dry $K_2Cr_2O_7$ at 103^0C for 2 hours and dissolve 1.226 g in 1 L. From this 20 mL dichromate solution is taken in a conical flask, add 10 mL of 5% KI followed by 3mL conc. H_2SO_2.Titrate against sodium thiosulphate and when the colour fades, add a few drops of starch. Disappearance of color marks the end point.

Procedure: Take water sample in a 300 ml BOD bottle very carefully to prevent air bubbles and add 1 mL of Winkler A, followed by Winkler B. The bottle is then glass stoppered and shaken well by placing the bottle upside down to mix the solution and allow the precipitation to settle. Add 1mL of conc. Sulfuric acid and shake well to dissolve the precipitation completely. The liberated iodine is estimated by titration against standard thiosulfate. Add one or two drops of starch indicator when color change to pale yellow. End point is the disappearance of blue color.

DO mg/L = strength of thiosulfate × volume of thiosulfate × 8×1000 × 298/ (300 × 300).

2.4.17 Biochemical Oxygen Demand (5210 B: APHA): Winkler's Iodometric Method

Principle: BOD determination is done using standard laboratory procedures by determining the relative oxygen requirements of wastewaters effluents and polluted waters. Identical test conditions should be provided to get the results in order to compare the BOD values. Keep the samples at or below $4^{o}C$ to minimize the change in oxygen demand between sampling and testing. Incubation should not exceed more than 24 hours after the sample is collected.

Apparatus: a) BOD bottles of 300 mL capacity with ground glass stoppers. Before use clean bottles using good detergent, rinsed thoroughly with distilled water for two to three times and drained well.

Incubator: Gambak Enterpries Madras 94

Reagents: 1) Distilled water: The distilled water should be free of copper chloramines chlorine, caustic alkalinity and organic material. 2) Phosphate buffer solution: Dissolved 8.5g of KH_2PO_4, 21.75g K_2HPO_4, 33.4g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl in about 500 mL distilled water and make it to 1L with distilled water. The pH of this buffer solution should be 7.2 without any adjustment. 3) Magnesium sulphate solution: Dissolved 22.5 g of $MgSO_4$. 7H $_2O$ in distilled water and diluted to 1L. 4) Calcium chloride solution: Dissolved 27.5g $CaCl_2$ (anhydrous) in distilled water and dilute to 1L. 5) Ferric chloride solution: Dissolved 0.25g $FeCl_3.6H_2O$ in distilled water and make it to 1L. 6) Seeding: Seeding is not needed for natural water samples. 7) Acid and alkali solutions (1N).

Procedure: Preparation of dilution water: Dilution water is prepared by saturating DO using aerators. Take desired volume of dilution water in a suitable container and add phosphate buffer, magnesium, calcium and iron salt solutions, 1mL each in 1liter. 1) Pretreatment of sample: Use 1N H_2SO_4 or NaOH to neutralize acidic or alkaline samples. 2) Dilution: Suitable amounts of sample taken into the BOD bottle using a large tip volumetric pipette and fill rest of the volume with dilution water leaving air bubbles. Two bottles should be prepared with same sample, one for incubation and the other for initial DO determination. Incubate one bottle for 5 days at 20°C, with water seal in the flared mouth of the bottle. 3) Glucose glutamic acid check: Being a bioassay procedure, the results from BOD test are influenced critically by the presence of toxic substances or the use of poor seeding material. Even distilled water is frequently contaminated with toxic substances like copper. Hence, it is necessary to check the quality of the dilution water, the effectiveness of the seed and the technique of the analyst using pure organic compounds having a known BOD. Prepare a standard solution with regent grade glucose and glutamic acid of 150 mg/L each dried at 103°C for 1 hour. Take 5 mL of this mixture and fill with dilution water to the neck of the BOD bottles. Found the initial DO and final DO after 5 days incubation at 20°C was evaluated.

$$BOD_5\,(mgO_2/L) = \text{(Initial DO-Final DO) x Dilution factor}$$

2.5 Hydrogeochemistry

2.5.1 Hill-Piper Trilinear Diagram

Hill-Piper Trilinear Plot is a diagrammatic representation of chemical composition of soil or water samples. It consist of two ternary diagrams, one for major cations (calcium, magnesium and sodium & potassium) and other for anions (carbonate, bicarbonate, chloride and sulphate). There is a diamond plot in the middle of both anion-cation triangles. The combined behaviour of relative percentage of cations and anions are reflected in the diamond plot [19,20] (Figure 2.14).

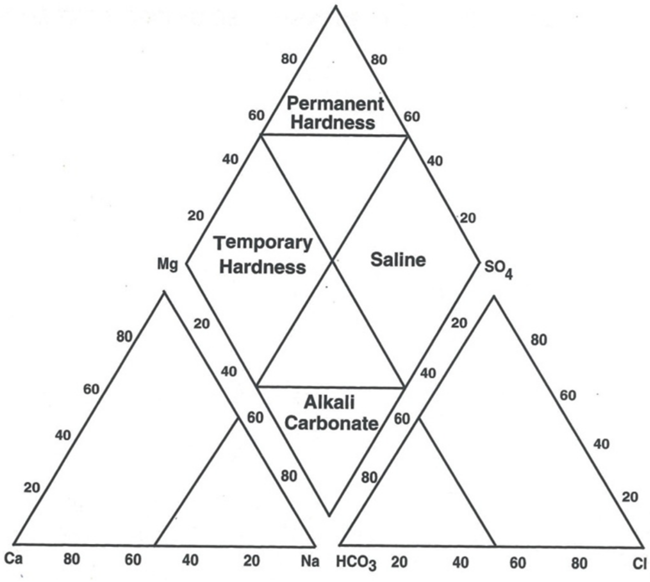


Figure 2.14: Water type classification as per diamond portion of Hill-Piper Trilinear diagram

According to Piper plot water belongs to four major water types based on their positions near the four corners of the diamond plot.

i) *Permanent hardness water type:* Water plott at top of the diamond plot is high in both [Ca^{2+} +Mg^{2+}] and [Cl^- +SO_4^{2-}]. These ions indicate character of permanent hardness.

ii) *Temporary hardness water type:* Water falls in the left corners of the diamond has character of temporary hardness. The prominent ions are [Ca^{2+} +Mg^{2+} and HCO_3^-.

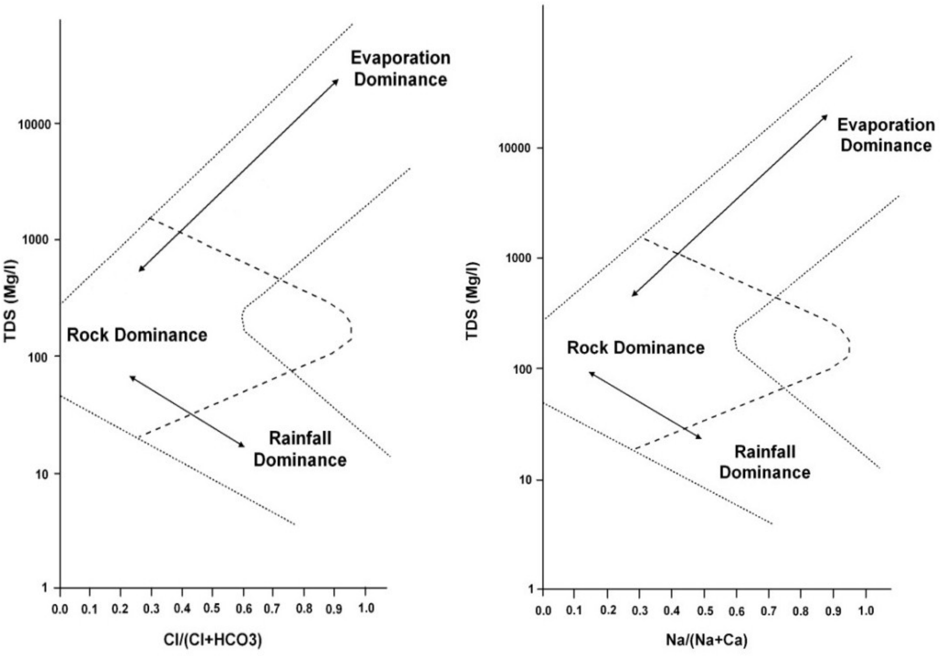
iii) *Alkali carbonate water type:* Water with plot data at lower corner of the diamond. This type of water type is derived from hardness due to soft ions like alkali carbonates [Na^+ +K^+] and [HCO_3^- + CO_3^{2-}] ions.

iv) *Saline water type:* Water with plot data at right corner of the diamond plot. In saline water type [Na^+ +K^+] and [Cl^- +SO_4^{2-}] ions are prominent.

The percentage composition of different anions and cations can be evaluated from the position of corresponding data points in the cation and anion triangles.

2.5.2 Gibb's Plot

Gibb's plot is a diagramatic representation that depicts the mechanisms that control the chemical composition of groundwater [21]. It is an effective tool to assess the influence of precipitation (rainfall), rock weathering and evaporation on groundwater system. In Gibb's plot of anion ratio, ($Cl/Cl+HCO_3$) is plotted against total dissolved solids (TDS) and in cation ratio (Na/Na+Ca) is plotted against TDS in mg/l [22,23]. From the position of the point in the diagram inferences can be drawn about the chemical nature of water (Figure 2.15). The primary mechanism that controls the chemistry of water is *rainfall dominance*. If the water is plotted on the rainfall dominant area on the Gibb's diagram, the water is characterised as low saline water, having dissolved salts furnished by precipitation. Quantity and quality of rainfall is the major factor influencing rainfall dominant water. The second mechanism that governs the chemistry of water is *rock dominance*. In water plotted on the rock dominant area, the salts are derived from dissociation of rock forming minerals. In rock dominant groundwater the amount and nature of dissolved salts depends up on the climate and relief of the region. Here calcium rich, medium saline fresh water is the end member. The third mechanism is the *evaporation dominance* where the end member is sodium rich, high saline water. Sea water mixing with fresh water increases the salinity and sodium concentration.



(a) (b)

Figure 2.15: Gibb's plot for a)anion and b) cation ratios

2.5.3 Ionic Ratios

In order to understand the ionic interactions that prevails in the study area that determine the hydrogeochemical processes and extend of sea water intrusion various ionic ratios are calculated [24,25]. The ratio of sodium to chloride (Na/Cl) is very useful in order to find the ion exchange process prevailed in the study area. The incidence of seawater is checked using the ratio of $Cl^-/(HCO_3^-+CO_3^{2-})$, also known as Revelle co-efficient [26]. Ca^{2+}/Mg^{2+} molar ratio ≤ 1 indicates dissolution of dolomite, whereas higher ratio may represent the contribution through weathering of carbonate and silicate bearing rocks. Plot of $Ca^{2+}+Mg^{2+}$ vs $HCO_3^-+SO_4^{2-}$ helps to identify the ion exchange process active in the study area as calcium and magnesium ions in groundwater are attributed to leaching from limestone, dolomites and gypsum bearing rocks. The plot for (Na^++K^+) and total cations gives insight into the silicate weathering involved in the geochemistry of the study area. The plot for total cations to $Ca^{2+}+Mg^{2+}$ is used to understand the geological origin of calcium and magnesium in the groundwater [27,28].

2.6 Statistical Analysis

The statistical analysis of water quality data is done using t-test, correlation matrix and ANOVA.

2.6.1 t-test

For each parameter limited set of data is obtained by representative sampling. In statistics mean and standard deviation are determined. Student’s t-test is a statistical tool used most frequently to express confidence intervals and to compare results from different experiments. The confidence interval is an expression stating that the true mean, μ, is likely to lie within a certain distance from the measured mean, $\bar{x}$. The confidence interval of μ is given by

$$\mu = \bar{x} \pm t\sigma/\sqrt{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.1)$$

σ is the measured standard deviation, n is the number of observations, and t is Student's t, taken from t- table

2.6.2 Correlation Study

Statistical analyses are very useful in groundwater research in order to explore the interconnections between parameters (variables) in a large sized data set. The most commonly used statistical method involving these stochastic connections is the Pearson's correlation matrix. In this, the correlation co-efficient 'r' shows the strength and direction of the linear relationship between parameters. This could be positive or negative depending on the direction of relationship. If both the parameters under investigation tend to increase or decrease together, the correlation coefficient 'r' is positive. If one parameter increases as the other decreases, r is negative. The correlation co-efficient 'r' is calculated using the following formula

$$r_{(x,y)} = \frac{\sigma_{(x,y)}}{\sigma_x \sigma_y}$$

Where σ_x, σ_y are the standard deviation of variables X and Y; $\sigma_{(x,y)}$ is the co-variance.

In correlation analysis, $-1 \leq r_{(x,y)} \leq +1$ and if the relationship between variables X and Y is positive, then $r_{(x,y)} > 0$ where as if this relationship is negative, $r_{(x,y)} < 0$. If $r_{(x,y)}$ is exactly equal to ±1, then there exist a linear fundamental relation between the two given variables. Any variable's correlation to itself is 1. If $r_{(x,y)}$is zero or near to zero (both positive and negative values), the two variables are said to be uncorrelated but it doesn't mean they are independent. If two variables are independent then correlation coefficient, $r_{(x,y)}$= 0 [29]. In this study SPSS software is used in correlation matrix calculation. The correlation co-efficient r > 0.71 are considered as strong linear relation between parameters under consideration [30].

2.6.3 Analysis of Variance (ANOVA)

The collected data for the study were compiled and statistically analysed using Two Factor and Three Factor Analysis of Variance Technique to draw conclusions. The mathematical model employed for the two factor ANOVA is

$$X_{ij}=\mu+\alpha_i+\beta_j+\epsilon_{ij}$$

Where, X_{ij} -is the observation on the j^th^ parameter on i^th^ strata, μ- overall effect, αi-i^th^ strata effect, βj- j^th^ parameter effect and ϵ_{ij}- Random error
The model used in the construction of Three Factor ANOVA is

$$X_{ijk}= \mu+\alpha_i+\beta_j+\gamma_k+\epsilon_{ij}$$

Where, X_{ij} -is the observation on the i^{th} strata of the j^{th} month for the k^{th} parameter, μ- overall effect, αi-i^{th} strata effect, βj- j^{th} time effect, γ_k –k^{th} parameter effect and ϵ_{ij}- Random error

Wherever the effects were found to be significant, Least Significant Difference (LSD) was calculated at 5% level of significance to separate out the significant treatment effect. Results of the analysis of the data are given below

Abbreviations used in the ANOVA table and their expansions are given below

ss - sum of squares

df - degrees of freedom

ms - mean square

F - variance ratio

p-value and the level of significance in ANOVA analysis are given in Table 2.2

Table 2.2: p-value and the level of significance in ANOVA analysis

p-value	**Level of significance**
p>0.05	No significant difference at 5% level of significance
p<0.05	Significant difference exist at 5% level of significance
p<0.01	Significant difference exist at 1% level of significance
p<0.001	Significant difference exist at 0.1% level of significance

2.7 Water Quality Index

The water quality index is a mathematical tool [31] to convert quantitative measurements of water quality data into a single number. It is very useful for assessing the suitability of water for human consumption and effective method to communicate the overall water quality from a complex multiple parameters to a dimensionless single number. Hence this method is readily understandable to public as well as policy makers [32-34]. Water quality index can be calculated using several methods such as National Sanitation Foundation Water Quality Index (NSFWQI), Canadian Council of Ministries of the Environment Water Quality Index (CCMEWQI), Oregon Water Quality Index (OWQI) and Weighted Arithmetic Water Quality

Index Method (WAWQI) [35]. In this present study water quality index is calculated using *weighted arithmetic water quality index method* [2,36,37] with 11 prominent water quality parameters - pH, EC, total dissolved solids (TDS), total hardness (TH), Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, Cl^{-} & SO_4^{2-}. This method comprises following steps

The overall quality of water can be assessed by using following the equation given below,

$$WQI = WiQi/Wi \qquad (2.1)$$

$$W_i = K/S_i. \qquad (2.2)$$

Where W_i is the relative unit weight. K= proportionality constant, for the sake of simplicity K is taken as 1.

S_i= standard permissible value of particular parameter.

$$Qi = 100[V_o - V_i] / [V_s - V_i] \qquad (2.3)$$

Qi is the quality rating for the ith water quality parameters (i= 1, 2, 3, …., N)

V_o= observed value or mean of the observed values of any parameter.

V_i= ideal value of that particular parameter, zero for all parameters except pH & DO. V_i for pH= 7 & for DO= 14.6 mg/l.

V_s= Standard permissible value of particular parameter, determined by WHO.

The overall water quality of any water body is assessed by using following gradation Table 2.3.

Table 2.3: Classification of groundwater on the basis of Water Quality Index, WQI (Brown et al. 1972).

WQI Level	Water Quality	Grading
0-25	Excellent	A
25-50	Good	B
51-75	Poor	C
76-100	Very Poor	D
>100	Unfit for Drinking Purpose	E

In other words

a) $0 < WQI < 100$ Fit for human use

b) $0 > WQI > 100$ Unfit for drinking use

2.8 Irrigation Quality Evaluation

Soil characters both physical and chemical are affected directly by the quality of irrigation water which in turn affects the growth and development of flora population. The poor quality irrigation water may leads to the accumulation of ions and trace elements in unacceptable concentration in the soil and water affecting soil fertility[38]. For the proper management and effective utilization of the groundwater resources it is necessary to consider the irrigation water quality to assess the nature of water as different crops have different requirements $_6$.

The irrigation quality can be evaluated by various calculated parameters [39] such as sodium adsorption ratio (SAR), sodium percentage (Na %), permeability index (PI), Kelley's index (KI), magnesium adsorption ratio (MAR) and residual sodium carbonate (RSC). Concentrations of various ions obtained from chemical analysis are converted to milli equivalents per litre (meq/L) and the different parameters are calculated as per the equations given below.

- **Sodium Adsorption Ratio (SAR)** [40,41].

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}} \quad \text{...(2.4)}$$

- **Sodium Percent (Na %)** [42,43].

$$Na\% = \frac{Na^{+} \text{ x } 100}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \quad \text{...(2.5)}$$

- **Permeability Index (PI)** [44,45].

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{Ca^{2+} + Mg^{2+} + Na^{+}} \text{ x } 100 \quad \text{..(2.6)}$$

- **Kelley's Index (KI)** [46-48].

$$KI = \frac{Na^{+}}{\left(Ca^{2+} + Mg^{2+}\right)} \quad \text{...(2.7)}$$

- **Magnesium Adsorption Ratio (MAR)** [49]

$$MAR = \frac{Mg^{2+} \text{ x } 100}{Ca^{2+} + Mg^{2+}} \quad \text{..(2.8)}$$

- **Residual Sodium Carbonate (RSC)** [50]

$$RSC = (CO_3^{2-} + HCO_3^{-}) - \left(Ca^{2+} + Mg^{2+}\right) \quad \text{.....................................(2.9)}$$

The following tables give the classification of water based on these parameters (Table 2.4).

In addition to these irrigation water quality parameters chloroalkalinity indices, CAI 1 & CAI 2 are evaluated to find the ion-exchange between groundwater and the host aquifer [51,52].

$$\text{CAI 1} = \frac{Cl^{-} - (Na^{+} + K^{+})}{Cl^{-}}$$

$$\text{CAI 2} = \frac{Cl^{-} - (Na^{+} + K^{+})}{(SO_4^{2-} + HCO_3^{-} + CO_3^{2-} + NO_3^{-})}$$

Table 2.4: Classification of groundwater on the basis of irrigation water quality parameters

SI No:	Parameters	Unit	Range	Remarks
1	SAR	meq/l	< 10	Excellent
			10 – 18	Good
			19 – 26	Doubtful
			> 26	Unsuitable
2	Na%	%	<20	Excellent
			20-40	Good
			40-60	Permissible
			60-80	Doubtful
			>80	Unsuitable
3	PI	%	> 75	Suitable for irrigation
			25-75%	Suitable for irrigation
			0-25%	Unsuitable for irrigation
4	KI		< 1	Suitable for irrigation
			> 1	Indicates an excess level of sodium
5	MAR	meq/l	< 50%	Suitable for irrigation
			> 50%	Adversely affect soil
6	RSC	meq/l	< 1.25	Suitable
			1.25- 2.50	Marginally suitable
			> 2.50	Unsuitable

2.8.1 USSL Diagram

The USSL diagram was developed by United States Salinity Laboratory Staff under United States Department of Agriculture [53] (1954). This diagram is widely accepted and used in water quality studies related to irrigation purposes [54,55]. In this plot Sodium Adsorption Ratios (SAR) are plotted along y axis and Electrical Conductivity (EC) on X-axis. According to the combined effect of these two prominent irrigation water quality parameters, the plot is subdivided into 16 sections with varying degrees of salinity and sodium hazards (Figure 2.16). The salinity hazard divides the plot in 250, 750 and 2250 µmhos, resulting in four categories (Table 2.5)

Table 2.5: Classification of groundwater on the basis of salinity hazard

	EC (µmho)	Inference	Class
1	<250 µmho	Low-salinity water	C1
2	250-750 µmho	Medium-salinity water	C2
3	750-2250 µmho	High- salinity water	C3
4	>2250 µmho	Very high- salinity	C4

The sodium hazard is a function of both SAR and salinity. The dividing lines are

$$S = 43.85 - 8.87 \log C$$
$$S = 31.31 - 6.66 \log C$$
$$S = 18.87 - 4.44 \log C$$

Where S is the SAR and C is the conductivity.

The resulting four categories are given in the Table 2.6

Table 2.6: Classification of groundwater on the basis of sodium hazard

	Class	Inference
1	S1	Low-sodium water
2	S2	Medium-sodium water
3	S3	High-sodium water
4	S4	Very high-sodium water

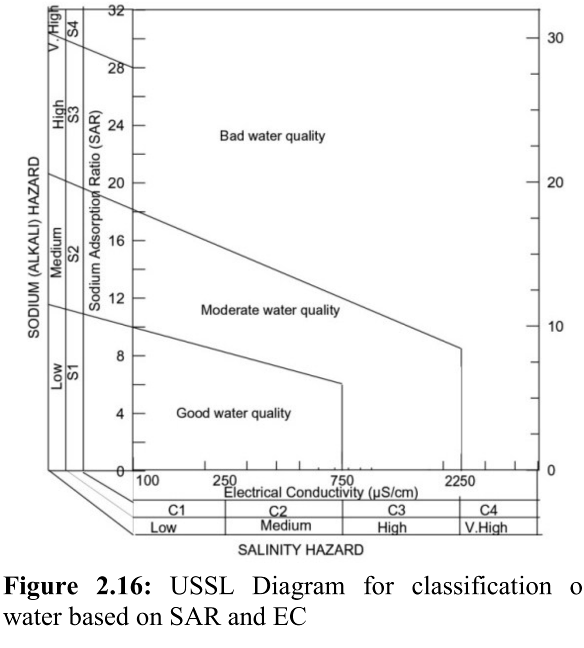


Figure 2.16: USSL Diagram for classification of water based on SAR and EC

2.8.2 Wilcox diagram

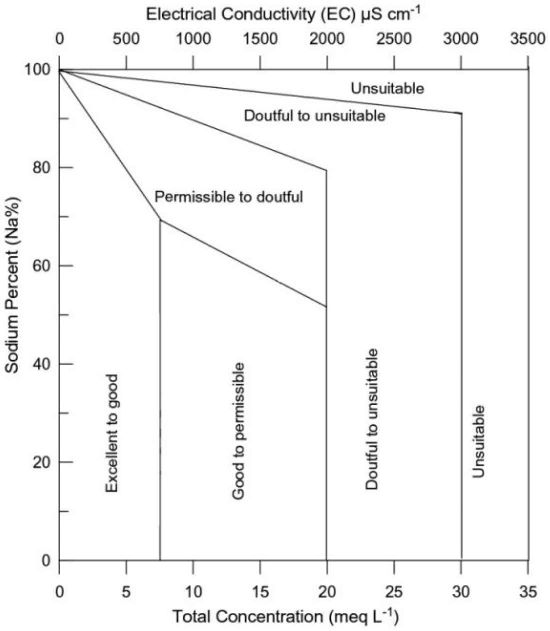


Figure 2.17: Wilcox Diagram for classification of water based on Na% and EC

In Wilcox diagram (Figure 2.17) sodium percent (Na%) [24,56] is plotted against electrical conductivity in order to draw inferences on suitability of water for irrigation.

2.9 Corrosion Study

Corrosion indices are useful to predict the tendency of water to dissolve $CaCO_3$ or scale formation[43]. They are derived from chemical equilibrium equations for the $CaCO_{3(s)}$ system. Corrosion is accelerated by low pH values, so that in water of low alkalinity and high free carbon dioxide, the attack is much more rapid as compared to water which is high in alkalinity and low in carbon dioxide content.

2.9.1 Langelier Saturation Index (LSI)

Langelier Saturation Index (LSI) is used to predict the tendencies of a water to precipitate or dissolve calcium carbonate, the main parameter for determining the corrosivity of water. According to Langelier, the corrosive action of water is principally due to an excess of free CO_2 and its interaction with calcium and magnesium carbonates [57].

Langelier Saturation Index (LSI or Saturation index) and the Ryznar Stability Index (RSI or Stability index) are used in common and combined use of these two indices gives better results. These indices are based upon a calculated pH of saturation for calcium carbonate (pHs). The pHs value is then subtracted with the water's actual pH (measured pH) to calculate the value of the index as follows:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pHs} \quad \text{......} \quad (2.15)$$

$$\mathrm{pHs} = (9.3 + A + B) - (C + D) \quad \text{......} \quad (2.16)$$

Where:

A = [log (TDS) -1)/10], TDS in ppm

B = [-13.12 log (T + 273)) + 34.55], Temperature, T in °C

C = [log (calcium hardness) - 0.4], Ca hardness in ppm (as $CaCO_3$)

D = log (alkalinity), alkalinity in ppm (as $CaCO_3$)

Classification of water based on LSI in given in Table 2.7

Table 2.7: Classification of groundwater on the basis of LSI

LSI**	**Tendency of water**
$< {}^{-}2$	Intolerable corrosion (IC)
${}^{-}2$ - ${}^{-}0.5$	Serious corrosion (SC)
${}^{-}0.5$ - 0	Slightly corrosive but non scale forming (SCNSF)
0	Balanced but pitting (BP)
0 – 0.5	Slightly scale forming and corrosive (SSFC)
0.5 - 2	Scale forming but non corrosive (SFNC)

2.9.2 Ryznar stability index (RSI)

Ryznar Stability Index (RSI) is an empirical index developed by Ryznar in 1944 and this is generally used for flowing water systems such as flowing water through pipe system. This index works on the assumption that the water with scale forming properties can control the rate of corrosion while non-scaling water is considered as corrosive (Table 2.8).

$$RSI = 2pHs - pH \quad \text{.......} \quad (2.17)$$

Table 2.8: Classification of groundwater on the basis of RSI

	RSI	**Remarks**
1	4.0- 5.0	Severe scaling
2	5.0- 6.0	Moderate to slight scaling
3	6.0- 7.0	Stable water, slight tendency for dissolving of scale
4	7.0- 7.5	Dissolving of scale, corrosive
5	7.5- 9.0	Intense dissolving of scale and corrosion
6	>9.0	Very intense dissolving of scale and corrosion

2.9.3 Aggressiveness Index (AI)

The American Water Works Association formulated an empirical indicator for water's aggressiveness towards the corrosion of Asbestos-Cement pipes. Potential primary contamination associated with asbestos-cement pipes are the release of asbestos fibres, increase in pH of the water, and calcium. Aggressive water leads to leaching of calcium, silicates and aluminosilicates. Aggressiveness Index (AI) is calculated as,

$$AI = pH + \log(AH) \quad \dots\dots (2.18)$$

Where A- Alkalinity in ppm as ($CaCO_3$), H- Ca hardness in ppm (as $CaCO_3$)

Table 2.9 give the tendency of water based on AI

Table 2.9: Classification of groundwater on the basis of AI

AI*	**Tendency of water**
< 10.0	Highly aggressive (HA)
10.0-11.9	Moderately aggressive (MA)
> 12.0	Non-aggressive (NA)

2.9.4 Larson-Skold index

Larson-Skold index is used to calculate the corrosion induced by anions in the groundwater. This index was developed by Larson and Skold in 1958. They found that in the case of mild steel alkalinity in water reduces the corrosive tendency whereas chloride and sulphate promote corrosion. The Larson-Skold index is calculated using the following formula,

$$\text{Larson-Skold Index} = (SO_4^{2-} + Cl^-)/ (HCO_3^- + CO_3^-) \dots\dots\dots\dots (2.19)$$

Table 2.10 give the corrosive nature of water based on this index

Table 2.10: Classification of groundwater on the basis of Larson-Skold Index

	Larson- Skold Index	**Remarks**
1.	Index< 0.8	Chlorides and sulphate probably will not interfere with natural film formation.
2.	0.8< Index< 1.2	Chlorides and sulphate may interfere with natural film formation. Higher than desired corrosion rates might be anticipated.
3.	Index> 1.2	The tendency towards high corrosion rates of a local type should be expected as the index increases.

2.10 Total Organic Carbon Analysis (TOC)

Organic carbon is widely distributed in large varieties in the simple to complex form of carbohydrates, proteins, fats, wax, organic acids etc., highly water soluble as well as insoluble. Due to its special properties to bind with clay particles and ability to form complexes with metal ions, the determination of total organic carbon (TOC) is significant in soil and groundwater studies [61]. The TOC analysis is based on the principle of oxidation of the carbon in the sample to carbon dioxide. In the present study Elementar Vario TOC Cube (made in Germany, Model No.38092033) is used for the detection of total organic carbon content in the groundwater samples.

2.11 Trace Element Study

Inductively Coupled Plasma–Mass Spectrometer capable of scanning the mass range 5 to 250 amu with a minimum resolution capability of 1 amu peak width at 5 % peak height is used to determine the concentration of various trace elements in the groundwater sources. The trace metals such as Lithium (Li), Aluminium (Al), Vanadium (V), Chromium (Cr), Manganese (Mn), Nickel (Ni), Cobalt (Co), Copper (Cu), Zinc (Zn), Gallium (Ga), Arsenic (As), Selinium (Se), Rubidium (Rb), Strontium (Sr), Silver (Ag), Cadmium (Cd), Indium (In), Cesium (Cs), Barium (Ba), Lead (Pb) and Bismuth (Bi) are determined.

The groundwater samples for the analysis of trace elements are collected in separate 250 mL capacity bottles. Samples are fixed with supra-pure nitric acid immediately after collection. Samples are introduced by pneumatic nebulization into radiofrequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are detected by a continuous dynode electron multiplier assembly and the ion information processed by a data handling system. Interferences relating to the technique are recognized and corrected.

2.12 Microbiological Analysis

A broad spectrum of microorganisms are present in water bodies. While analyzing the presence of microorganisms in fresh water sources, major consideration is given to pathogens that are harmful to human beings as well as livestock. Total coliform bacteria are generally considered as the potential indicator of faecal contamination. The presence of total coliforms and specifically *E.coli* is determined using the method most probable number (MPN) using replicate liquid broth growth in ten-fold dilutions. This test consists of three steps, first is the presumptive test which is a screening test to check the presence of coliform organisms, second is the confirmatory test and the third and final step is the completed test for the presence of *E.coli* [16,17].

2.13 Designated Best Use of Water

Central Pollution Control Board, India classifies water into five classes i.e.; from A to E on the basis of their designated best use [62] (Table 2.11). Through designated best use (DBU) of water, CPCB means to identify the highest quality of the water body in terms of water quality requirements for specific use. Class A includes all water bodies used for drinking without any conventional treatment but after disinfection. Water sources that are used for outdoor bathing belongs to class B. Drinking water sources after conventional treatment and disinfection are included in class C and propagation of wild life and fisheries is termed in class D. Class E comprises those water bodies which are used in irrigation, industrial cooling and controlled waste disposal. Boron is determined using spectrophotometer at 420 nm. The criteria for these classifications are taken on the basis of important physico-chemical and biological parameters specific to various purposes of water usage under the given classifications.

Table 2.11: Classification of water based on designated best use by CPCB

Designated-Best-Use	Class of water	Criteria
Drinking Water Source without conventional treatment but after disinfection	A	• Total Coliforms Organism MPN/100ml shall be 50 or less • pH between 6.5 and 8.5 • Dissolved Oxygen 6mg/l or more • Biochemical Oxygen Demand 5 days 20°C 2mg/l or less
Outdoor bathing (Organised)	B	• Total Coliforms Organism MPN/100ml shall be 500 or less • pH between 6.5 and 8.5 • Dissolved Oxygen 5mg/l or more • Biochemical Oxygen Demand 5 days 20°C 3mg/l or less
Drinking water source after conventional treatment and disinfection	C	• Total Coliforms Organism MPN/100ml shall be 5000 or less pH between 6 to 9 • Dissolved Oxygen 4mg/l or more • Biochemical Oxygen Demand 5 days 20°C 3mg/l or less
Propagation of Wild life and Fisheries	D	• pH between 6.5 to 8.5 • Dissolved Oxygen 4mg/l or more • Free Ammonia (as N) 1.2 mg/l or less
Irrigation, Industrial Cooling, Controlled Waste disposal	E	• pH betwwn 6.0 to 8.5 • Electrical Conductivity at 25°C micro mhos/cm Max.2250 • Sodium absorption Ratio Max. 26 • Boron Max. 2mg/l
	Below-E	**Not Meeting A, B, C, D & E Criteria**

2.14 Conclusion

The significant features of the study area is discussed in this chapter including the geology, hydrogeology, climate, groundwater potential zones as well as land use- land cover pattern with specially constructed maps for this research work. The physico-chemical parameters of groundwater samples were analysed using scientific analytical protocols and standard procedures prescribed by APHA. The analysis of the groundwater samples from the study area, the relevance of the prominent water quality parameters selected, statistical methods adopted, various ionic and diagrammatical plots used and the guidelines of Central Pollution Control Board (CPCB), BIS and WHO classification are systematically presented through the sections placed above. The results and outcome of the research work with inferences are presented in the following chapters, with interpretation of the pertinent features.

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Chapter **3**

HYDROGEOCHEMISTRY OF SHALLOW AND DEEP GROUNDWATER OF ALAPPAD COAST, KOLLAM, KERALA, INDIA DURING THE YEAR 2012

3.1 Introduction

Study of groundwater quality to understand hydrogeochemistry and freshwater availability in coastal aquifers is of primary importance in the coastal regions which faces numerous natural as well as anthropogenic threats. Groundwater is an important resource for economic growth. Its per capita availability 1000 m^3/year (water scarcity limit) and 500 cm^3/year (water stress limit) is an indicator of a stable society. Rigorous assessment of groundwater quality is becoming increasingly important in a local perspective for proper management of available groundwater resources and to prevent their over exploitations. To determine the groundwater quality of a region, a large number of prominent water quality parameters have to be analysed followed by correct interpretation of analysed data[1].

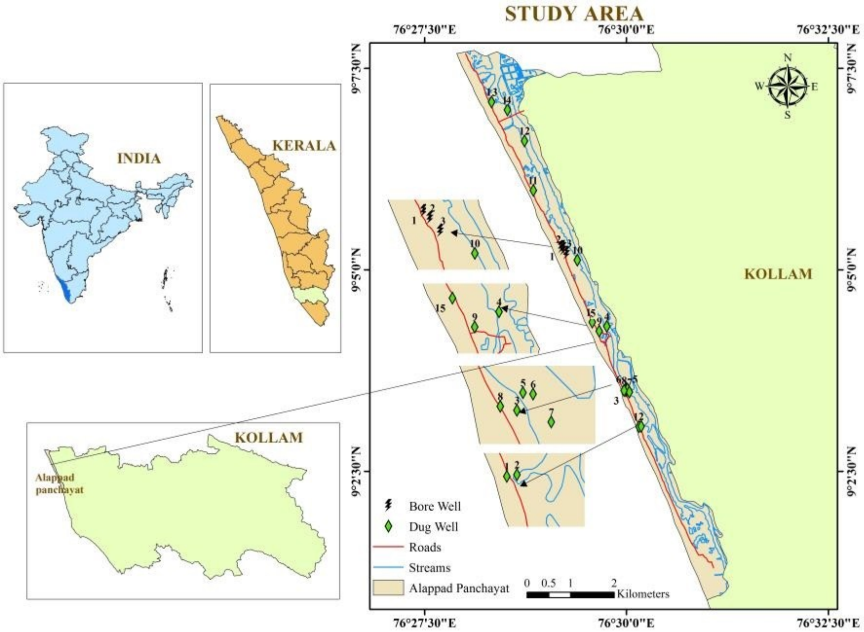

Figure 3.1: Location map of Alappad coast with shallow dug well and deep bore well sampling stations in Kollam, Kerala, India.

This chapter of the thesis mainly comprises of major results of physico-chemical parameters of groundwater analysed in the laboratory sampled from the shallow dug wells and deep bore wells in the study area during the months of year 2012. From this original (primary) data, the hydrogeochemistry of the region is evaluated using the major anion and cation chemistry including hydrochemical facies and water types. The data is derived from the critical analysis of eighteen groundwater sources from the Alappad region comprises of fifteen (15) dug wells and three (3) bore wells. Graphical representation of each physico-chemical parameters includes control well (CW) separately both in dug well and bore well strata as the present work is a continuation of post tsunami water quality study of Alappad coast initiated in the year 2005. The control well (CW) marked is considered as one with highest stable water quality and maintaining good water quality in the year 2005, least affected by the giant tsunami waves[2].

Table 3.1: Location details of Dug wells (DW) and bore wells (BW) in Alappad coast, Kollam, Kerala, India.

Station no:	Description	Remarks	Location (Degree Decimal)
1	Temple well(Control well)	Dug well (DW1)	09.05089 76.50257
2	Temple well	Dug well (DW2)	09.05097 76.50303
3	Private owned well	Dug well (DW3)	09.05830 76.49986
4	Private owned well	Dug well (DW4)	09.07164 76.49596
5	Private owned well	Dug well (DW5)	09.05868 76.49999
6	Private owned well	Dug well (DW6)	09.05865 76.50021
7	Private owned well	Dug well (DW7)	09.05805 76.50060
8	Private owned well	Dug well (DW8)	09.05839 76.49950
9	Temple well	Dug well (DW9)	09.07067 76.49438
10	Temple well	Dug well (DW10)	09.08535 76.48987
11	Private owned well	Bore well (BW1)	09.0524 76.2920
12	Private owned well	Bore well (BW2)	09.0523 76.2923
13	Private owned well	Bore well (BW3)	09.08668 76.47214
14	Temple well	Dug well (DW11)	09.09978 76.48079
15	Temple well	Dug well (DW12)	09.1100 76.47895
16	Private owned well	Dug well (DW13)	09.11805 76.47214
17	Private owned well	Dug well (DW14)	09.11641 76.47543
18	Temple well	Dug well (DW15)	09.07253 76.49294

The prominent parameters analysed includes physico-chemical parameters such as pH, redox potential (Eh), electrical conductivity (EC), total dissolved solids (TDS), alkalinity, total hardness, calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), potassium (K^{+}), bicarbonate (HCO_3^{-}), chloride (Cl^{-}), sulphate (SO_4^{2-}), phosphate (PO_4^{3-}), nitrate (NO_3^{-}), iron, dissolves oxygen (DO), biological oxygen demand (BOD). From these analysed parameters hydrochemical facies and hydrogeochemistry of the groundwater is assessed depending on the interaction of various ions.

3.2 Physico-chemical Parameters

3.2.1 Temperature (°C)

Temperature of the source water body has very significant effect on most of the physico-chemical parameters, especially in ion retention. It is known that the monovalent ions such as sodium, potassium and chloride show decrease in retention at higher temperature of water (26°C to 30°C) leading to increase in diffusion rates. The multivalent ions (sulphate, calcium, magnesium etc.) have high retention in aquifers at temperature range 10°C to 30°C, hence low rate of diffusion is inferred[3]. Retention and diffusion of ions plays an important role in rate of ionic interactions in the hydrogeochemistry of groundwater.

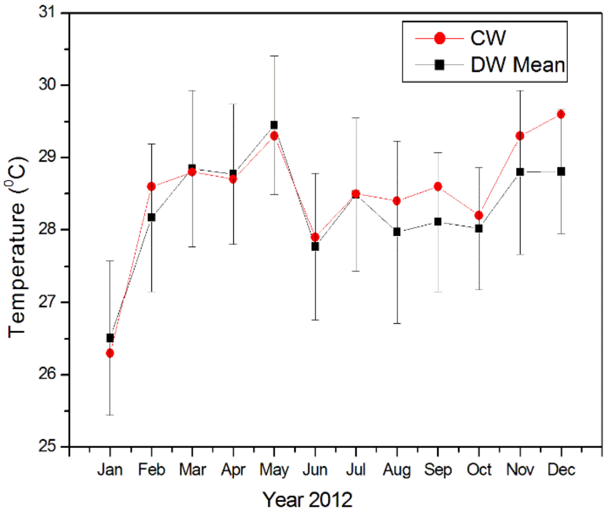

Figure 3.2: Monthly variation of temperature (°C) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Temperature of the study area for control well ranges from a minimum temperature of 26.3°C in January 2012 to 29.6°C in December

2012. The annual mean of CW is 28.5±0.8 not having much variation in temperature profile in the case of dug well samples of the region with a confidence interval of 28.0°C - 29.0°C, at 95% significant limit.

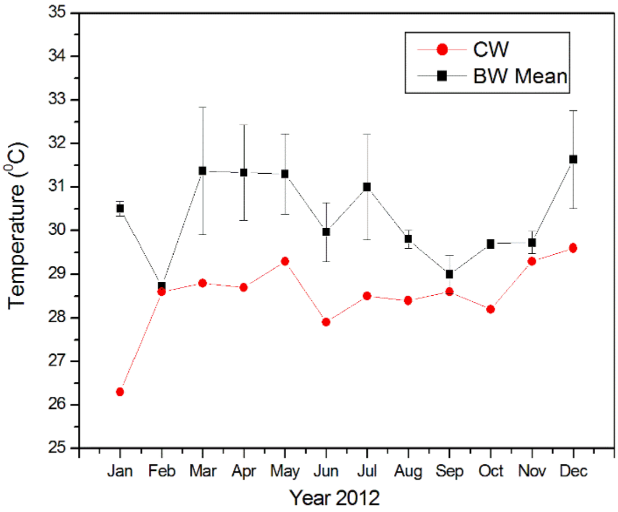

Figure 3.3: Monthly variation of temperature (°C) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

There is no much variation between the temperature profile of shallow and deep groundwater sources. The dug wells shows annual mean temperature of 28.3±1°C and annual mean of temperature in bore wells is 30.34±1°C.

3.2.2 pH

Acidic or basic character of water is primarily predicted in terms of pH of the water. Most natural water is considered of having pH value in the range of 4 to 9. Low pH range (below 6.5) is the indication of acidic nature of water and imparts corrosive behaviour[4]. The control well has annual pH of 7.7±0.2, with a confidence interval of 7.6 – 7.8 at 95%

confidence interval. During pre-monsoon a maximum pH of 8.0 (March 2012) and post-monsoon period (November 2012) for control well. pH of the groundwater collected from shallow dug well sources ranges from 7.4 to 8.0, with annual mean 7.8±0.4 with 7.6 – 8.1 level of confidence at 95% significance.

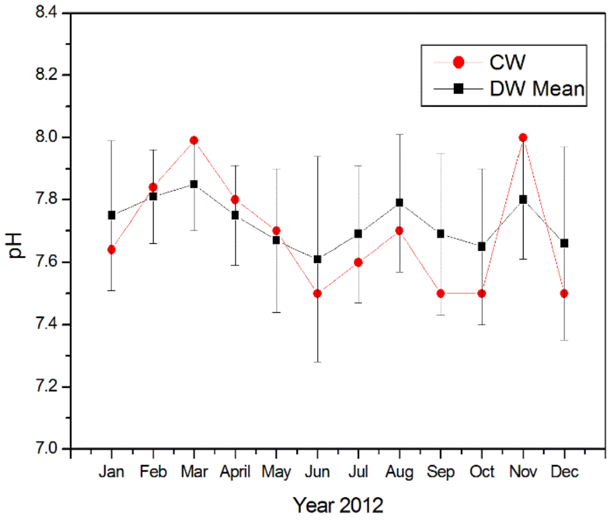

Figure 3.4: Monthly variation of pH of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In the case of bore wells, minimum pH drops to 6.8 (during July 2012) and maximum pH is 7.9 (in November). For both dug wells and bore wells, slightly alkaline behaviour become visible and pH is maximum during November 2012, but all are within the permissible limit prescribed by BIS (2012)[5] and WHO (2011)[6] standards (pH 6.5 to 8.5). The annual mean of pH for bore wells are 7.3±0.3 with CI of 7.1 – 7.4 at 95% level of significance.

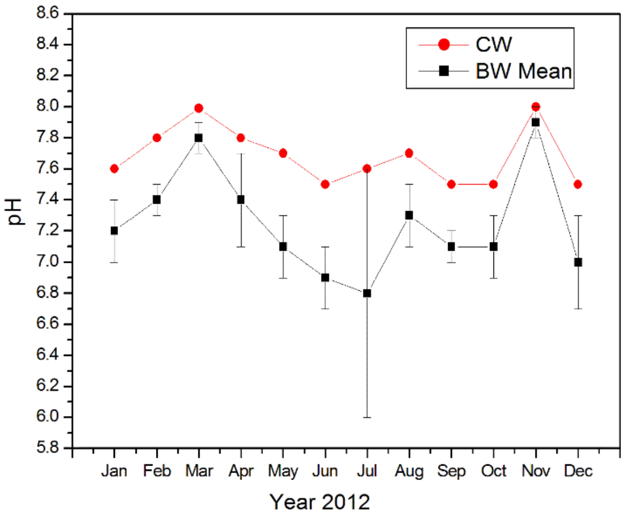

Figure 3.5: Monthly variation of pH of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

In the study area, all the groundwater sources have pH ≤ 8. This indicates that bicarbonate (HCO_3^-) is not converted into carbonate (CO_3^-) during the study period as the reaction takes place only in high pH (above pH 8). Hence there is no reaction of carbonate with cations and there by calcium carbonate ($CaCO_3$) is not precipitated[7]

3.2.3 Redox Potential (Eh)

Redox potential is used to foresee the electrochemistry of groundwater[8]. System being it measure the electrical energy transferred between water and standard reference electrode cell. It plays a special role in predicting instances of groundwater pollution occurred due to source contaminants especially heavy metal mobility[9] and organic matter trash sources[10]. Long term evaluation of Eh is most likely for monitoring fate of iron and sulphate in groundwater[11]. Eh of groundwater is affected by dissolved oxygen, iron and sulphate.

Redox potential for control well and dug well strata is limited to the negative range by the reduction of H_2O to H_2. It shows that, shallow groundwater sources are under reducing environment throughout the study period [12]. Control well and dug well mean shows similar pattern being annual mean of control well -42±10 mV with confidence interval CI -48.3 mV to -35.7 mV at 95% level of significance.

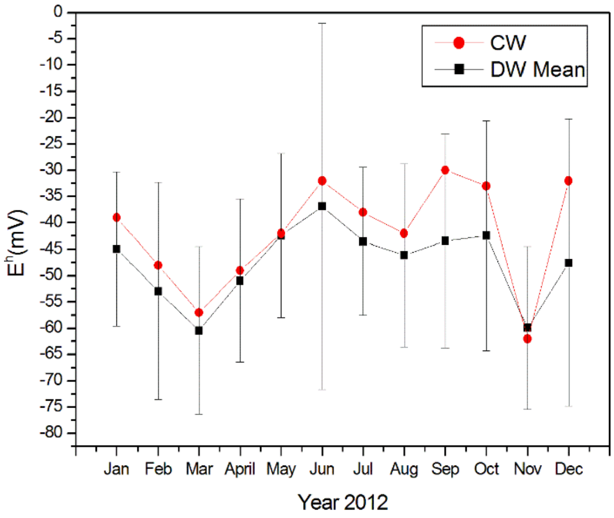

Figure 3.6: Monthly variation of redox potential (Eh) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

From January 2012 Eh of dug wells shows a gradual decrease till March, 2012 for shallow dug well sources and then increases to -37 mV in June 2012. Again there is a slow decrease in Eh throughout the monsoon but a sudden fall in Eh is observed during post monsoon season in the month of November (-60 mV). Finally in December, 2012 Eh reaches -48 mV. Annual mean of Eh in groundwater from dug wells is -48±20 mV with confidence interval CI, -60 to -35 mV at 95% significant level.

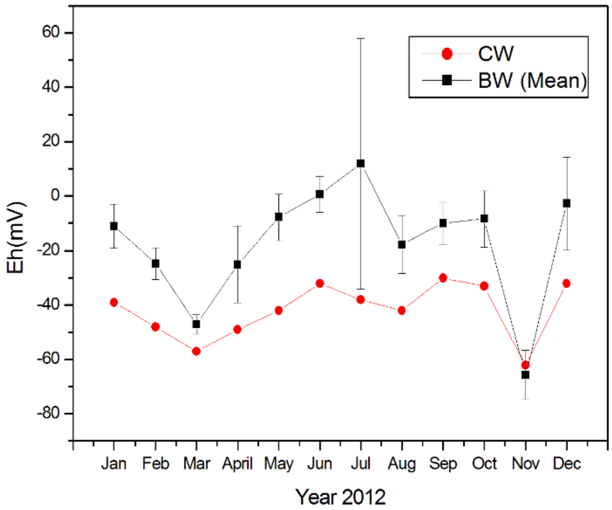

Figure 3.7: Monthly variation of redox potential (Eh) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

The deep bore wells in the study area also shows a similar trend as in the case of shallow dug wells throughout the study period. But during June and July 2012, groundwater exhibits oxidation nature as Eh increases to positive range by the oxidation of H_2O to O_2. The annual mean of Eh for bore well is -17±16 mV with CI of -27 to -7.2 mV at 95% significant level.

3.2.4 Electrical Conductivity (EC)

Electrical conductivity keeps close relationship with TDS and temperature[13]. Incidence of mixing of fresh water with sea water could be monitored using EC measurement[14]. Conductivity is correlated to salinity which in turn affects dissolved oxygen concentration of the water source. EC of groundwater is contributed by the geology of aquifers it contained, as water reacts with the surrounding rocks and diffuses minerals in varying degrees. Water having greater ionic strength also contains higher electrical conductivity. It is also used for identification of contamination occurred in groundwater[15]. The control well have electrical conductivity annual mean of 403±139 µS/cm with a confidence interval of 317– 488 µS/cm at 95% significant level.

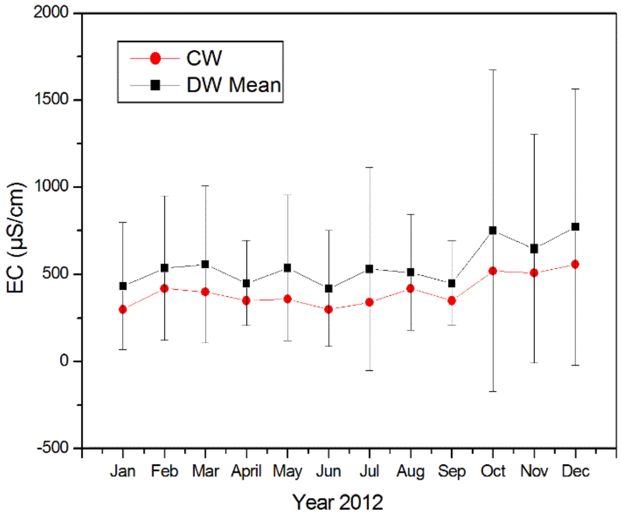

Figure 3.8: Monthly variation of electrical conductivity (EC) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Dug wells are not having variation in its monthly mean of electrical conductivity in January 2012 with a monthly mean of 433±364 µS/cm and in September 2012 (450±243 µS/cm). But during October 2012 quick increase in EC is observed (751±922 µS/cm). This relatively high standard deviation marks the spacial variation in EC between different sampling locations. The sudden increase in EC implies contamination of water sources. The annual mean of dug wells is 550±521 µS/cm with a confidence interval, CI of 229– 871 µS/cm at 95% level of significance.

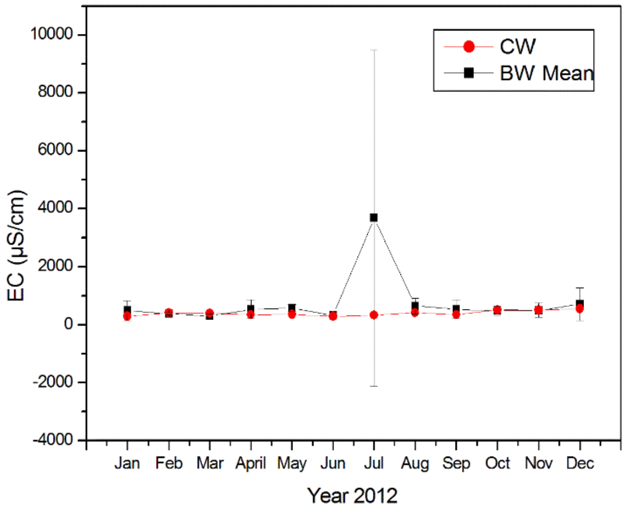

Figure 3.9: Monthly variation of electrical conductivity (EC) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

From Figure 3.9 it is clear that electrical conductivity of bore wells in the study area are within the range of 313 µS/cm to 720 µS/cm, except in July 2012 that is well below the WHO standard [6] (1500 µS/cm). During monsoon season (July 2012), there is an abrupt increase in electrical conductivity to a monthly mean of 3680± 5811 µS/cm. May be due to substantial volumes by monsoon dilution and reaches the deep groundwater sources and this huge variation in turn reflects in annual mean of 768±1698 µS/cm in bore well waters during the year 2012. This high standard deviation indicates the wide range of EC among different sampling locations in the study period.

3.2.5 Total Dissolved Solids (TDS)

Total dissolved solids in water may be defined as the sum of concentrations of all dissolved constituents in the water. TDS have very strong correlation with electrical conductivity of water. According to BIS (2012)[5] and WHO (2011)[6], total dissolved solids in a given water sample should not exceed 500 mg/L (desirable limit), but TDS of up to 2000 mg/L is permissible by BIS standards, if alternative sources are unavailable.

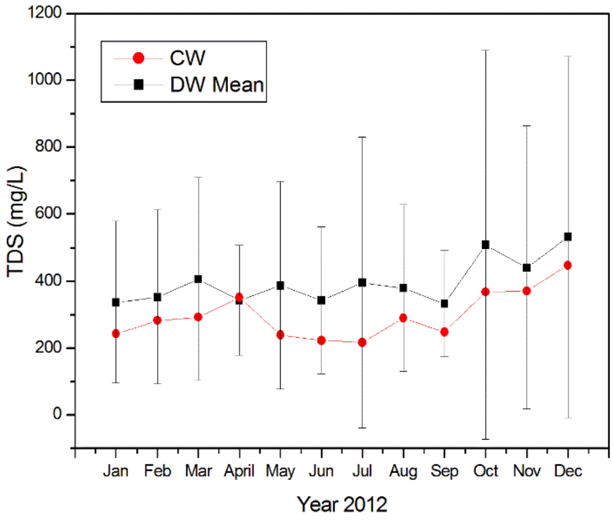

Figure 3.10: Monthly variation of total dissolved solids (TDS) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

The annual mean of control well water samples for total dissolved solids is 298±72 mg/L with a confidence interval of 316– 488 mg/L (95% significance level), which is well under the desirable limit prescribed by BIS and WHO for drinking water standards. In January 2012, dug well source water has 337.4±243 mg/L and it slowly increases to 406.8±293 mg/L in March 2012. TDS decreases to 342.5±352 mg/L in April, but again increase to 387.50±240 mg/L in May 2012. This continues until TDS rise to cross the desirable concentration in October 2012 with 509±368 mg/L and reaches the maximum concentration (532±448 mg/L) of the study period. Dug wells have annual average of 396.76±350.36 with confidence interval of 181– 612 mg/L at 95% significance level.

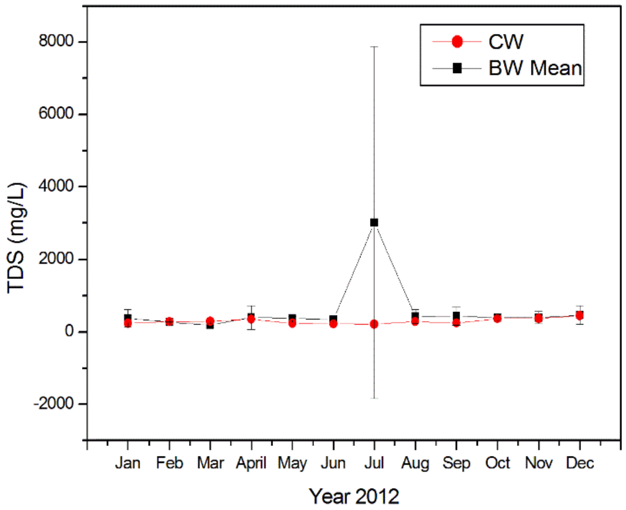

Figure 3.11: Monthly variation of total dissolved solids (TDS) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Both control and bore well waters measured in different strata shows similar trend in TDS concentration, being control well has lower concentrations than the later throughout the study period. A non-uniform feature occurs in July 2012, as in the case of EC, TDS also hikes up to 3018.67±4861.39 mg/L may be as a cause of monsoon dilution of mineral particles along with the mobility of contaminants. Hence, the annual mean of TDS in bore wells is 591.86±1414.34 mg/L, which is beyond the desirable limit prescribed by BIS and WHO standards[5,6] for drinking water.

3.2.6 Alkalinity

Alkalinity is the quantity of base present in water. Alkalinity and hardness of groundwater is because of the interaction of carbon dioxide, water and limestone[16]. The prominent components of alkalinity are carbonates and bicarbonates. The chemical reactions triggered by CO_2 contained water with the aquifer rock formations (containing limestone - calcite and dolomite) forms calcium bicarbonate and magnesium bicarbonate salts.

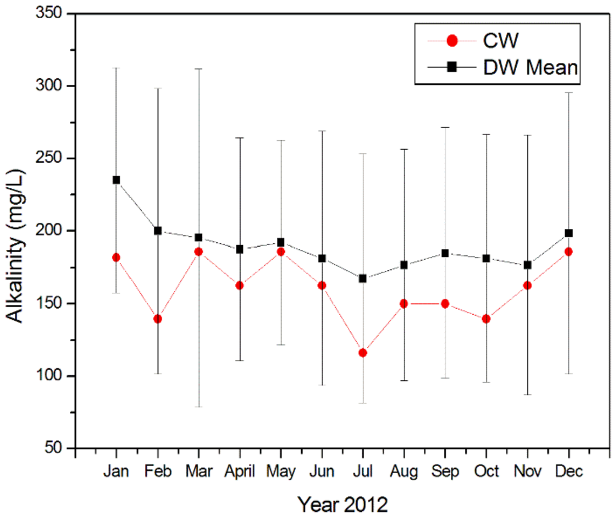

Figure 3.12: Monthly variation of alkalinity of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

The control well has total alkalinity (182 mg/L) in January 2012 and it decreases to 139.5 mg/L in February 2012. The highest concentration of 186 mg/L is observed in March, May and December 2012. In July 2012, total alkalinity falls down to 116 mg/L but increases gradually from October to December 2012. The annual mean of alkalinity in control well is 160.3±22.3 mg/L with a confidence interval of 146.5 - 174.0 mg/L, with 95% significant level. The dug wells show a maximum alkalinity (monthly mean of 235±77.7 mg/L) in January 2012. Thereafter, the concentration gradually declines (187.5±76.9 mg/L) till April 2012 but slightly increases

(192±70.6 mg/L) May 2012 and drops to minimum concentration (167.4±85.7 mg/L) in July 2012. From August 2012 alkalinity and remains somewhat steady (176±89.5 mg/L) till November 2012 and reaches a mean of 198±97 mg/L in December 2012. According to BIS (2012)[5], desirable limit of alkalinity in drinking water is 200 mg/L and monthly mean for dug well sources in the year 2012 is within this limit except in the month of January 2012. The annual mean of dug well strata is 189.7±88.4 mg/L with confident interval, CI of 135 – 244 mg/L at 95% level of significance.

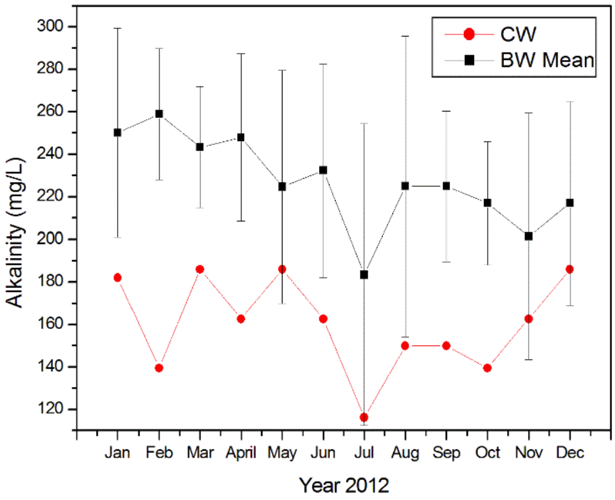

Figure 3.13: Monthly variation of alkalinity of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Bore well sources show a high alkalinity compared to dug wells with maximum monthly mean of 258.9±30.9 mg/L in February 2012. The alkalinity shows an oscillating but decreasing trend till July 2012 (183.5±71 mg/L) but raises eventually to 216.97±47.80 mg/L in December 2012. The monthly mean of bore wells in the study area is beyond the desirable limit prescribed by BIS (2012)[5], except in July 2012, which shows a monthly mean of 167.4±85.7 mg/L. The annual mean of alkalinity for water from bore wells is 227.2±60.3 mg/L with 190 - 264 mg/L confidence interval (at 95% significant level).

3.2.7 Total Hardness (TH)

Hardness is typically known as the sum of calcium and magnesium content of water. Hardness is defined as the concentration of all multivalent metallic cations in solution[17]. In natural water these ions react with soap to form a scum that is difficult to remove. Thus hardness in water is mainly due to calcium bicarbonate, magnesium bicarbonate, calcium sulphate and magnesium sulphate[18].

Hardness (mg/L) of water is classified into a range of extremely soft to too hard for ordinary domestic use[19]. Water with hardness 0 to 45 mg/L $CaCO_3$ is *extremely soft to soft water* (ESS). Hardness of 46 mg/L to 90 mg/L $CaCO_3$ is considered as *soft to moderately hard water* (SMH). *Moderately hard to hard water* (MHH) has hardness in the range 91 mg/L to 130 mg/L $CaCO_3$. Hardness between 131 mg/L to 170 mg/L $CaCO_3$ is categorised as *hard to very hard water* (HVH) and hardness of 171 mg/L to 250 mg/L is *very hard to excessively hard* (VHEH) water. A water sources with hardness > 250 mg/L are *too hard for ordinary domestic use*. Generally, water is treated for hardness levels above 120 mg/L as $CaCO_3$[20].

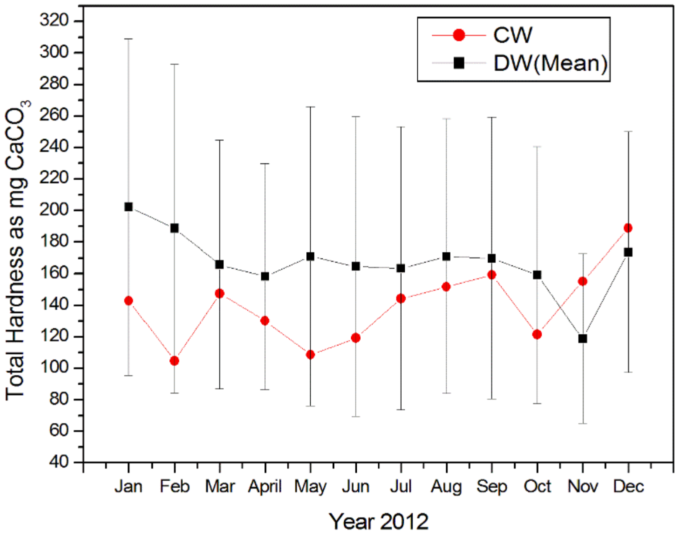

Figure 3.14: Monthly variation of total hardness (TH) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Control well has total hardness with annual mean of 139.6±23.9 mg/L with a confidence interval, CI of 124.8 mg/L – 154.3 mg/L. Minimum total hardness is observed in the month of February (104.8 mg/l) and maximum total hardness as $CaCO_3$ in December 2012 (188.8 mg/L). Total hardness for shallow dug well strata in January 2012 is high (202.2±106.7 mg/L) compare to rest of the months of the year that comes in category *very hard to excessively hard* (VHEH). From February onwards, total hardness is decreased gradually and reached more or less uniform till October 2012. In November 2017, a sudden decrease to 118.9±53.7 mg/L is observed, but in December 2012, total hardness increased to 173.7±76.2 mg/L. Annual mean for total hardness as $CaCO_3$ for dug wells is 167.25±86.9 mg/L with confidence interval (CI) 113 mg/L – 220 mg/L. From the graph it is clear that control well and dug wells has *hard to very hard water* (HVH).

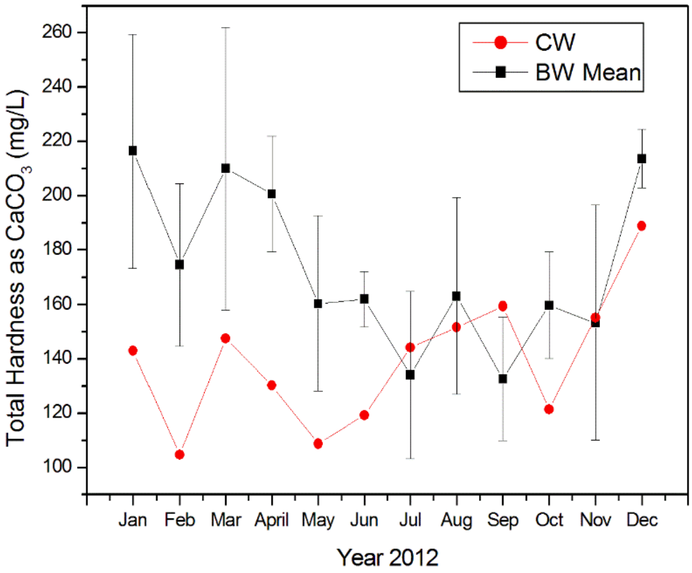

Figure 3.15: Monthly variation of total hardness (TH) of control well (CW) and bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

In the case of bore wells hardness is observed maximum in January 2012 with a monthly mean of 216.5±43 mg/L and minimum concentration of 132±22.9 mg/L in September 2012. No particular trend is noticed in the concentration throughout the year. Total hardness in deep groundwater sources comes in very *hard to excessively hard* (VHEH) water having annual mean of total hardness 173.4±31.9 mg/L as $CaCO_3$, with confidence interval, CI of 153.8 mg/L – 193 mg/L. All the groundwater sources show an increasing trend of total hardness in December 2012 compared to the preceding month (November 2012). This increasing trend of total hardness concentration in fresh water aquifers in coastal regions can be recognized as a result of mixing of brine and subsequent ion exchange process. The annual mean of total hardness in control well, dug wells and bore wells are within the desirable limit prescribed by BIS[5] (200 mg/L).

In natural water, typically hardness is broadly classified into two types of, namely carbonate hardness and non-carbonate hardness. Carbonates and bicarbonates of calcium [$CaCO_3$ & $Ca(HCO_3)_2$] and magnesium [$MgCO_3$ & $Mg(HCO_3)_2$] causes carbonate hardness. *Carbonate hardness is also known as temporary hardness* as this type of hardness can be removed through raising the temperature of water (heating) that leads to precipitation. But calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) if present in water sources cannot precipitate by simply heating. In such cases total hardness is less than or equal to alkalinity.

Table 3.2: Comparison of TH, AL, Te H and Pe H in mg/L $CaCO_3$ for the control well (CW) in the year 2012

Month	TH (mg/L)	Inference	TA (mg/L)	Te H (mg/L)	Pe H (mg/L)
Jan	142.99	HVH	182	142.99	-39.01
Feb	104.75	MHH	139.5	104.75	-34.75
Mar	147.51	HVH	186	147.51	-38.49
Apr	130.29	MHH	162.7	130.29	-32.41
May	108.71	MHH	186	108.71	-77.29
Jun	119.31	MHH	162.7	119.31	-43.39
Jul	144.23	HVH	116.2	116.2	28.03
Aug	151.71	HVH	150	150	1.71
Sep	159.45	HVH	150	150	9.45
Oct	121.50	MHH	139.5	121.50	-18
Nov	155.26	HVH	162.7	155.26	-7.44
Dec	188.84	VHEH	186	186	2.84
$\bar{x} \pm \sigma$	139.5±□3.9	HVH	160.3±22.3	□36.0±23.5	-20.7±29.0
μ	139.5±14.7		160.3±13.7	136□0±14.5	-20.7±17.8
CI	124.8-154.3		146.5-174.0	121.6-150.5	-38.5- -2.9

Non-carbonate hardness also known as permanent hardness is caused due to chlorides and sulphates of calcium and magnesium. This hardness cannot be precipitate and removed through heating. If alkalinity is greater than total hardness (TH) then all the hardness is regarded as temporary hardness (TeH). If alkalinity is less than TH, then alkalinity is considered as TeH. Permanent hardness (PeH) is calculated from the difference between total hardness (TH) and temporary hardness (TeH)[21].

Table 3.3: Comparison of TH, AL, Te H and Pe H in mg/L $CaCO_3$ for the dug wells (DW) in the year 2012

Month	**TH (mg/L)**	**Inference**	**TA (mg/L)**	**Te H (mg/L)**	**Pe H (mg/L)**
Jan	202.2	VHVH	235.1	202.2	-32.8
Feb	188.7	VHVH	199.9	188.7	-11.3
Mar	165.8	HVH	195.3	165.8	-29.5
Apr	158.3	HVH	187.5	158.3	-29.2
May	171.1	VHVH	192.2	171.1	-21.1
Jun	164.7	HVH	181.3	164.7	-16.6
Jul	163.4	HVH	167.4	163.4	-4.0
Aug	171.1	VHVH	176.7	171.1	-5.6
Sep	169.9	HVH	185.0	169.9	-15.1
Oct	159.2	HVH	181.4	159.2	-22.1
Nov	118.9	MHH	176.7	118.9	-57.7
Dec	173.7	VHVH	198.4	173.7	-24.7
$\bar{x} \pm \sigma$	167.3±19.7	HVH	189.7±17.3	167.3±19.7	-22.5±14.4
μ	167.3±12.1		189.7±10.6	167.3±12.1	-22.5±8.9
CI	155.1-179.4		179.1-200.4	155.1-179.4	-31.4- -13.6

For control well alkalinity is greater than hardness for most of the months in the year 2012 except in July, August and September and hence the water during this period consists of both temporary as well as permanent hardness (Table 3.2). The annual mean of temporary hardness of control well is 136.0±23.5 mg/L. The dug well and bore well strata have total hardness less than the alkalinity for the entire study period in the year 2012. So the groundwater sources contains only temporary hardness with an annual mean of 167.3±19.7 mg/L for dug wells and 173.4±29.8 mg/L for bore wells.

Table 3.4: Comparison of TH, AL, Te H and Pe H in mg/L $CaCO_3$ for the bore wells (BW) in the year 2012

Month	TH (mg/L)	Inference	TA (mg/L)	Te H (mg/L)	Pe H (mg/L)
Jan	216.5	VHEH	250.2	216.5	-33.7
Feb	174.6	VHEH	258.9	174.6	-84.3
Mar	210.1	VHEH	243.4	210.1	-33.4
April	200.7	VHEH	248.0	200.7	-47.3
May	160.4	MHH	224.7	160.4	-64.3
Jun	162.1	MHH	232.5	162.1	-70.4
Jul	134.1	HVH	183.5	134.1	-49.4
Aug	163.1	HVH	225.0	163.1	-61.9
Sep	132.7	HVH	225.0	132.7	-92.3
Oct	159.8	MHH	217.0	159.8	-57.2
Nov	153.3	HVH	201.5	153.3	-48.2
Dec	213.6	VHEH	217.0	213.6	-3.3
$\bar{x} \pm \sigma$	173.4±29.8	VHEH	227.2±21.4	173.4±29.8	-53.8±24.0
μ	173.4±18.3		227.2±13.2	173.4±18.3	-53.8±14.8
CI	155.1-19□.7		214.0-240.4	155.1-191.7	-68.6--39.0

Usually water salinity decreases as the temporary hardness increases. This is mainly attributed to the effect of leaching and dissolution of salts leading to increase of hardness and ionic strength effect on increasing solubility of Ca^{2+} and Mg^{2+} in water[22].

3.2.8 Calcium (Ca^{2+})

The control well has a calcium concentration with an annual mean of 40.2±8.4 mg/L with a CI of 35 mg/L – 45.3 mg/L. In January 2012 the shallow groundwater sources have calcium concentration of 55.8±29.7 mg/L. A slight increase in calcium is observed in February 2012 (56.36±33.8 mg/L). After that a gradual decrease in the calcium concentration is noticeable from the graph (Figure 3.16) having almost uniform concentration of 48.7±23.5 mg/L and 48.6±21.2 mg/L in month of March and April 2012 respectively.

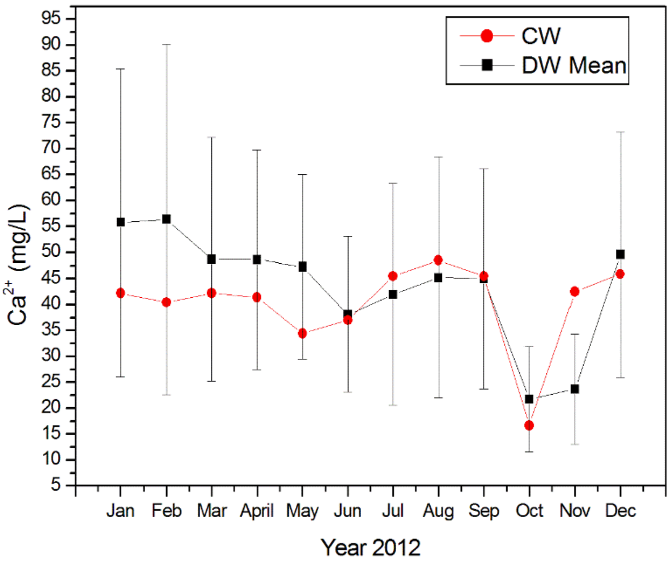

Figure 3.16: Monthly variation of calcium (Ca^{2+}) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In May 2012 calcium lowered to 47.24±17.8 mg/L of dug wells in the study area and reaches to monthly average of 38.1±37 mg/L in June 2012. But in July 2012, slight increase in calcium is observed (41.9±21.38 mg/L) and this trend is noticeable in August 2012 with monthly mean of 45.2±23.2 mg/L and in September month with a concentration of 45±21.2 mg/L. A sudden decrease in calcium ions is visible in October with 21.75±10.1 mg/L and 23.6±10.6 mg/L in November; those are minimum calcium concentrations in the year 2012. In December 2012, there is a hike in calcium with a monthly mean of 49.6±23.6 mg/L. The annual mean of calcium ion concentrations in dug wells is 43.5±2 mg/L with a confidence interval (CI) 30 mg/L – 57 mg/L.

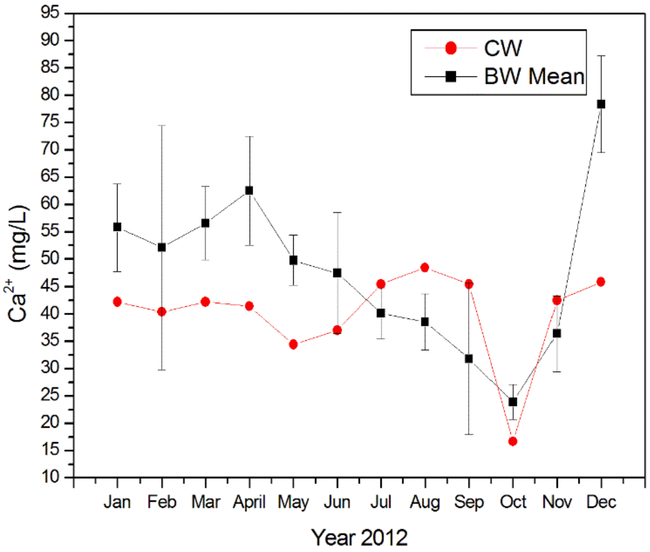

Figure 3.17: Monthly variation of calcium (Ca^{2+}) of control well (CW) and bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In the case of bore well strata, January 2012 have calcium concentration of 55.2±8 mg/L. A drop to 52.3±22.3 mg/L is observed in February with high standard deviation compared to other months indicating special variability of calcium in shallow groundwater sources during this month. In March calcium slightly increased to 56.6±6.7 mg/L and reaches 62.5±10 mg/L in April 2012. From May 2012 onwards, calcium decreases gradually and attains a minimum concentration of 23.9±3.2 mg/L in October 2012. But in November 2012, calcium increase to 36.4±7 mg/L and calcium concentration shot out to a maximum level of 78.4±8.9 mg/L in December 2012 which is beyond desirable limit prescribed by WHO[6] and BIS[5] standards (75 mg/L). The annual mean of calcium in bore well strata is 47.8±10.1mg/L with a confidence interval, CI of 54±41.6 mg/L. But the annual mean of calcium in both deep and shallow groundwater sources are < 75 mg/L that is considered with in the BIS[5] (2012) and WHO[6] (2011) standard limit.

3.2.9 Magnesium (Mg^{2+})

The control well in the study area has very low concentration of magnesium compared to calcium with annual average of 9.5±5.2 mg/L and confidence interval, CI of 12.6 mg/L - 6.3 mg/L.

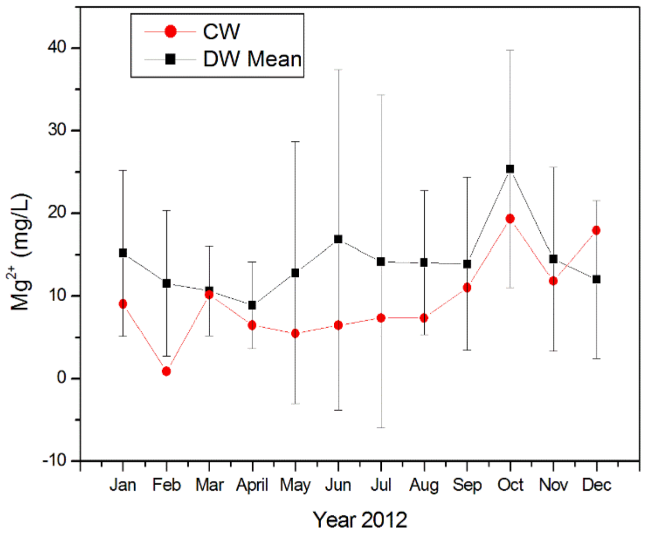

Figure 3.18: Monthly variation of magnesium (Mg^{2+}) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In the case of dug well strata, January 2012 has Mg^{2+} 15.2±10 mg/L which decreases gradually from February (11.6±8.8 mg/L) till a minimum magnesium concentration of the year 2012 reported in April (12.8±15.9 mg/L). Then it increases to 12.8±15.9 mg/L in May to 16.8±20.6 mg/L in June 2012. After that, there is a minor decrease in magnesium during July, August and September 2012. A sudden increase in magnesium is evident in October 2012 with 25.4±14.3 mg/L attaining the maximum concentration in the study region during the year 2012. It is then gradually reduced to 12±9.5 mg/L in December 2012. According to BIS and WHO standards, the permissible limit of magnesium in water is 30 mg/L and here the shallow dug wells have annual mean of 14.2±12.7 mg/L with CI, 6.4 mg/L – 21.9 mg/L at 95% significant level.

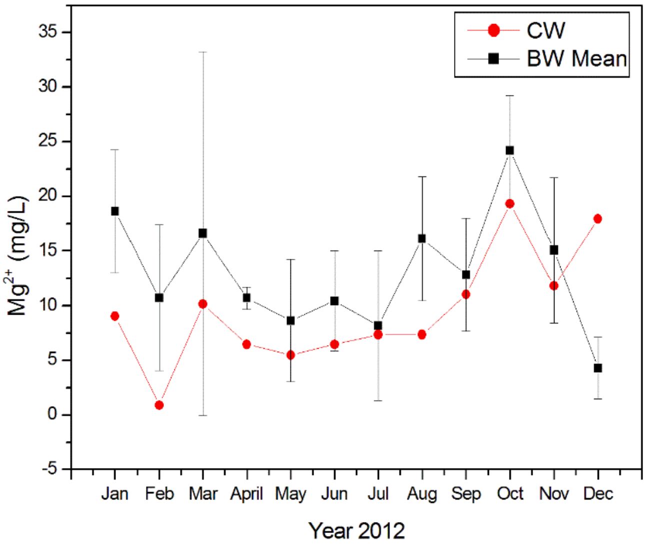

Figure 3.19: Monthly variation of magnesium (Mg^{2+}) of control well (CW) and bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In January 2012, the bore wells have magnesium ion 18.6±5.6 mg/L. It decreases to 10.7±6.7 mg/L in February 2012 and again upswing to 16.6±16.6 mg/L. After that, slightly fall down May and April months of year 2012. From April to October 2012 an irregular zigzags pattern is recognizable from the graph (Figure 3.19) having maximum magnesium concentration of 24.2±5 mg/L in October, as seen in monthly mean of dug wells. Magnesium concentration falls to 15.1±6.6 mg/L in November and reaches the minimum concentration (4.3 ±2.8 mg/L) of the year in December 2012. Bore wells have an annual mean of 13±7 mg/L, with CI having confidence interval at 95% significant level of 8.7 mg/L to 17.3 mg/L.

3.2.10 Sodium (Na^+)

During the first few months starting from January 2012 to May 2012 the control well and monthly mean of dug wells shows similar trend for Na^+ concentration. Highest concentration during the pre-monsoon period is 78.3±58.8 mg/L reported in March 2012 for dug wells and 72.4 mg/L for control well. The control well has annual mean of 53.4±12.1 mg/L and confidence interval with 95% significance level of 60.9 mg/L - 46 mg/L. For dug wells lowest concentration of Na^+ in the year 2012 is observed in May (49.2±44.7 mg/L). In the beginning of monsoon Na^+ concentration increase to 52.8±36.5 mg/L in June 2012 and reaches the maximum concentration (78.1±103.2 mg/L) again in July 2012. This outsized standard deviation in July is due to the variability in sodium content in between different dug well sources of the study area during monsoon season. From August 2012 onward Na^+ decrease gradually with 59.3±48.8 mg/L in October 2012 and then a slight increase is noticeable till it reaches 78.7±69 mg/L in December 2012. The annual mean of dug wells is 64.25±59.34 mg/L with a confidence interval, CI of 27.7 mg/L – 100.8 mg/L (95% significant level).

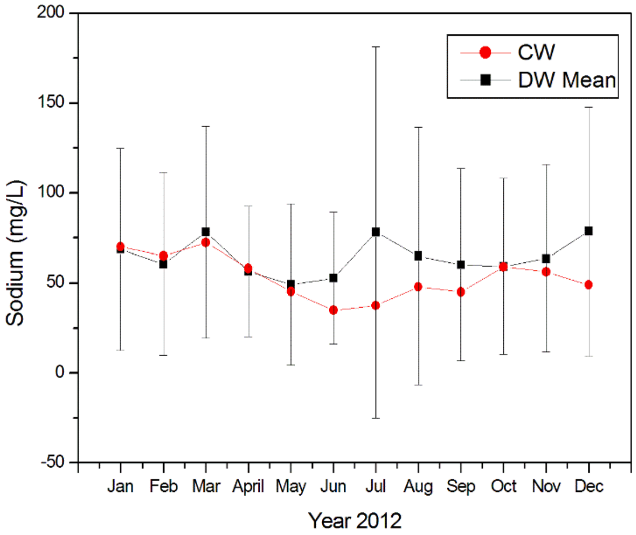

Figure 3.20: Monthly variation of sodium (Na^+) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Bore wells have a high sodium concentration in January 2012 (84.4±72.2 mg/L) which is gradually decreases to the minimum concentration of the year 2012 in March (32.90±30.9 mg/L). It then increases to maintain a steady concentration for the next two months and then drops to 48.37±28.9 mg/L in June 2012. During the course of monsoon period Na^+ increases gradually to attain a maximum of 89±35 mg/L in August 2012. For both dug well and bore well strata, sodium concentration is found maximum during monsoon period. In September 2012, Na^+ decreases to 46±8.7 mg/L and gradually reaches 86.2±88 mg/L with extreme variations between stations in December 2012. The annual mean for concentration of sodium in bore wells during the study period is 62.5±45 mg/L, with confidence interval of 34.9 mg/L - 90.1 mg/L in 95% significant level.

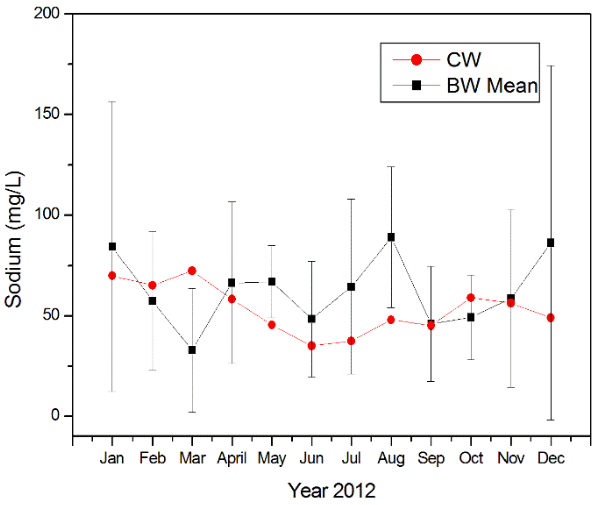

Figure 3.21: Monthly variation of sodium (Na^+) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

3.2.11 Potassium (K^+)

The source of potassium in groundwater is from of potash feldspar and usually they are resistant to chemical weathering[23]. Annual mean of potassium for control well is 12.3±3.5 mg/L with confidence interval of 95% significant level from 10.1 mg/L – 14.4 mg/L. According to WHO[6] standards the desirable limit of potassium in drinking water is up to 12 mg/L and control well has exceed this limit in pre-monsoon and post-monsoon periods. Potassium is high in control well compared to both dug well and bore well strata.

The concentration of potassium in dug wells and bore wells follows to some extent a similar trend. From January 2012 onwards dug wells shows a gradual increase in potassium concentration till May 2012 with a maximum of 13±6.3 mg/L. Concentration of potassium is decreases in monsoon season (8±4.4 mg/L in June, 2012) with minimum oscillation in the following months with a slight increase to 8.8±7.8 mg/L in December 2012. The dug wells have annual mean of 8.4±4.9 mg/L with CI of 5.4 mg/L - 11.4 mg/L at 95% significant level.

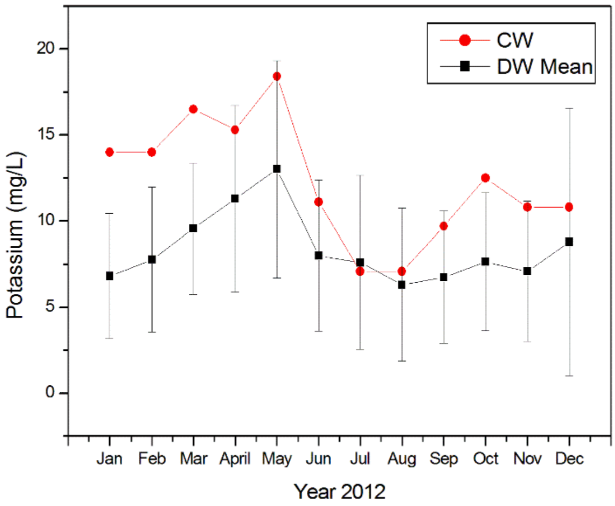

Figure 3.22: Monthly variation of potassium (K^+) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

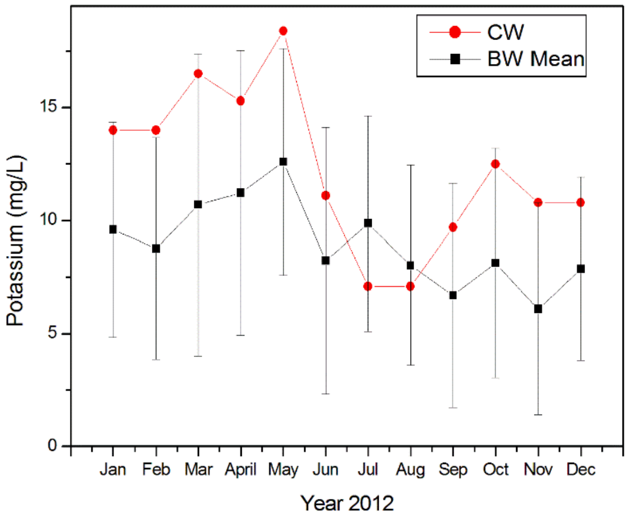

Figure 3.23: Monthly variation of potassium (K^+) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

In the case of bore wells, the annual mean for the study period is 9±5.2 mg/L with a CI of 5.8 mg/L – 12.2 mg/L at 95% level of significance. It has a maximum concentration of potassium of 12.6±5mg/L in May 2012 and minimum 6.1±4.7 mg/L in November 2012.

3.2.12 Bicarbonate (HCO_3^-)

In fresh water, the most abundant anion found is bicarbonate[2]. High content of HCO_3^- in the groundwater source is an evidence for the nature of water sources is having fresh quality in natural coastal environmental condition. The desirable limit for bicarbonate in drinking water suggested by WHO[6] is 500 mg/L. Control well have annual mean of 195.5±27.3 mg/L with a confidence interval of 178.8 mg/L – 212.3 mg/L at 95% level of significance.

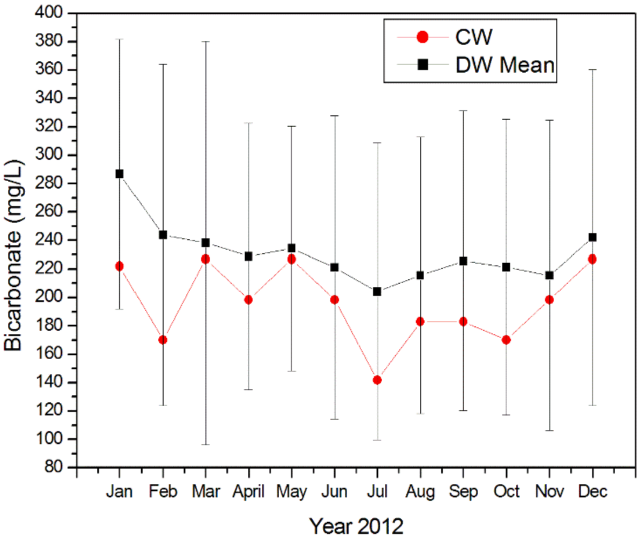

Figure 3.24: Monthly variation of bicarbonate (HCO_3^-) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

For dug wells January, 2012 has the maximum bicarbonate concentration with a monthly mean of 286.8±94.8 mg/L. Higher concentration of HCO_3^- in groundwater expect a dominance of mineral dissolution[24]. Then February to March 2012 it decreases gradually and slightly increase in May 2012 to 234.4±86.1 mg/L. But during May 2012 the concentration again decrease reaching the minimum bicarbonate of 204.2±104.6 mg/L in June 2012. July and August 2012 witness an increase in bicarbonate nevertheless a minor drop in bicarbonate seen in following months till November 2012 (215.5±109.2 mg/L). In December 2012 concentration of bicarbonate rises to 242±118.3 mg/L. The annual average of bicarbonate content in dug wells are 231.5±107.9 mg/L at 95% significant level of 165.1 mg/L – 297.8 mg/L confidence interval.

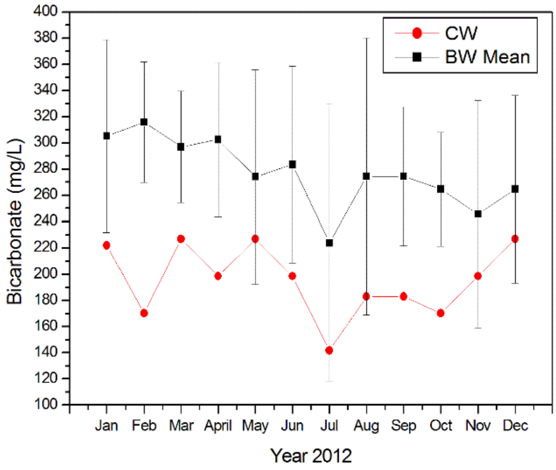

Figure 3.25: Monthly variation of bicarbonate (HCO_3^-) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

In the case of bore wells, maximum bicarbonate concentration is observed during February 2012 (315.9±46.1 mg/L). From the graph (Figure 3.25) it is clear that a wavering nature along with decreasing trend is observable till a minimum concentration of the study period, 204.2±104.6 mg/L in July 2012 is reached. But during August 2012 bicarbonate increases to 274.5±105.7 mg/L and maintained the same monthly mean in September also with slight differences between the different sources. A gradual decrease in concentration is noticed till November (245.8±86.7 mg/L), but attains 264.7±71.4 mg/L in December 2012. Annual mean of bicarbonate in deep bore wells during the study period is 277.2±73.5 mg/L with CI of 322.4 mg/L – 232 mg/L at 95% significant level.

3.2.13 Chloride (Cl^-)

Chloride is usually derived from non-lithological origin[23] it is the most abundant anion found in sea water[25]. The control well has annual mean of chloride concentration 45.6±20.1 mg/L, with very low concentration of 3.1 mg/L and 6.3 mg/L observable in May and June 2012 respectively. The confidence level at 95% significant level for control well is 58 mg/L - 33.3 mg/L which is below the desirable limit for chloride recommended by WHO[6] guide lines of 250 mg/L.

From the graph (Figure 3.26) it is clear that for dug wells, July and August 2012 has maximum mean and out ranging standard deviation (85.6±164.4 mg/L and 86.8±155.7 mg/L respectively) inferring wide variation in chloride concentration between different shows dug well sources during monsoon. This higher concentration of chloride ion is because of the influence of marine environment over this coastal aquifer as the proximity of sea and back waters in the study area is evident for the marine origin of Cl^-. Also high solubility of chloride ions facilitates to mix readily with the fresh groundwater sources. The annual mean of chloride in dug wells are 65.5±83.6 mg/L, with a confidence interval of 14.1 - 116.9 mg/L at 95% significant level.

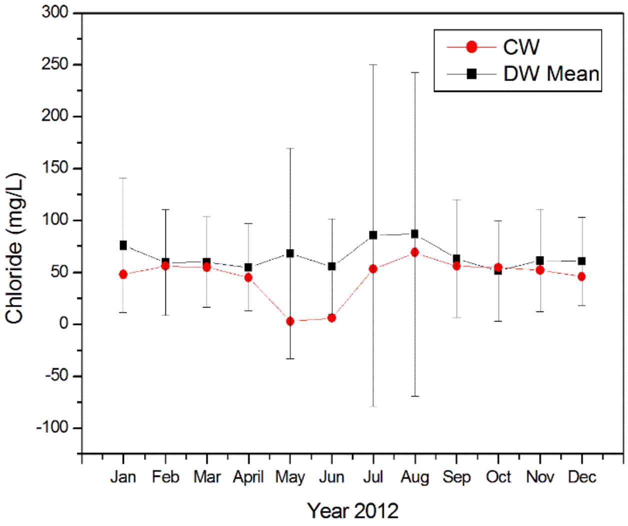

Figure 3.26: Monthly variation of chloride (Cl^-) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

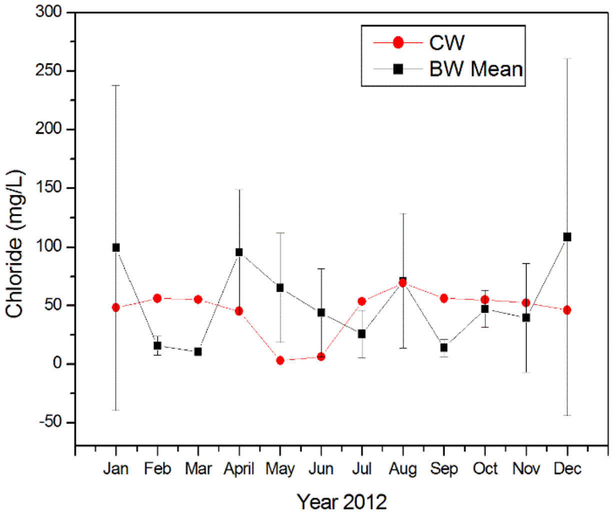

Figure 3.27: Monthly variation of chloride (Cl^-) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Bore wells depicts very uneven distribution of chloride concentration throughout the study period (Figure 3.27) being the lowest concentration of 10.6±3.2 mg/L in March 2012 and highest chloride content of 108.4±152.2 mg/L in deep groundwater sources during December 2012. The bore wells have chloride with annual mean of 53±67.7 mg/L with 11.3 mg/L – 94.7 mg/L of confidence interval at 95% level of significance.

3.2.14 Sulphate (SO_4^{2-})

Sulphate is found in groundwater usually from weathering of sulphate minerals present in sedimentary rocks. In natural conditions, groundwater may contain 2 to 80 mg/L sulphate[26].

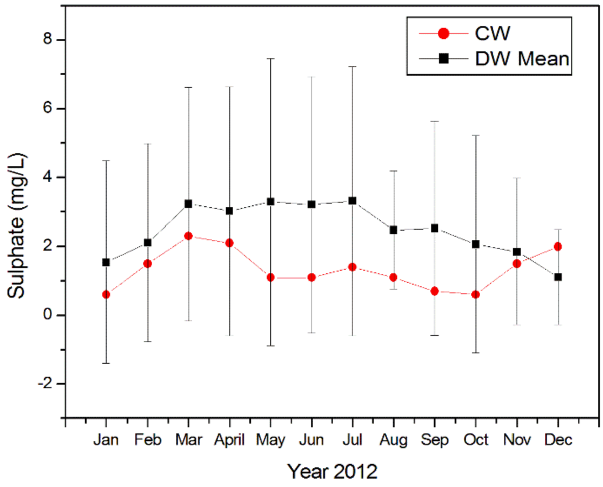

Figure 3.28: Monthly variation of sulphate (SO_4^{2-}) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

According to BIS[5] standard, the desirable concentration of sulphate in drinking water must be within 200 mg/L and that of WHO[6] is 250 mg/L. In the Alappad coast the amount of sulphate is very low throughout the study period. The control well has annual mean of 1.3±0.6 mg/L.

The control well have less sulphate compare to the dug well strata but more than that of the bore wells. The dug wells has a concentration of sulphate 1.5±2.9 mg/L in January 2012 that gradually increases till March 2012 with a maximum monthly mean of 3.3 ±4.2 mg/L. This condition sustains to July 2012, there after decreases with minimum concentration reported in December 2012 (1.1±1.4 mg/L). The annual mean of dug wells during the study period is 2.5±3.1 mg/L with confidence interval of 0.6 mg/L – 4.4 mg/L at 95% confidence interval.

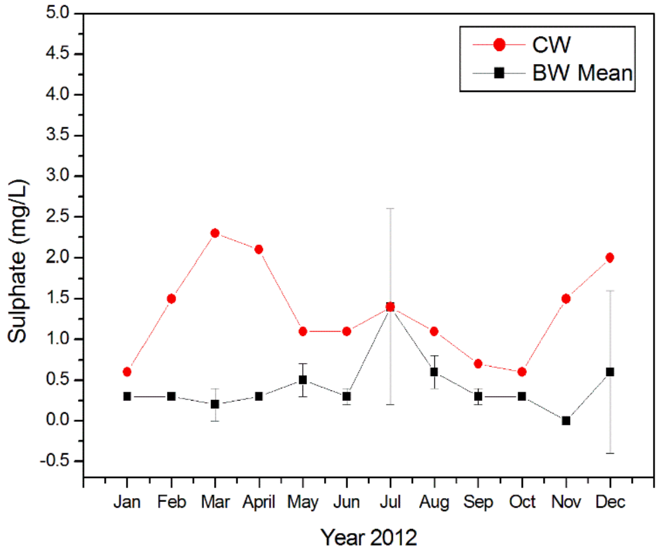

Figure 3.29: Monthly variation of sulphate (SO_4^{2-}) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Sulphate concentrations in bore wells are negligible amount throughout the study period. A maximum concentration of 1.4±1.2 mg/L is observed in monsoon period during July 2012 that reaches the sulphate concentration in control well in the same month. This may be infer as during monsoon season along with the downward motion of water, sulphate spreads more or less uniformly irrespective of vertical stratification. The annual mean of bore wells is 0.4±0.5 mg/L with 0.1 mg/L – 0.7 mg/L confidence level at 95% level of significance.

3.2.15 Phosphate (PO_4^{3-})

Phosphorus is present in water as orthophosphate ion or phosphate (PO_4^{3-}). Under natural condition, phosphate reaches groundwater through weathering of sedimentary rocks containing phosphate minerals and through anthropogenic intervention by the addition of chemical fertilizers and manures. These phosphates beyond the adsorption capacity of soil particles will dissolve with the percolating water and reaches the groundwater[27].

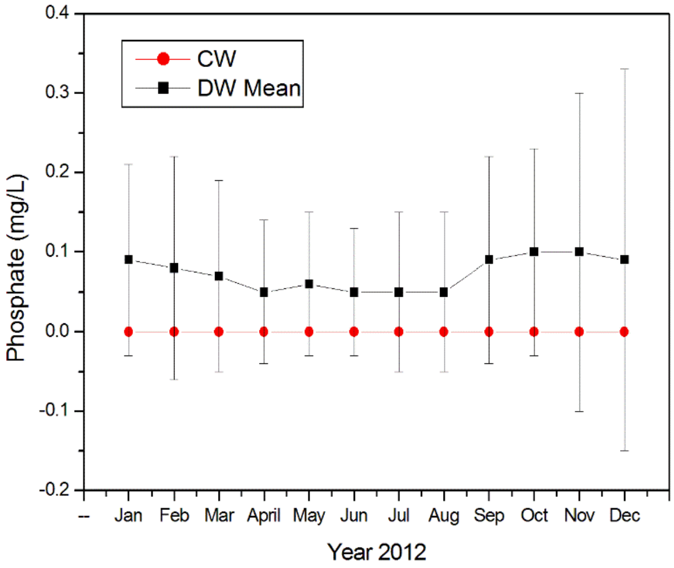

Figure 3.30: Monthly variation of phosphate (PO_4^{3-}) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

In control well, there is no phosphate even though other dug wells have shown very minute concentration of monthly mean up to 0.1 mg/L. The annual average of phosphate for shallow dug well sources is 0.1±0.1 mg/L with confidence interval, CI of 0 – 0.2 mg/L at 95% significant level. Phosphate is absent in bore wells, as adsorption and mineralization leads to immobilisation of phosphate that in turn limits its movement within or below the root zone. This prevents this nutrient to infiltrate through soil and reach the deep groundwater aquifers.

3.2.16 Nitrate (NO_3^-)

Nitrate in groundwater is generally from a non-lithological source that can be attributed to fertilizers and sewage waste. Nitrate is used as an indicator of groundwater pollution as it is highly soluble in water and non-reactive under oxidizing conditions[28]. Ingestion of nitrate by infants cause methemoglobinema, a disease results from low oxygen level in blood[29]. Monitoring of nitrate in groundwater is inevitable for the long-term management of water resources.

The control well has annual mean of nitrate concentration 0.9±0.3 mg/L with a confidence interval of 0.7 mg/L –1.1 mg/L at 95% level of significance. For dug wells most of the months, nitrate concentration is below detectable limit and the high standard deviation is due to the variation in nitrate distribution among sampling locations. Concentration of nitrate is minimum in July 2012, with a monthly mean of 0.2±0.6 mg/L for dug well strata and not detectable in control well. This may be due to monsoon dilution of nitrate. In the case of bore wells, nitrate is not identified throughout the study period supporting that nitrate has not entered the deep aquifers of study area.

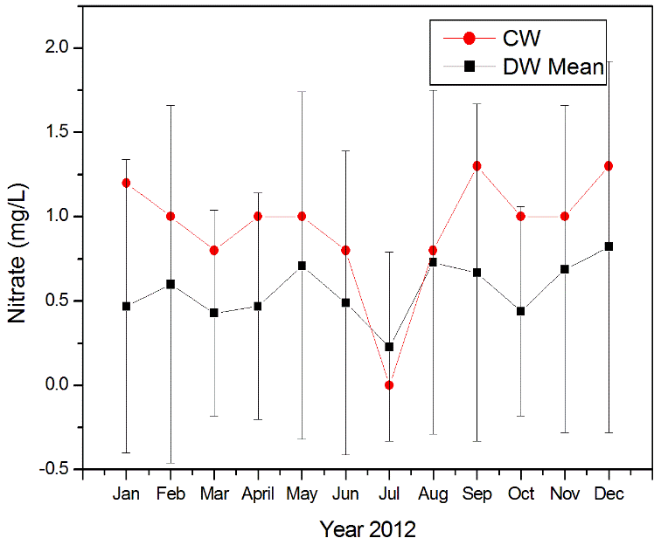

Figure 3.31: Monthly variation of sodium (NO_3^-) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

3.2.17 Iron (Fe)

The ecological effects of iron contamination not only include the chemical toxicity but also iron act as a mediator on geochemistry of other potentially toxic metals present in the soil or water. When bound with iron, Selenium, a rare earth element found in and around the study area can form a poorly soluble complex during rainy season[30].

Iron is not detected in the control well throughout the study period. Only few dug wells sources show the presence of iron but in insignificant concentration. The high standard deviation infers the wide variation in iron concentration among the dug well sources. The annual mean of iron in dug wells is 0.06±0.1 mg/L.

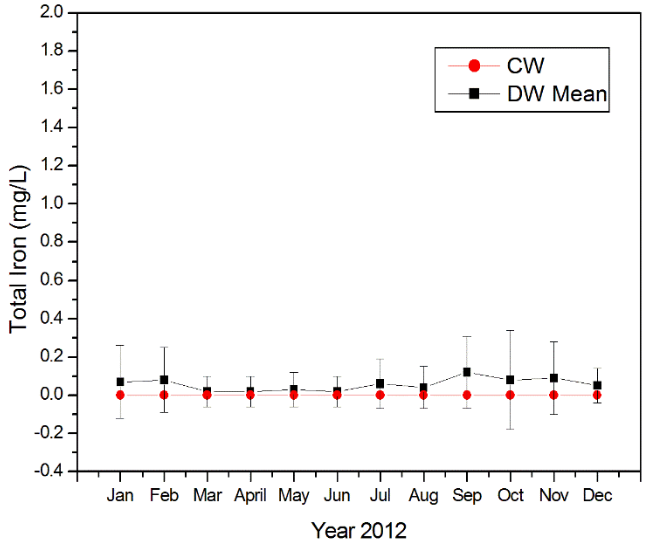

Figure 3.32: Monthly variation of iron (Fe) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

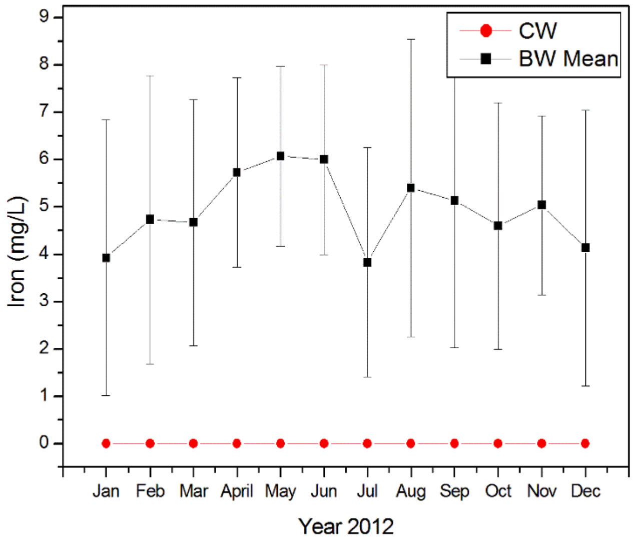

Figure 3.33: Monthly variation of iron (Fe) of control well (CW) and deep bore well (BW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Bore wells displays high iron content, exceeding the permissible limit (0.3 mg/L) prescribed by BIS standard[5] (BIS, 2012) throughout the study period. A minimum range of 3.9±2.9 mg/L is noticed in January 2012 which rises to 4.7±3.0 mg/L in February 2012 and remained same till March 2012. The concentration gradually increases during April 2012 and reaches a maximum of 6.1±1 and 6.0±2 mg/L in May and June 2012 respectively. In July 2012 the iron concentration falls to 3.8±2.4 mg/L but uphold 5.4±3.14 mg/L in August 2012 and remains in the comparable trend until December 2012 with a monthly ion concentration of 4.13±2.9 mg/L. The annual mean of iron during the year 2012 is 4.9±2.6 mg/L, with a confidence interval, CI of 3.3– 6.5 mg/L, at 95% significant level.

Exposure of pyrite to oxygenated water or contact of ferric-oxide or hydroxide minerals with reducing substances can cause high iron concentration in groundwater[31]. A concentration of iron greater than 0.3 mg/L leads to staining of clothes, fixtures in plumbing, encrustation of well screens, and plugging of pipes. Excessive quantities can stimulate growth of iron bacteria[32].

3.2.18 Dissolved Oxygen (DO)

Monitoring and assessment of dissolved oxygen (DO) is significant as it plays a major role in physical and biological processes prevalent in water[33]. It controls the solubility of many naturally occurring polyvalent trace elements and regulates them in groundwater[8]. In water containing sufficient DO, the concentration of iron is noted within the limit of drinking water quality standards as it precipitated to iron oxyhydroxides. These oxyhydroxides are found to act as important heavy metal absorbents[34].

DO is also an important geochemical oxidant. It is utilized in weathering mechanism such as oxidation of the ferrous silicates[35].

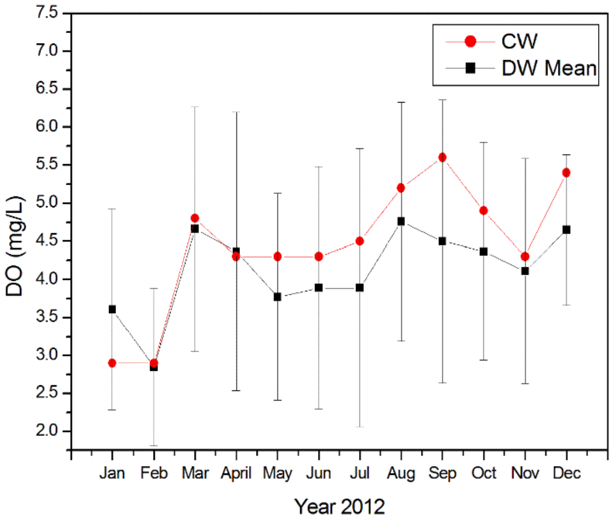

Figure 3.34: Monthly variation of dissolved oxygen (DO) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012

Control well has an annual mean of dissolved oxygen 4.5±0.9 mg/L, with a confidence interval CI of 3.9– 5.0 mg/L, at 95% level of significance. The dug wells have annual DO of 4±1.52 mg/L, with a confidence interval of 3.2 – 5 mg/L, at 95% level of significance. Low DO level (< 3 mg/L) make the water unfit for drinking purposes.

The bore wells show a gradual increase in DO from January 2012 (1.7±1.5 mg/L) to March 2012 (2.9±0.8mg/L) and regularly decreases to 1.6±0.2 mg/L in May 2012. A slight increase is observed in July 2012 with a monthly mean of 2.1±1.8 mg/L but falls to 1.8±0.8 mg/L. After that, a progressive increase in the subsequent months till November 2.7±1.7 mg/L is seen finally 1.6±1.3 mg/L in December 2012. The annual mean of DO in deep bore wells is 2.1±1.3 mg/L, with confidence interval of 2.9 - 1.3 mg/L at 95% significant level.

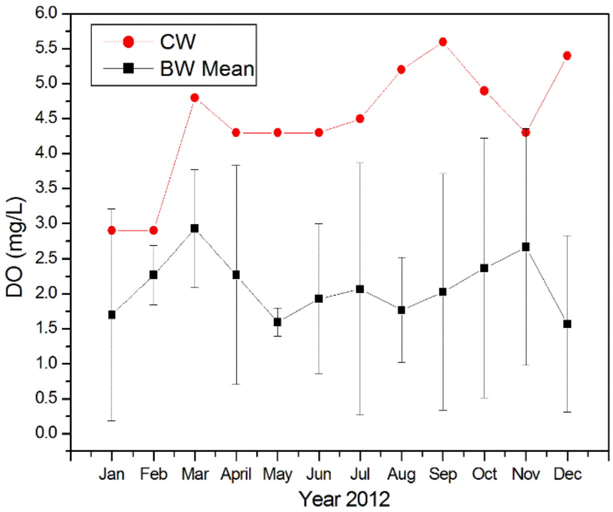

Figure 3.35: Monthly variation of dissolved oxygen (DO) of control well (CW) and deep bore well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

3.2.19 Biological Oxygen Demand (BOD)

Biological oxygen demand (BOD) is a measure of bacterial load in water and it is linked to the oxidation of biodegradable organic materials[36]. BOD is also considered as an indicator of contamination of water through human and animal waste[37].

The control well has annual mean of 0.26±2.04 mg/L and this unusually large standard deviation infer the temporal and special variability in BOD concentration. The dug wells have a high BOD concentration of 7.9±6.9 mg/L in January 2012 exceeding the permissible limit for BOD is 5 mg/l prescribed by WHO[6]. However, the annual mean of BOD is low, 4.12±1.5 mg/L with a confidence interval CI of 1.4 - 5.4 mg/L, at 95% significant level.

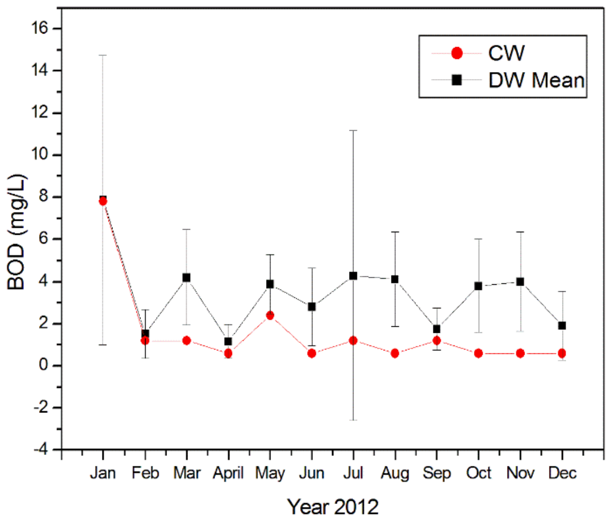

Figure 3.36: Monthly variation of biological oxygen demand (BOD) of control well (CW) and dug well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

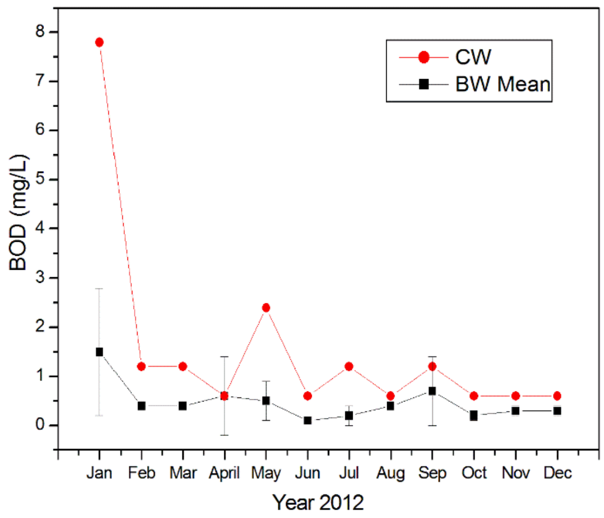

Figure 3.37: Monthly variation of biological oxygen demand (BOD) of control well (CW) and deep bore well (DW) water sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

The bore wells display notably low BOD compare to shallow groundwater sources. The annual mean of BOD is 2.1±1.3 mg/L, well within the permissible limit recommended by WHO standards with a confidence interval of 0.2 – 0.8 mg/L, at 95% level of significance. This low concentration of BOD in deep bore well sources can be attributed to low organic loads[38].

3.3 Hydrochemical Facies and Water Types

Hill-Piper Trilinear diagram consist of a combination of anion and cation equilateral triangles that lies on a common baseline. The diamond plot between these anion and cation triangles is used to designate different water types [21,39-40]. The relative proportion of each cations and anions are plotted in percentages and the concentrations are expressed in milliequivalent per litre. These relative proportions of cation-anion combination of particular water samples are intertwined in the diamond plot and gives specific water types based on the prominent hydrochemical facies. The piper classifies water into four basic types according to their position near the four corners of the diamond plot. Water with a plot at the top corner of the diamond is the permanent hardness water type with high Ca^{2+} + Mg^{2+} and high Cl^- + SO_4^{2-} concentration. The water plots near left corner are rich in Ca^{2+}, Mg^{2+} and HCO_3^- and are a character of temporary hardness. Alkali carbonate water type is showed at the bottom corner of the plot (Na^++ K^+ and HCO_3^- + CO_3^{2-}) and the plot near the right corner represents saline water type (Na^++ K^+ and Cl^- + SO_4^{2-})[21]. Hence the four facies of hill-piper trilinear plot are as follows:

i) Facies I: Ca^{2+}-Mg^{2+}-HCO_3^- (*Temporary hardness type)*
ii) Facies II: Na^+-K^+- Ca^{2+} -HCO_3^- *(Alkali Carbonate type)*
iii) Facies III: Na^+-K^+-Cl^--SO_4^{2-} (*Saline type*) and
iv) Facies IV: Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-} (*Permanent hardness type)*

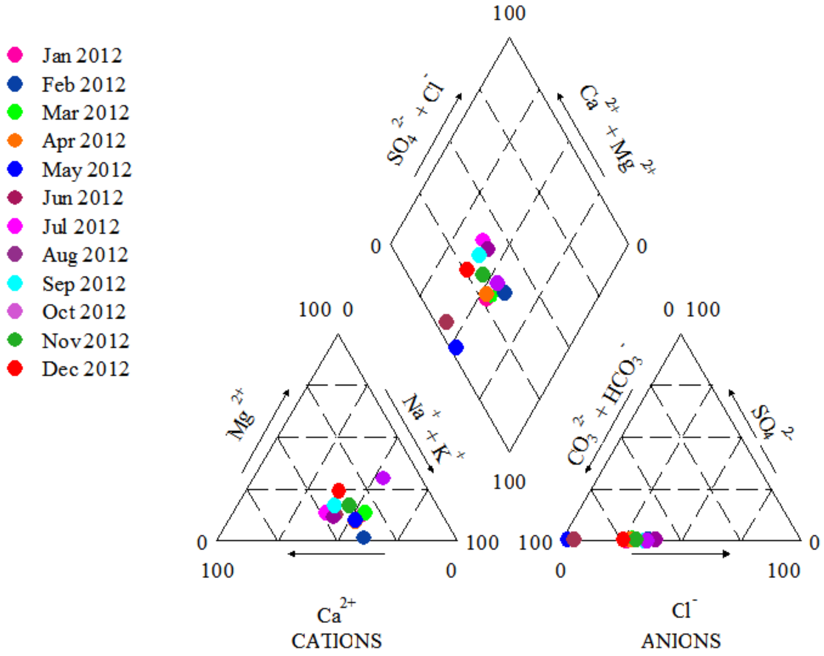

Figure 3.38: Hill-Piper trilinear plot for control well (CW) along the Alappad coast, Kollam, Kerala, India during the year 2012.

From the Hill-Piper trilinear plot, it is clear that control well (CW) in the year 2012 about 50% (Six months) of the monthly data comes in *Temporary Hardness water type*. Specifically the months June, July, August, September, November and December 2012, falls near the left corner of the diamond plot. This implies, the hydrochemical facies during these months are Ca^{2+}- Mg^{2+}- HCO_3^-. During these months no cations exceeds 50% of the total cation concentrations and all of them have more than 50% bicarbonate out of total anion concentration. The rest of the months, that is, January, February, March, April, May and October 2012 data are spread in the non-dominant area of the diamond plot, with sodium type cations to bicarbonate anion type. Here no specific water type can be distinguished as the sodium is more dominant than calcium, but not in considerable proportion so it holds a mixed type (Ca^{2+}- Na^{+}- HCO_3^-). But the overall hydrochemical facies (mean) of control well in the year 2012 is **Ca^{2+}- Mg^{2+}- HCO_3^-** and the water type being *Temporary Hardness water type*, with non-dominant cation to bicarbonate anion type water. The relative proportion of cation concentration are Na^{+} (48%), Ca^{2+} (38%), Mg^{2+} (12%) and that of anion concentration are HCO_3^- (71.5%), Cl^- (28%) and with a very negligible amount of sulphate.

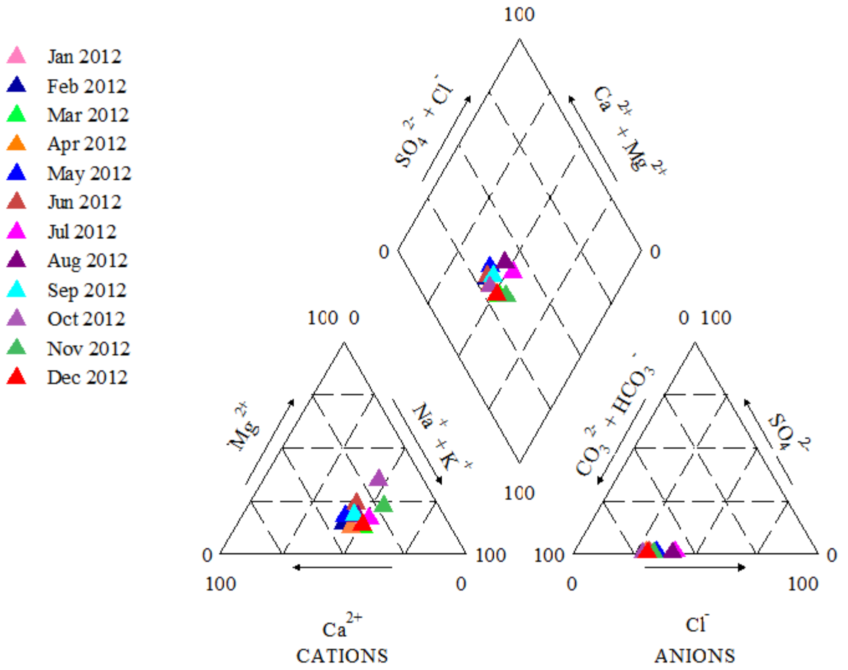

Figure 3.39: Hill-Piper trilinear plot for shallow dug well (DW) sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Most of the dug wells fall in *temporary hardness water type* with non-dominant cations and bicarbonate anion type water. In January, February, April, May, June, August, September and October 2012 no cations exceeds 50% of the relative proportion of total cation concentration, whereas all the months show dominants of bicarbonate over other anions. But in March, July, November and December 2012 the water type shifts slightly to a mixed or field of diamond plot. During these months the relative proportion of concentration of sodium is more than 50% of the total cations concentration compared to rest of the months. The relative percentage of sodium in March 2012 is 52%, July (51%), November 2012 (56%) and December (51%). This slight increase in sodium during these months leads to a swing in the water type to mixed water type (Ca^{2+}- Na^{+}- HCO_3^{-}). The prominent hygrochemical facies of shallow dug wells during the study period is **Ca^{2+}- Mg^{2+}- HCO_3^{-}** with *Temporary Hardness water type.* The annual mean of cations are in the order Na^{+} (48%)> Ca^{2+} (33%) > Mg^{2+} (19%) and anion are HCO_3^{-} (68%)> Cl^{-} (31%)> SO_4^{2-} (1%).

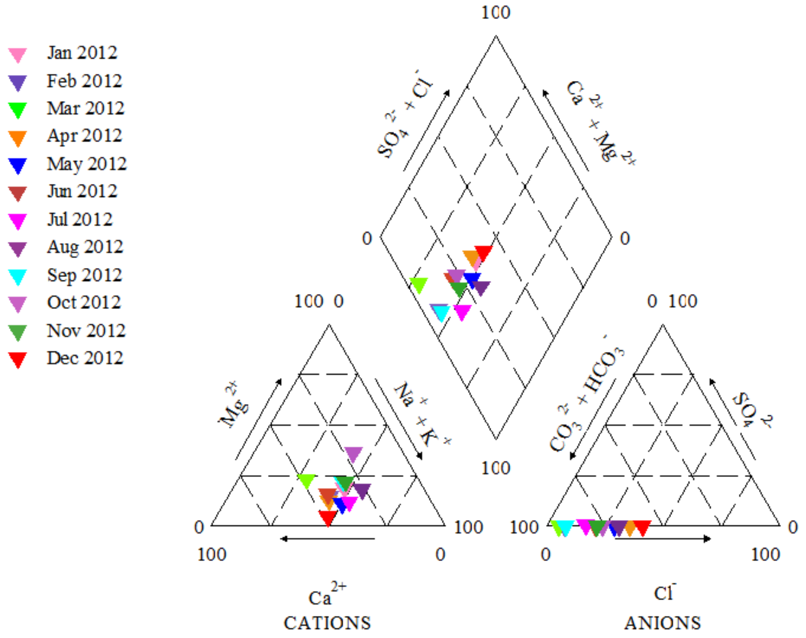

Figure 3.40: Hill-Piper trilinear plot for the deep bore well (BW) sources along the Alappad coast, Kollam, Kerala, India during the year 2012.

Deep bore wells in most of the months fall in the left corner of the diamond plot, central inverted triangle in cation triangle and left corner of the anion triangle. All these leads to the conclusion that bore well strata come in *temporary hardness water type* with non-dominant cations to bicarbonate anion water during most of the study period. But during July and August 2012, mixed water type (Ca^{2+}- Na^{+}- HCO_3^{-}) exhibits with sodium type cation but bicarbonate type anion water. This temporary shift in hydrochemical facies is attributed to the interaction of water with the aquifer[41]. The hydrochemical facies of annual mean of bore wells during the year 2012 is **Ca^{2+}- Mg^{2+}- HCO_3^{-}**, with *Temporary Hardness water type.* The relative percentages of cations are in the order Na^{+} (45%), Ca^{2+} (38%) and Mg^{2+} (17%) whereas the anions are HCO_3^{-} (75%) and Cl^{-} (25%) with a negligible proportion of sulphate.

The overall hydrochemical facies of both dug well and bore well strata suggests the dominance of bicarbonate in the groundwater throughout the study period. This leads to propose that under the natural environment pertain in the hydrogeological settings, the groundwater actually originate from fresh water source which is altered subsequently due to recurrent marine activities in the hydrogeological system.

3.4 Gibb's Diagram

It is known that the relationship and interaction between groundwater and the aquifer formed minerals shapes the water quality[42]. Gibbs[43] (1970) proposed a diagram that represents the interaction and controlling mechanisms of groundwater chemistry. The mechanisms controlling the water chemistry are classified into three types: Evaporation dominance, rock dominance and rainfall dominance. The Gibbs plot illustrates the ratios for dominant anions and cations plotted against the TDS.[44]

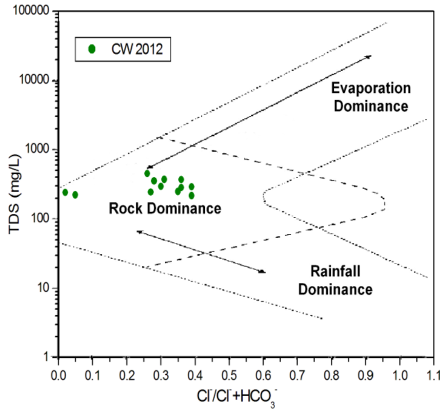

Figure 3.41: Gibbs a for control well (CW) in the Alappad coast, Kollam, Kerala, India, during the year 2012.

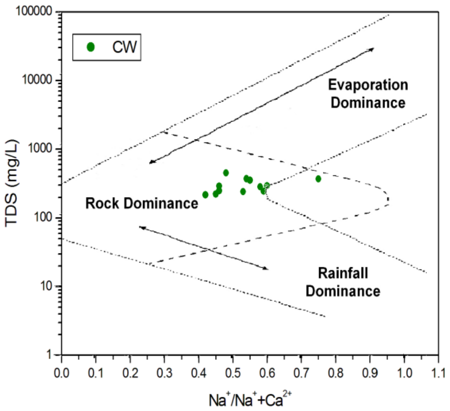

Figure 3.42: Gibbs b for control well (CW) in the Alappad coast, Kollam, Kerala, India, during the year 2012.

Gibbs diagram (Figure 3.41 & Figure 3.42) for control well shows that all the months fall in the rock dominant area reveals rock-water interaction form the hydrochemistry of the water. The anion ratio is less than 0.5, indicating the low concentration of chloride ions and high concentration of bicarbonates. This means the study area is predominantly dominated by dissolution of rock forming minerals.

The dug wells also fall in the rock dominant field of Gibbs plot revealing the rock dominant nature of water. The sources of mineral constituents in water are mainly contributed from the dissolution of rock through which water percolates. In the case of bore wells, in July 2012 high TDS value shifts to evaporation dominant field of the Gibbs diagram. The evaporation dominance of the water can be attributed to the mixing of sea water[45].

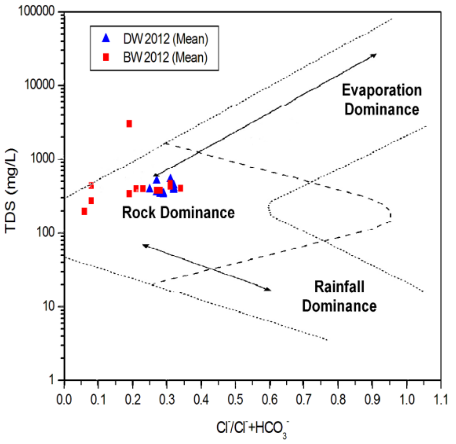

Figure 3.43: Gibbs a for dug wells (DW) and bore wells (BW) in the Alappad coast, Kollam, Kerala, India, during the year 2012.

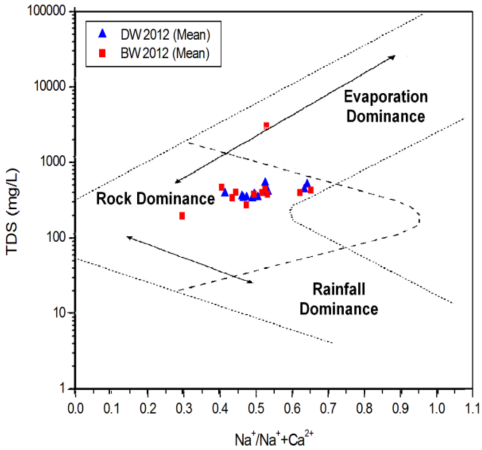

Figure 3.44: Gibbs b for dug wells (DW) and bore wells (BW) in the Alappad coast, Kollam, Kerala, India, during the year 2012.

3.5 Major Ionic Ratios in Groundwater

Water does not exist in its pure form when it comes in contact with the lithosphere as it can dissolve many ionic compounds and salts. The water chemistry of natural system is very complex to explain and description of hydrology under dynamic natural environment is unlike any controlled conditions in the laboratory can describe only by taking other such systems into consideration such as geology[46]. Major dissolved components of groundwater include cations such as sodium, calcium, magnesium and potassium and anions like bicarbonates, chloride and sulphate. When water percolates and infiltrates through the soil, it reacts with the soil particles in varying degrees depending on the chemical nature of the rock containing minerals and the residence time. Hence there is a considerable interdependence between the water and the natural geological settings for the development of the hydrochemistry of groundwater in a particular region[47]. The processes that can modify the chemistry of groundwater are mineral precipitation, ion exchange and evaporation[48]. In this section of the chapter major ionic interactions are taken into consideration to explain the hydrogeochemistry of the study area.

3.5.1 Sodium versus Chloride

The ratio of sodium to chloride is very useful in order to find the ion exchange process prevailed in the study area. If $Na^+/Cl^- > 1$ and $Na^+/(Na^++Cl^-) > 0.5$, then the calcium from water is exchanged with the sodium from clay and the process is said to be *ion-exchange* whereas the ratio of sodium to chloride is less than one ($Na^+/Cl^- > 1$) then it indicate contamination with brine and the water contains more sodium which is exchanged with calcium from clay minerals. This phenomenon is known as *reverse ion exchange*.

Table 3.5: The ratio of Na^+ to Cl^- of control well (CW), dug well (DW) and bore well (BW) of Alappad coast, Kollam, Kerala, India during the year 2012.

Year 2012	CW Na^+/Cl^-	Inference	DW Na^+/Cl^-	Inference	BW Na^+/Cl^-	Inference
Jan	2.24	IE	1.48±0.5	IE	3.19±3.6	IE
Feb	1.78	IE	1.63±0.5	IE	8.44±7.4	IE
Mar	2.02	IE	1.95±0.8	IE	6.19±7.4	IE
Apr	1.98	IE	1.85±1.2	IE	1.08±0.6	IE
May	2.60	IE	1.68±1.1	IE	2.26±1.5	IE
June	8.57	IE	2.23±2.1	IE	2.27±1.0	IE
July	1.08	IE	1.68±0.7	IE	6.45±7.2	IE
Aug	1.07	IE	1.52±0.7	IE	5.73±7.4	IE
Sep	1.24	IE	1.90±1.6	IE	7.43±6.6	IE
Oct	1.66	IE	1.93±1.3	IE	1.80±1.2	IE
Nov	1.66	IE	1.69±1.2	IE	3.64±3.5	IE
Dec	1.64	IE	1.88±0.9	IE	2.35±2.4	IE
	2.30±2	IE	1.79±1.2	IE	4.24±5.1	IE

**IE – Ion Exchange*

Table 3.6: The ratio of Na$^+$ to Na$^+$+Cl$^-$ of control well (CW), dug well (DW) and bore well (BW) of Alappad coast, Kollam, Kerala, India during the year 2012.

Year 2012	CW Na$^+$/Na$^+$+Cl$^-$	Inference	DW Na$^+$/Na$^+$+Cl$^-$	Inference	BW Na$^+$/Na$^+$+Cl$^-$	Inference
Jan	0.69	IE	0.58±0.1	IE	0.64±0.2	IE
Feb	0.64	IE	0.61±0.08	IE	0.79±0.2	IE
Mar	0.67	IE	0.64±0.09	IE	0.75±0.2	IE
Apr	0.66	IE	0.6±0.14	IE	0.50±0.1	IE
May	0.96	IE	0.59±0.22	IE	0.65±0.1	IE
Jun	0.90	IE	0.59±0.18	IE	0.67±0.1	IE
Jul	0.52	IE	0.61±0.09	IE	0.75±0.2	IE
Aug	0.52	IE	0.58±0.1	IE	0.71±0.2	IE
Sep	0.55	IE	0.6±0.12	IE	0.77±0.2	IE
Oct	0.62	IE	0.62±0.15	IE	0.60±0.2	IE
Nov	0.62	IE	0.59±0.11	IE	0.71±0.2	IE
Dec	0.62	IE	0.62±0.12	IE	0.61±0.2	IE
	0.69±0.1	IE	0.60±0.1	IE	0.68±0.2	IE

**IE – Ion Exchange* ***RIE – Reverse Ion Exchange*

Reverse ion exchange is observed in dug wells near to the proximity of sea especially in station 18 (DW 15) where there is Na$^+$/Cl$^-$ < 1 in most of the months. In the case of bore wells, station 12 (BW 2) shows *reverse ion exchange* during April 2012.

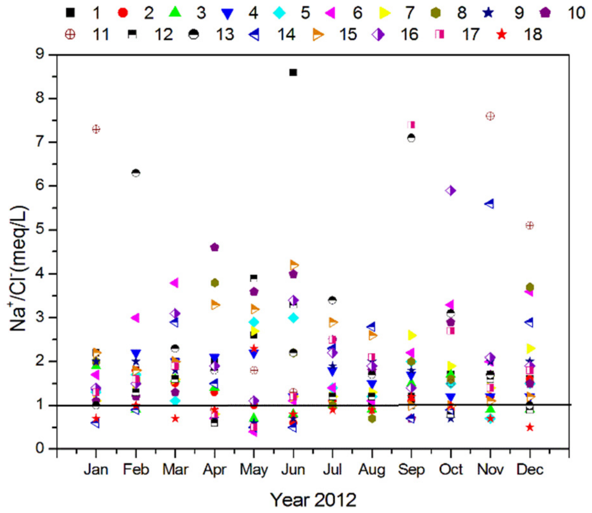

Figure 3.45: Na/Cl for all the individual groundwater sources in each months of year 2012 in Alappad coast, Kollam, Kerala, India.

In Alappad coast the interface between sea water and groundwater is too small because of the geological position of this narrow land between estuary and vast sea on both sides. The up-coning of sea water break this interface and readily mix with fresh water leading to high concentration of sodium and potassium in groundwater aquifers[49]. The average Na/Cl is greater than 1 throughout the study period with intermittent reverse ion exchange in different locations irrespective of seasons suggesting that rainfall does not have direct influence on the concentration except may be as a carrier of sea spray aerosol[50].

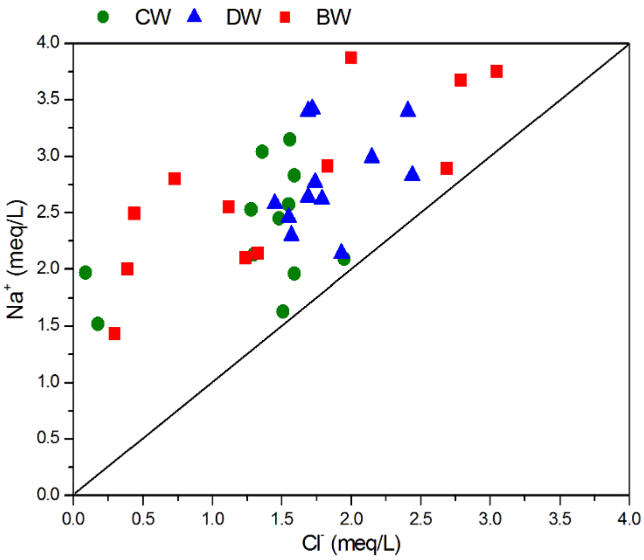

Figure 3.46: Scatter plot Na vs Cl for control well (CW), dug wells (DW) and bore wells (BW) in the Alappad coast, Kollam, Kerala, India during the year 2012

The molar ratio of sodium to chloride is plotted for control well, dug wells and bore wells (Figure 3.46). A non-linear trend is observed for shallow and deep groundwater sources, means both sodium and chloride not simultaneously increased or decreased throughout the study period. All the points fall above the equiline (1:1line) suggesting, Na^+ is excess over Cl^- and hence multiple sources of sodium is identified as silicate weathering of rocks[51]. On the other hand, no additional source for chloride can be considered. If additional sodium comes from the dissolution of halite minerals, the ratio of Na^+ to Cl^- is approximately equal to one.

3.5.2 Revelle's co-efficient and incidences of saltwater intrusion

Fresh groundwater sources contaminated by sea water are a major issue faced by coastal regions all around the world. According to Kallioras, A (2002)[52], the process of sea water intrusion contributes dissolved solids with in groundwater or soil due to any physical or anthropogenic activities. Excessive withdrawal of fresh water as a result of over pumping from potential groundwater sources and subsequent up-coning of seawater is the main reason of seawater intrusion in coastal regions. The incidence of seawater is checked using the ratio of $Cl^-/(HCO_3^- + CO_3^-)^,$ also known as Revelle's co-efficient. According to Revelle (1941)[53], increase in total dissolved solids is not sufficient proof for seawater encroachment. In his paper on the criteria for recognition of sea water in groundwater explains about the three types of modification in the composition of sea water when passes through the soil and reaches the fresh water sources as follows:

1) Modification that affect the proportion between cations along.
2) Modification that affect the proportion between anions along.
3) Modification that affect on both cations and anions equally.

The chloride ion is the most dominant anion in sea water and it is not affected by any of these above mentioned modification. In fresh water the concentration of chloride is very low; hence its increased proportion in fresh water is treated as an indicator of seawater intrusion. On the other hand, the concentration of bicarbonates along with carbonates is negligible in seawater as it is the most plentiful anion in fresh water[54]. So the ratio of chloride to sum of carbonate & bicarbonate is a useful index to check the incidence of seawater intrusion.

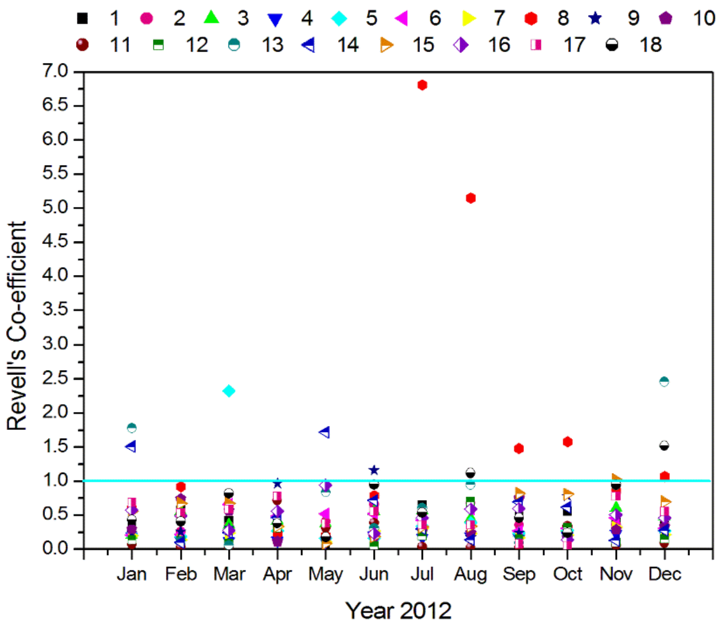

Figure 3.47: Revelle's co-efficient for each groundwater sources in Alappad coast, Kollam, India, during the year 2012

$$\textbf{The Revelle's coefficient R} = \frac{\mathbf{Cl^-}}{\mathbf{CO_3^{2-} + HCO_3^-}}$$

Based on the Revelle's coefficient, Kallergis (1986)[55] classified water into the following classification

Table 3.7: Classification of water based on Revelle's co-efficient

Revelle's coefficient 'R'	Degree of contamination
< 1	Fresh water
1-2	Slightly contaminated water
2-6	Moderately contaminated water
6-10	Seriously contaminated water
10-150	Dangerously contaminated water
>150	Sea water

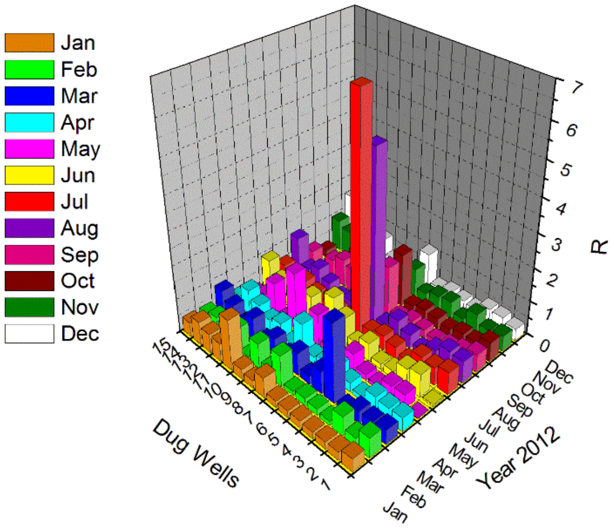

Figure 3.48: Revelle's co-efficient showing the instances of salt water intrusion in shallow dug wells in Alappad coast, Kollam, Kerala, India during the year 2012.

In January 2012, DW 14 and BW 3 have *slight contamination* with R values 1.5 and 1.78 respectively. No incidence of sea water intrusion is reported in February. But in March 2012, DW 5 is *moderately contaminated* with sea water, being R= 2.33 and in May 2012 DW 14 is *slightly contaminated* by saline water intrusion (R=1.72). In June DW 9 has R value 1.2, after that during July to Oct 2012 and in December 2012, DW 8 shows *slight to moderate contamination* due to seawater intrusion. DW 18 also shows moderate contamination by saline water intrusion in

August and December 2012. The rest of the sampling sites are free from saline water intrusion during the study period.

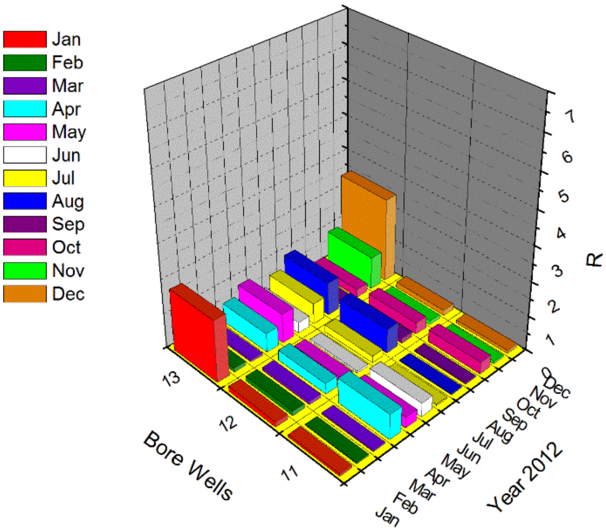

Figure 3.49: Revelle's co-efficient showing the instances of salt water intrusion in deep bore wells in Alappad coast, Kollam, Kerala, India during the year 2012.

The main roots of contamination of coastal aquifers by seawater are over pumping that lowers the water table of freshwater below sea level and the hydraulic continuity of poorly recharged aquifers with sea[56]. From the above observations it can be inferred that even though the entire study area is located in the proximity of brine, the natural hydrodynamics groundwater and seawater is balanced to some extend so that invasion of sea water is restricted.

3.5.3 Calcium Vs Magnesium

The dissolution of calcite and dolomite can be shown by Ca^{2+}/Mg^{2+} molar ratio[57]. Ca^{2+}/Mg^{2+} molar ratio ≤ 1 indicates dissolution of dolomite, whereas higher ratio may represent the contribution through weathering of carbonate and silicate bearing rocks[58]. Almost all the points are above the equiline that indicates $Ca^{2+}/Mg^{2+} > 1$ due to the dissolution of calcite minerals. In addition to this, it is clear from the Figure 3.50 that most of the groundwater sources from the study area are found near or greater than 2 ($Ca^{2+}/Mg^{2+} > 2$), that can be attributed to the dissolution of silicate minerals[59]. However in October 2012, all the groundwater sources irrespective of depth, falls below the equiline and in November 2012 only monthly mean of dug well sources falls on the 1:1 line, evidencing dissolution of dolomite during that period.

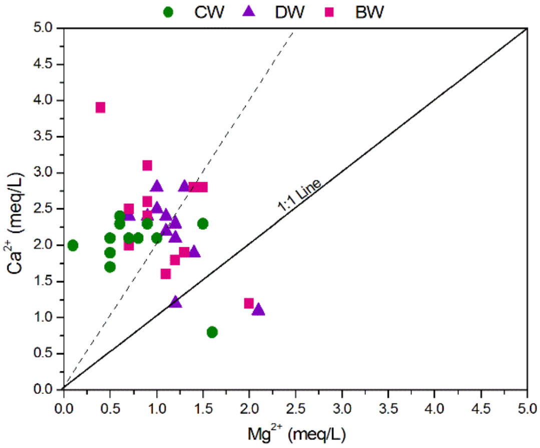

Figure 3.50: Scatter plot Ca^{2+} verses Mg^{2+} for control well (CW), dug wells (DW) and bore wells (BW) in the Alappad coast, Kollam, Kerala, India during the year 2012

3.5.4 Ca^{2+}+Mg^{2+} Versus HCO_3^-+SO_4^{2-}

This plot is also helps to identify the ion exchange process active in the study area. Calcium and magnesium ions in groundwater are attributed to leaching from limestone, dolomites and gypsum bearing rocks[60]. Calcium is also obtained from cation-exchange process where as in coastal areas a high concentration of magnesium ion points to saline intrusion[61].

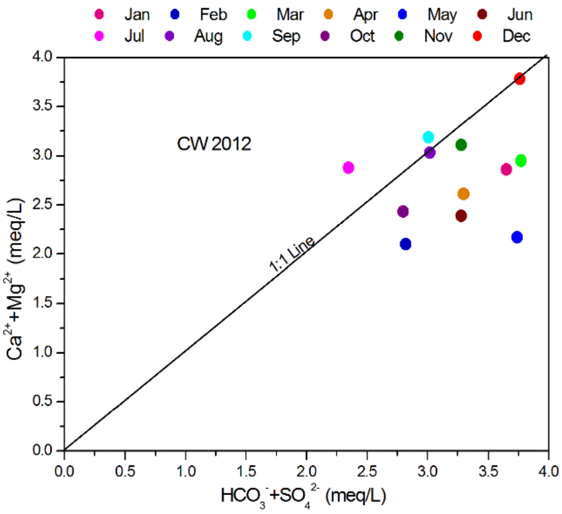

Figure 3.51: Scatter plot for $Ca^{2+}+Mg^{2+}$ verses $HCO_3^-+SO_4^{2-}$ for control well (CW) in the Alappad coast, Kollam, Kerala, India during the year 2012

From the Figure 3.51, it is clear that, control well in most of the month falls below the equiline indicating an excess amount of $HCO_3^-+SO_4^{2-}$. Increase in the concentration of bicarbonate is due to weathering and dissolution of silicate containing rocks. This situation occurs during the dominance of *ion-exchange process* in the study area. But during the months of July and September 2012 the ratio shifts above the equiline due to reverse ion-exchange reaction which leads to excess of $Ca^{2+}+Mg^{2+}$ over $HCO_3^-+SO_4^{2-}$. Increase in calcium and magnesium indicates carbonate weathering of minerals such as calcite, dolomite and gypsum. In August and December 2012 the data falls on the 1:1 line signifying dissolution of carbonate as well as silicate minerals. Also data falls on the equiline insinuations the origin of silicate weathering from igneous rocks[62,63].

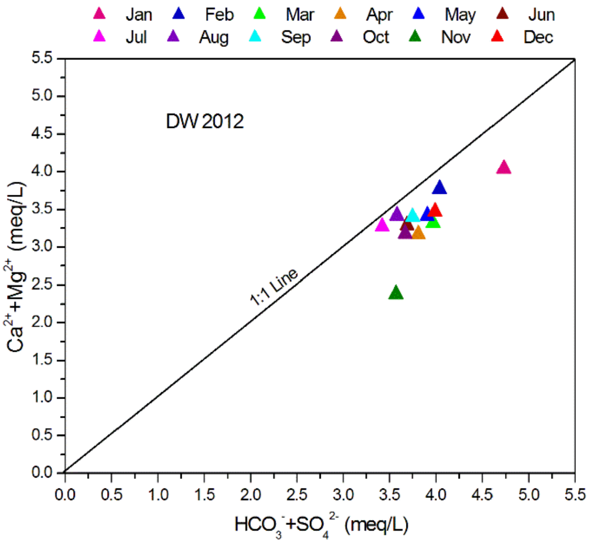

Figure 3.52: Scatter plot for Ca^{2+}+Mg^{2+} verses HCO_3^-+SO_4^{2-} for dug wells (DW) in the Alappad coast, Kollam, Kerala, India during the year 2012

The Figure 3.52 shows the ionic ratio between Ca^{2+}+Mg^{2+} and HCO_3^-+SO_4^{2-} for dug wells. During July and August 2012 the plots are near to 1:1 line which indicates dissolution of carbonate bearing rocks may be responsible for the calcium, magnesium, sulphate and bicarbonate in the shallow dug wells[57]. All other months in the year 2012 shift to the right of the equiline due to excess HCO_3^-+SO_4^{2-} over Ca^{2+}+Mg^{2+}. This happens when there is dominance of ion-exchange process succeed in the study area, along with silicate weathering.

For bore wells (Figure 3.53) all the months shifts to the right side of the equiline except during December 2012. Here ion-exchange reaction is active in the deep aquifers as HCO_3^-+SO_4^{2-} is excess over Ca^{2+}+Mg^{2+}. In December 2012 data falls on the equiline indicates, Ca^{2+}, Mg^{2+}, HCO_3^- and

SO_4^{2} in deep groundwater sources may be derived from the dissolution of carbonate also along with silicate weathering of rocks.

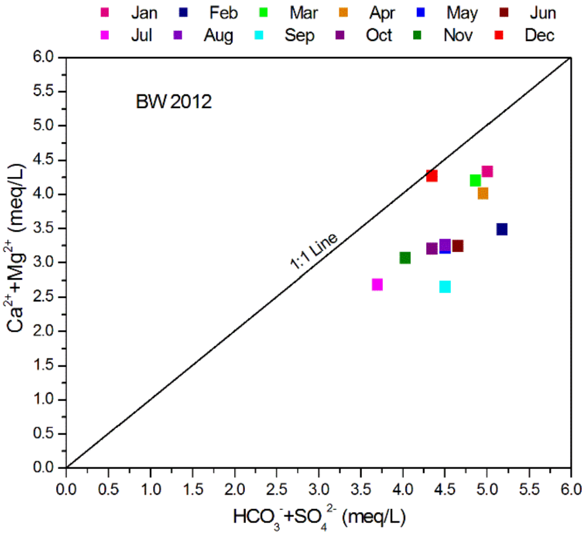

Figure 3.53: Scatter plot for Ca^{2+}+Mg^{2+} verses HCO_3^-+SO_4^{2-} for bore wells (BW) in the Alappad coast, Kollam, Kerala, India during the year 2012

3.5.5 (Na^++K^+) Versus Total Cations

The plot that illustrates the relationship between (Na^++K^+) and total cations (TZ) gives insight to the silicate weathering involved in the geochemistry of the study area. For this, Na^++K^+= 0.5*TZ (1:2 line) and Na^++K^+= TZ (1:1 line) are used to interpret the results[42] Elevation in the concentration of Na^++K^+ may results from weathering of silicate mineral containing rocks[61].

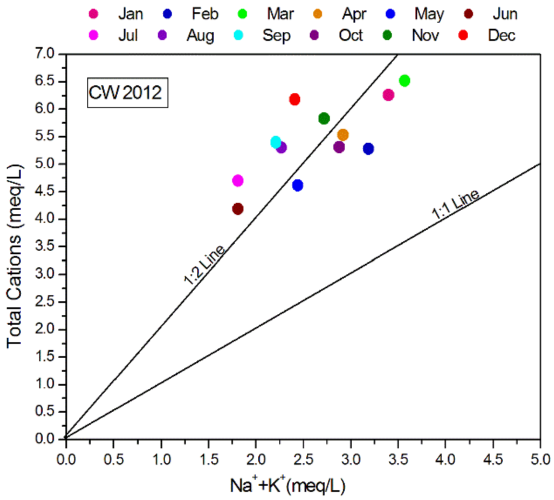

Figure 3.54: Scatter plot for TZ verses Na^++K^+ for control well (CW) in the Alappad coast, Kollam, Kerala, India during the year 2012

In control well all the points are clustered around the 1:2 line, indicates the contribution of cations are from silicate weathering. High ratio of (Na^++K^+) vs total cations are observed for six months as they are plotted above the 1:2 line, designates the contribution from silicate weathering are significant.

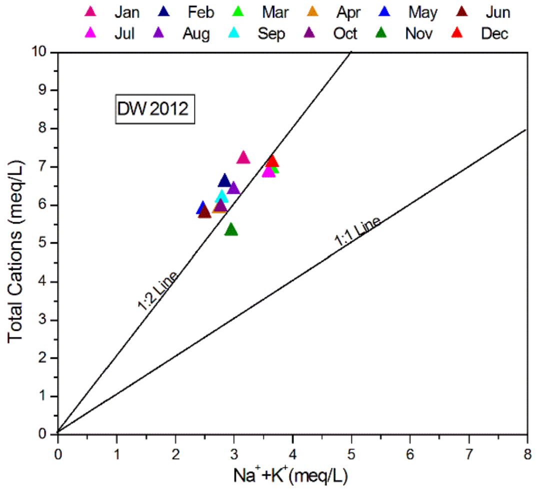

Figure 3.55: Scatter plot for TZ verses Na^++K^+ for dug wells (DW) in the Alappad coast, Kollam, Kerala, India during the year 2012

In the case of dug wells also irrespective of seasons all the points are clustered around 1:2 line proving the role of silicate weathering in the contribution of cations ions in the study area. High concentration of Na^++K^+ in March, July, November and December 2012 may attributes to additional sources such as saline water contamination and residence time.

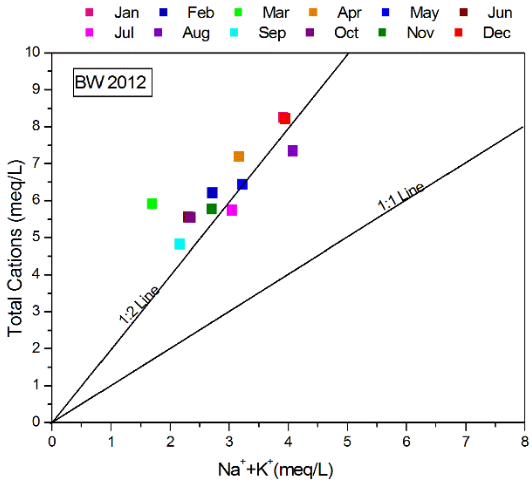

Figure 3.56: Scatter plot for TZ verses Na^++K^+ for bore wells (BW) in the Alappad coast, Kollam, Kerala, India during the year 2012

Deep bore wells in the year 2012 also clusters around the 1:2 line with addition sources for Na^++K^+ in July and August 2012. All these evidences the major role of weathering of silicate bearing rocks in the contribution of cations in all groundwater sources of Alappad region.

3.5.6 Total Cations Versus (Ca^{2+}+Mg^{2+})

The plot for total cations to Ca^{2+}+Mg^{2+} help us to find the geological origin of calcium and magnesium in the groundwater. If the ratio is high, the abundance of $Ca^{2+}$and Mg^{2+} is attributed to carbonate weathering whereas less concentration of $Ca^{2+}$and Mg^{2+} leads to high ratio which supports silicate weathering of rock[64].

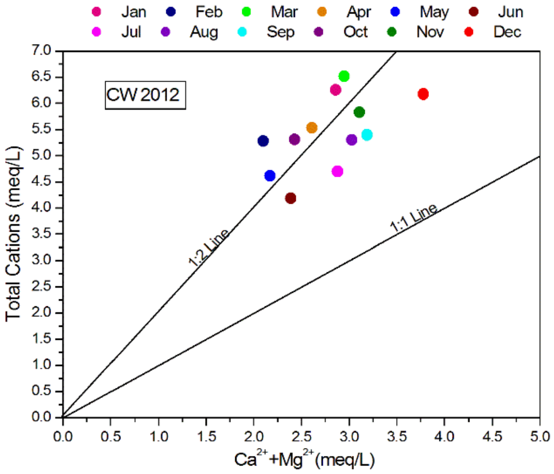

Figure 3.57: Scatter plot for Total Cations versus (Ca^{2+}+Mg^{2+}) for control well of Alappad coast, Kollam, Kerala, India, during the period 2012.

In the control well, the points are clustered around the 1:2 line, indicating the silicate weathering where as six months lies between 1:2 line and 1:1 line inferring the chances of excess $Ca^{2+}$and Mg^{2+} from carbonate weathering of rocks.

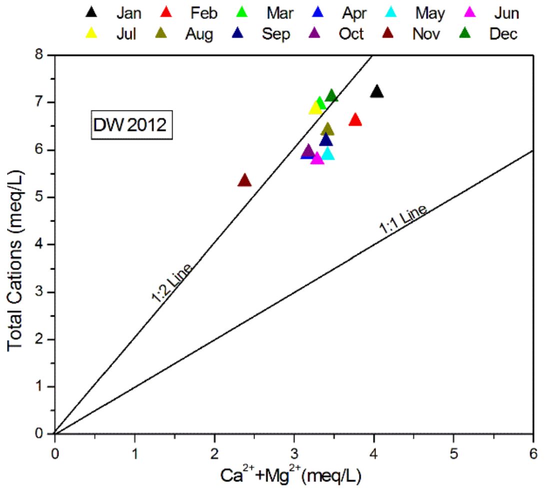

Figure 3.58: Scatter plot for Total Cations versus (Ca^{2+}+Mg^{2+}) for dug wells (DW) of Alappad coast, Kollam, Kerala, India, during the period 2012.

The dug wells shows a linear trend that indicats $Ca^{2+}$and Mg^{2+} are abundance in the study area with regression R=0.721. Here most of the points lies between the 1:2 line and 1:1 line, with clustering around the former line, indicating excess $Ca^{2+}$and Mg^{2+} from leaching of silicate weathering of rocks.

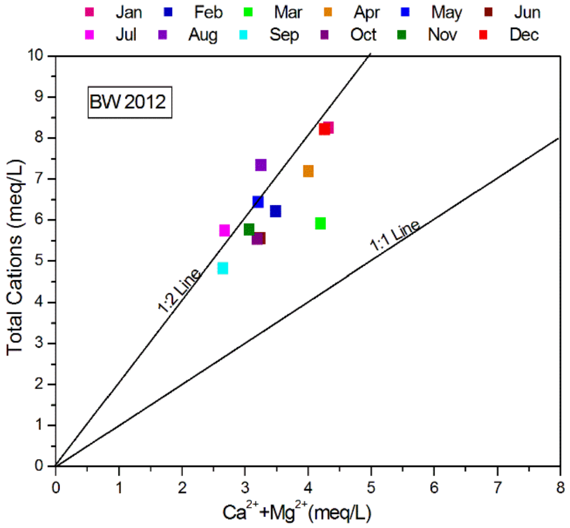

Figure 3.59: Scatter plot for Total Cations versus (Ca^{2+}+Mg^{2+}) for bore wells (BW) of Alappad coast, Kollam, Kerala, India, during the period 2012

Bore wells also shows a similar pattern that of dug wells with most of the points falls between 1:2 line and 1:1 line which suggest that addition of cations to the hydrogeochemistry of the study area is controlled by silicate weathering of rocks. All the plots are evidence for the influence of silicate weathering in the study area.

3.6 Statistical Analysis

3.6.1 Pearson's Correlation Matrix

Correlation analysis is used to find the degree of linear relationship between any of the two water quality parameters analysed[65]. The critical results of the physico-chemical parameters of groundwater sampled from control well, dug wells and bore wells are statistically correlated using correlation matrix and a coefficient > 0.5 are considered to be of an agreement with other variables[66]. Correlations among various parameters may be positive or negative depending up on the nature of the linear relationship. If the correlation coefficient <0.5, then no correlation is considered among that variables. The correlation analysis of analysed parameters for control well, dug wells and bore wells are performed separately and the correlation co-efficient are presented as correlation matrixes in the tables.

In the case of groundwater from control well, pH shows very strong negative correlation with Eh (-0.995) and moderate positive correlation with Na^+ (0.54) and SO_4^{2-} (0.524). EC have significant positive correlation with TDS (0.871) and moderate correlation with Mg^{2+} (0.665). Magnesium also has correlation with total hardness (0.578) and DO (0.574). DO express a negative correlation with BOD (-0.597) and positive relation with total hardness (0.574). Total hardness is correlated with Ca^{2+} (0.554). HCO_3^- is completely correlated with alkalinity and Ca^{2+}, with a correlation coefficient 1.0 each (p value = 0) and moderate positive correlation with K^+ (0.617) and NO_3^- (0.589). K^+ shows positive moderate correlation with alkalinity (0.617) and Na^+ (0.536). Chloride do not shows a correlation with any other water quality parameters analysed.

Results of correlation analysis for groundwater collected from dug wells reveal there is strong negative correlation with pH and Eh (-0.864). EC is strongly correlated with TDS (0.978) and moderately correlated with PO_4^{3-} (0.573) positively and negative relation with SO_4^{2-} (-0.522). Alkalinity gets positive correlation between TH (0.702), Ca^+ (0.605) and HCO_3^- (1.000). Mg^{2+} is negatively correlated to pH (-0.505) and Ca^+ (-0.701). Cl^- is correlated to BOD (0.516) and iron (total Fe) is negatively correlated to DO (-0.692). Sodium, potassium and nitrate don't show correlation with any other parameters.

Analysis of water from bore wells shows significant negative correlation (-0.993) between pH and Eh. pH is also negatively related to SO_4^{2-} (-0.700), but positively correlated to DO (0.746). On the other hand, Eh got positive correlation with SO_4^{2-} (0.700) and negatively correlated with DO (-0.721). There is a significant positive correlation exist between EC and TDS with a correlation coefficient of 0.998 and with EC and SO_4^{2-} (0.896). TDS is also correlated to HCO_3^- (-0.681) and SO_4^{2-} (0.878), while correlation coefficient between SO_4^{2-} and HCO_3^- is negative (-0.557). Total hardness is correlated to alkalinity (0.603), HCO_3^- (0.603), Ca^+ (0.799) and Cl^- (0.576), whereas Cl^- also correlated to Ca^{2+} (0.556), Na^+ (0.799) as well as with DO (-0.609). No correlation with any water quality parameters are displayed by potassium, iron and BOD, being correlation coefficient < 0.5 with all the parameters analysed.

Table 3.8: Pearson correlation matrix for control well (CW) along Alappad coast, Kollam, Kerala, India during year 2012.

Variables	**pH**	**Eh**	**EC**	**TDS**	**TA**	**TH**	**Ca^{2+}**	**Mg^{2+}**	**Na^+**	**K^+**	**HCO_3^-**	**Cl^-**	**SO_4^{2-}**	**NO_3^-**	**DO**	**BOD**
pH	1															
Eh	**-0.995**	1														
EC	0.145	-0.146	1													
TDS	0.147	-0.170	**0.871**	1												
TA	0.191	-0.185	0.040	0.237	1											
TH	-0.076	0.087	0.398	0.470	0.218	1										
Ca^{2+}	0.224	-0.192	-0.223	-0.131	0.100	**0.554**	1									
Mg^{2+}	-0.305	0.286	**0.665**	**0.655**	0.147	**0.578**	-0.359	1								
Na^+	**0.540**	**-0.540**	0.177	0.272	0.332	-0.063	-0.125	0.051	1							
K^+	0.332	-0.343	-0.134	0.011	**0.617**	-0.487	-0.360	-0.193	**0.536**	1						
HCO_3^-	0.191	-0.185	0.040	0.237	**1.000**	0.218	**0.100**	0.147	0.332	**0.617**	1					
Cl^-	0.220	-0.211	0.366	0.309	-0.399	0.440	0.265	0.234	0.428	-0.451	-0.399	1				
SO_4^{2-}	**0.524**	**-0.552**	0.237	0.425	0.278	0.249	0.377	-0.091	0.220	0.240	0.278	0.086	1			
NO_3^-	-0.069	0.109	0.278	0.434	**0.589**	0.186	-0.096	0.304	0.360	0.357	**0.589**	-0.037	-0.140	1		
DO	-0.308	0.306	0.364	0.317	-0.019	**0.574**	0.070	**0.576**	-0.444	-0.401	-0.019	0.155	0.101	0.025	1	
BOD	-0.072	0.081	-0.449	-0.366	0.346	-0.060	0.063	-0.129	0.401	0.283	0.346	-0.075	-0.414	0.217	**-0.597**	1

Table 3.9: Pearson correlation matrix for dug wells (DW) along Alappad coast, Kollam, Kerala, India during year 2012.

Variables	pH	Eh	EC	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	Cl^-	SO_4^{2-}	PO_4^{3-}	NO_3^-	Fe (t)	DO	BOD
pH	1																	
Eh	**-0.864**	1																
EC	-0.110	-0.234	1															
TDS	-0.207	-0.143	**0.978**	1														
TA	0.171	-0.065	-0.170	-0.185	1													
TH	-0.057	0.370	-0.333	-0.337	**0.702**	1												
Ca^{2+}	0.273	-0.028	-0.463	-0.483	**0.605**	**0.786**	1											
Mg^{2+}	**-0.505**	0.472	0.361	0.389	-0.163	-0.111	**-0.701**	1										
Na^{+}	0.324	-0.381	0.338	0.387	0.102	0.092	0.190	-0.199	1									
K^{+}	-0.109	-0.044	-0.008	0.006	0.043	-0.035	0.219	-0.393	-0.324	1								
HCO_3^-	0.171	-0.065	-0.170	-0.185	**1.000**	**0.702**	**0.605**	-0.163	0.102	0.043	1							
Cl^-	0.153	0.167	-0.273	-0.233	-0.038	0.261	0.281	-0.151	0.353	-0.293	-0.038	1						
SO_4^{2-}	-0.035	0.154	**-0.522**	-0.475	-0.465	-0.146	0.016	-0.195	-0.281	0.450	-0.465	0.088	1					
PO_4^{3-}	0.102	-0.341	**0.573**	0.484	0.308	-0.098	-0.275	0.329	0.203	-0.359	0.308	-0.407	**-0.736**	1				
NO3-	-0.001	-0.092	0.271	0.219	0.094	-0.049	0.093	-0.206	-0.204	0.044	0.094	-0.071	-0.481	0.283	1			
Fe (t)	0.316	-0.227	0.048	-0.130	0.197	0.321	0.318	-0.140	-0.065	-0.198	0.197	-0.153	-0.288	0.308	0.137	1		
DO	-0.047	-0.082	0.279	0.390	-0.330	-0.353	-0.276	0.036	0.297	-0.023	-0.330	-0.004	0.006	0.010	0.196	**-0.692**	1	
BOD	0.126	0.053	-0.111	-0.048	0.445	0.233	-0.017	0.296	0.255	-0.254	0.445	**0.516**	-0.138	0.056	-0.287	-0.330	-0.101	1

Table 3.10: Pearson correlation matrix for bore wells (BW) along Alappad coast, Kollam, Kerala, India during year 2012.

Variables	pH	Eh	EC	TDS	TA	TH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	Fe (t)	DO	BOD
pH	1															
Eh	**-0.993**	1														
EC	-0.480	0.462	1													
TDS	-0.485	0.464	**0.998**	1												
TA	0.243	-0.190	**-0.682**	**-0.681**	1											
TH	0.237	-0.197	-0.410	-0.435	**0.603**	1										
Ca^{2+}	-0.020	0.030	-0.138	-0.169	0.394	**0.799**	1									
Mg^{2+}	0.351	-0.313	-0.320	-0.300	0.151	0.008	**-0.595**	1								
Na^+	-0.317	0.282	0.135	0.094	-0.063	0.280	0.371	-0.243	1							
K^+	-0.134	0.189	0.133	0.111	0.296	0.330	0.381	-0.191	0.026	1						
HCO_3^-	0.243	-0.190	**-0.682**	**-0.681**	**1.000**	**0.603**	0.394	0.151	-0.063	0.296	1					
Cl^-	-0.242	0.218	-0.160	-0.189	0.131	**0.576**	**0.556**	-0.154	**0.799**	0.195	0.131	1				
SO_4^{2-}	**-0.700**	**0.700**	**0.896**	**0.878**	**-0.557**	-0.319	0.007	-0.439	0.338	0.243	**-0.557**	0.024	1			
Fe (t)	0.118	-0.131	-0.462	-0.452	0.230	-0.230	-0.114	-0.119	-0.190	0.195	0.230	-0.009	-0.336	1		
DO	**0.746**	**-0.721**	-0.105	-0.081	0.039	-0.018	-0.266	0.418	-0.732	-0.112	0.039	**-0.609**	-0.427	-0.057	1	
BOD	0.047	-0.036	-0.216	-0.225	0.476	0.440	0.227	0.211	0.367	0.183	0.476	0.403	-0.223	-0.227	-0.275	1

3.6.2 ANOVA Test

Hypothesis I

> *Whether there is any significant difference between mean values of various parameters in control well (CW) stratum at different months of 2012.*

Table 3.11: ANOVA table for the comparison of water quality parameters between different months of CW stratum in 2012.

Source	**SS**	**Df**	**ms**	**F**	**p- value**
Total	1683596.7004	227			
Between Months	8466.9089	11	769.7190	1.974	$p<0.05$
Between Parameters	1597929.5660	18	88773.8648	227.684	$p<0.001$
Residual	77200.2255	198	389.9001		

<u>Inferences</u>

1) There is significant difference between months, ($p<0.05$) Months of November and December experienced significantly lower values ($p<0.0$)
2) Parameters also differ significantly between them ($p<0.001$). TDS is significantly higher than all the rest followed by HCO_3^-. Eh is significantly lower compared to all other, followed by Mg^{2+}, SO_4^{2-}, PO_4^{3-}, total iron, DO and BOD.

Hypothesis II

Whether there is any significant difference between mean values of various parameters of dug well (DW) strata in each month of year 2012.

Table 3.12: ANOVA table for the comparison of water quality parameters between different months of DW strata in 2012.

Source	**SS**	**Df**	**ms**	**F**	**p- value**
Total	2898314.2216	251			
Between Months	4320.8501	11	392.8046	0.303	$p>0.05$
Between Parameters	2608929.4683	20	130446.7734	100.673	$p<0.001$
Residual	285063.9032	220	1295.7450		

Inferences

1) There is no significant difference between months with respect to the parameter values ($p<0.05$)

2) Parameters differ significantly between them ($p<0.001$). TDS is significantly higher than all others, followed by SO_4^{2-}, and TH, Eh, Temperature, pH, EC, DO, BOD, PO_4^{3-}, total iron and NO_3^- are significantly lower than all others ($p<0.001$).

Hypothesis III

> *Whether there is any significant difference between mean values of various parameters of bore well (BW) strata in each month of year 2012.*

Table 3.13: ANOVA table for the comparison of water quality parameters between different months of BW strata in 2012.

Source	**SS**	**df**	**ms**	**F**	**p- value**
Total	2994714.6701	251			
Between Months	80424.4411	11	7311.3128	22.893	$p<0.001$
Between Parameters	2844028.9802	20	142201.4490	445.257	$p<0.001$
Residual	70261.2488	220	319.3693		

Inferences

1) Months registered a significant difference between parameters ($p<0.001$). January and December showed significantly higher values for the parameters and March and April registered significantly lower values ($p<0.001$).

2) Parameters differ significantly between them ($p<0.001$).TDS is significantly higher an all the rest followed by HCO_3^-, TA and TH. Significantly lower values were observed in Eh, EC, TA, BOD, PO_4^{3-} and SO_4^{2-}.

Hypothesis IV

Whether there is any significant difference between mean values of various parameters of control well (CW), dug wells (DW) and bore wells (BW) in each month of year 2012.

Table 3.14: ANOVA table for the comparison of water quality parameters between different months of CW, DW and BW strata in 2012.

Source	**SS**	**df**	**ms**	**F**	**p- value**
Total	766426.9487	62			
Between Wells	6946.5782	2	3473.2891	4.578	$p<0.05$
Between Parameters	713961.6794	20	3568.0840	47.55	$p<0.001$
Residual	45518.6911	60	758.6449		

Inferences

1) There is significant difference between wells ($p<0.05$). BW showed significantly higher values followed by DW and CW ($p<0.05$).

2) Parameters also exhibited a significant difference between them ($p<0.001$). TDS is significantly higher among all the parameters, followed by TA, TH and CaH. ($p<0.001$). Significantly lower parameter values was registered by Eh, followed by PO_4^{3-}, NO_3, EC, BOD and SO_4^{2-}.

Table 3.15: Over all groundwater quality of control well (CW), dug wells (DW) and bore wells (BW) of the Alappad coast, Kollam, Kerala, India during the year 2012

Water Quality Parameters	**Annual mean Control Well (CW)**	**Annual mean Dug Wells (DW)**	**Annual mean Bore Wells (BW)**	**BIS (IS 10500:2012) Acceptable Limit**	**BIS (IS 10500:2012) Permissible Limit**	**WHO (2011)**
pH	7.7±0.2	7.8±0.4	7.2±0.3	6.5-8.5	No relaxation	6.5-8.5
Eh (mV)	-42.0±10.3	-47.6±20	-17.3±16.3			
EC (µS/cm)	403±139	550±521	768±1698			1500
Alkalinity (mg/L)	160.3±22.3	189.7±88.4	227.2±60.3	200	600	
TDS (mg/L)	298±72	396.8±350.4	592±1414.3	500	2000	
TH (mg/L)	139.5±24	167.3±86.9	173.4±32	200	600	100
Ca^{2+} (mg/L)	40.2±8.4	43.5±22	47.8±10	75	200	75
Mg^{2+} (mg/L)	9.5±5.2	14.2±12.7	13±7	30	100	30
Na^+ (mg/L)	53.4±12	64.3±59.3	62.5±45			
K^+ (mg/L)	12.3±3.5	8.4±4.9	9.0±5.2			
Cl^- (mg/L)	45.6±20	65.5±83.6	53±67.7	250	1000	
HCO_3^- (mg/L)	195.5±27	231.5±108	277.2±73.5			
SO_4^{2-} (mg/L)	1.3±0.6	2.5±3	0.4±0.5	200	400	
PO_4^{3-} (mg/L)	ND	0.1±0.1	ND			
Iron (mg/L)	ND	0.1±0.6	4.9±2.6	0.3	No relaxation	0.1
NO_3^- (mg/L)	0.9±0.3	0.6±0.9	ND	45	No relaxation	
DO (mg/L)	4.5±0.9	4.1±1.5	2.1±1.3			
BOD (mg/L)	0.3±2.0	3.4±3	0.5±0.5			

Table 3.16: Physico- chemical characteristics of groundwater from dug well sources of Alappad coast, Kollam, Kerala, India, during each month of year 2012

2012	DW	Temp (⁰C)	pH	Eh	EC (µS/cm)	TDS (mg/L)	TA (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^{-} (mg/L)	Cl^{-} (mg/L)	SO_4^{3} (mg/L)	PO_4^{3} (mg/L)	NO_3^{-} (mg/L)	Fe (mg/L)	DO (mg/L)	BOD (mg/L)
Jan	$\bar{x} \pm \sigma$	26.51±1.07	7.75±0.24	-44.93±14.67	0.43±0.36	337.4±241.3	235.07±77.69	202.25±106.67	55.77±29.71	15.2±10	68.73±56.04	6.82±3.63	286.78±94.78	76.17±64.45	1.54±2.9	0.09±0.12	0.47±0.87	0.07±0.19	3.61±1.32	7.9±6.87
	CI	25.93-27.10	7.61-7.88	-53.01--36.86	0.23-0.63	204.63-470.17	192.3-277.81	143.55-260.94	39.42-72.12	9.69-20.72	37.89-99.56	4.8-8.8	234.63-338.9	40.7-111.6	-0.08-3.16	0.02-0.2	-0.01-0.95	-0.03-0.18	2.89-4.34	4.1-11.66
Feb	$\bar{x} \pm \sigma$	28.17±1.02	7.81±0.15	-52.93±20.65	0.54±0.41	353.33±259.24	199.93±98.55	188.67±104.06	56.36±33.8	11.56±8.8	60.63±50.7	7.78±4.2	243.9±120.23	59.83±50.83	2.11±2.9	0.09±0.15	0.6±1.06	0.64±2.18	2.85±1.04	1.5±1.15
	CI	27.61-28.73	7.73-7.9	-64.29-41.57	0.31-0.76	210.69-495.97	145.7-254.16	131.4-245.92	37.76-74.96	6.7-16.4	32.73-88.54	5.47-10	177.77-310.1	31.9-87.8	0.53-3.7	0.01-0.2	0.02-1.2	-0.56-1.84	2.28-3.43	0.9-2.15
Mar	$\bar{x} \pm \sigma$	28.85±1.08	7.85±0.15	-60.4±15.9	0.56±0.45	406.8±303.38	195.3±116.5	165.78±78.9	48.7±23.5	10.65±5.4	78.27±58.77	9.57±3.81	238.27±142.15	60.13±43.4	3.23±3.39	0.08±0.13	0.43±0.6	0.02±0.08	4.66±1.6	4.2±2.26
	CI	28.25-29.44	7.77-7.94	-69.17--51.63	0.31-0.81	239.87-573.73	131.2-259.41	122.35-209.2	35.77-61.65	7.68-13.6	45.93-110.6	7.48-11.67	160.1-316.5	36.25-84	1.37-5.1	0.01-0.2	0.09-0.8	-0.02-0.07	3.77-5.55	2.96-5.44
Apr	$\bar{x} \pm \sigma$	28.77±0.97	7.75±0.16	-50.9±15.46	0.45±0.24	342.5±164.38	187.53±76.85	158.3±71.66	48.62±21.17	8.9±5.27	56.49±36.22	11.3±5.42	228.79±93.76	55.13±41.69	3±3.6	0.05±0.09	0.47±0.67	0.02±0.08	4.37±1.83	1.16±0.8
	CI	28.23-29.30	7.66-7.84	-59.44-42.43	0.32-0.58	252.06-432.94	145.25-229.82	118.9-197.73	36.97-60.27	6-11.79	36.56-76.42	8.32-14.28	177.20-280.4	32.19-78.1	1.03-5.01	0-0.1	0.11-0.8	-0.02-0.06	3.37-5.38	0.7-1.6
May	$\bar{x} \pm \sigma$	29.45±0.96	7.67±0.23	-42.4±15.6	0.54±0.42	387.5±309.03	192.17±70.55	171.07±94.84	47.24±17.76	12.82±15.85	49.17±44.7	13±6.3	234.44±86.07	68.6±101.4	3.3±4.17	0.06±0.09	0.7±1.03	0.03±0.09	3.77±1.36	3.9±1.4
	CI	28.92-29.97	7.54-7.79	-50.99--33.81	0.31-0.77	217.47-557.53	153.35-230.99	118.89-223.26	37.46-57	4.1-21.54	24.58-73.77	9.55-16.5	187.08-281.8	12.82-124.4	0.1-5.58	0.01-0.1	0.14-1.3	-0.02-0.08	3.02-4.52	3.1-4.66
Jun	$\bar{x} \pm \sigma$	27.77±1.01	7.61±0.33	-36.87±34.82	0.42±0.33	342.67±219.87	181.32±87.52	164.67±95.05	38.07±15	16.82±20.6	52.8±36.55	8±4.38	221.2±106.78	55.7±45.89	3.2±3.73	0.05±0.08	0.5±0.9	0.02±0.08	3.89±1.59	2.8±1.85
	CI	27.22-28.33	7.43-7.79	-56.03--17.71	0.24-0.60	221.69-463.64	133.7-229.47	112.37-216.96	29.82-46.32	5.47-28.16	32.7-72.92	5.59-10.4	162.46-279.96	30.47-80.97	1.16-5.27	0.01-0.1	0-1	-0.02-0.06	3.01-4.76	1.8-3.82
Jul	$\bar{x} \pm \sigma$	28.49±1.06	7.69±0.22	-43.47±14.05	0.53±0.58	396.13±434.67	167.37±85.73	163.42±89.75	41.92±21.38	14.19±20.15	78.13±103.2	7.6±5.04	204.2±104.59	85.6±164.39	3.3±3.9	0.05±0.1	0.23±0.56	0.06±0.13	3.89±1.8	4.28±6.9
	CI	27.90-29.07	7.57-7.81	-51.19--35.74	0.21-0.85	156.97-635.3	120.2-214.54	114.04-212.8	30.15-53.68	3.1-25.28	21.37-134.89	4.84-10.39	146.65-261.7	-4.84-176.1	1.15-5.46	0-0.1	-0.07-0.5	-0.01-0.1	2.88-4.89	0.49-8.07
Aug	$\bar{x} \pm \sigma$	27.97±1.26	7.79±0.22	-46.13±17.37	0.5±0.33	379.47±249.1	176.67±79.88	171.09±87.04	45.22±23.22	14.05±8.7	65±71.5	6.32±4.44	215.53±97.45	86.76±155.74	2.47±1.71	0.05±0.1	0.73±1.02	0.04±0.11	4.76±1.57	4.12±2.23
	CI	27.28-28.67	7.66-7.91	-55.69--36.57	0.33-0.69	242.41-516.52	132.7-220.62	123.2-218.98	32.44-57.99	9.25-18.84	25.67-104.36	3.88-8.76	161.9-269.2	1.07-172.5	1.5-3.4	0-0.1	0.17-1.3	-0.02-0.1	3.89-5.63	2.89-5.35
Sep	$\bar{x} \pm \sigma$	28.11±0.96	7.69±0.26	-43.4±20.33	0.45±0.24	333.47±158.77	185±86.5	169.92±89.2	44.98±21.2	13.9±10.44	60.15±53.34	6.75±3.84	225.7±105.53	63.55±56.72	2.53±3.11	0.09±0.13	0.67±1	0.12±0.19	4.5±1.86	1.8±1
	CI	27.58-28.63	7.54-7.83	-54.58--32.22	0.32-0.58	246.11-420.83	137.41-232.59	120.8-219.01	33.31-56.65	8.16-19.66	30.8-89.5	4.64-8.87	167.64-283.8	32.35-94.8	0.8-4.24	0.02-0.2	0.12-1.2	0.01-0.2	3.48-5.52	1.21-2.31
Oct	$\bar{x} \pm \sigma$	28.02±0.84	7.65±0.25	-42.4±21.83	0.75±0.92	508.93±581.45	181.35±85.3	159.23±81.4	21.75±10.1	25.38±14.35	59.26±48.79	7.65±3.99	221.25±104.05	51.6±48.25	2.06±3.16	0.1±0.13	0.44±0.62	0.08±0.3	4.37±1.43	3.8±2.2
	CI	27.56-28.48	7.51-7.79	-54.41--30.39	0.24-1.26	189-828.86	134.42-228.28	114.44-204	16.19-27.3	17.48-33.27	32.4-86.1	5.45-9.84	163.99-278.5	25.06-78.2	0.32-3.8	0.03-0.2	0.1-0.8	-0.06-0.2	3.59-5.16	2.59-5.01
Nov	$\bar{x} \pm \sigma$	28.8±1.13	7.8±0.19	-59.93±15.49	0.65±0.66	441.2±423.06	176.67±89.5	118.94±53.71	23.65±10.6	14.47±11.1	63.71±51.99	7.1±4.07	215.53±109.24	61.7±49.31	1.85±2.12	0.1±0.2	0.7±0.97	0.09±0.2	4.11±1.48	4±2.35
	CI	28.18-29.42	7.7-7.9	-68.46-51.41	0.29-1.01	208.42-673.98	127.4-225.94	89.39-148.49	17.81-29.49	8.36-20.59	35.-92.3	4.86-9.34	155.4-275.6	34.6-88.9	0.7-3	-0.01-0.2	0.15-1.2	-0.01-0.2	3.29-4.92	2.71-5.3
Dec	$\bar{x} \pm \sigma$	28.81±0.86	7.66±0.3	-47.53±27.29	0.77±0.79	531.73±539.86	198.39±97	173.69±76.27	49.6±23.6	12±9.54	78.69±68.96	8.8±7.77	242±118.35	60.97±42.23	1.11±1.38	0.09±0.24	0.82±1.10	0.1±0.24	4.65±0.99	1.92±1.64
	CI	28.33-29.28	7.49-7.83	-62.55--32.52	0.33-1.2	234.69-828.77	145.01-251.76	131.7-215.65	36.6-62.6	6.78-17.27	40.74-116.63	4.54-13.1	176.9-307.2	37.74-84.2	0.35-1.9	-0.04-0.2	0.2-1.4	-0.03-0.2	4.11-5.2	1-2.8
Annual Mean	$\bar{x} \pm \sigma$	28.31±1.02	7.83±0.37	-47.61±20.34	0.55±0.52	396.76±350.36	189.7±88.4	167.25±86.85	43.5±21.96	14.2±12.66	64.25±59.34	8.4±4.88	231.5±107.85	65.5±83.56	2.5±3.12	0.1±0.14	0.6±0.89	0.1±0.65	4.1±1.52	3.4±3.2
	CI	27.7-28.9	7.6-8.1	-60.1--35.1	0.2-0.9	181.2-612.3	135.3-244.1	113.8-220.7	30-57	6.4-21.9	27.7-100.8	5.4-11.4	165.1-297.8	14.1-116.9	0.6-4.4	0-0.2	0-1.1	-0.3-0.5	3.2-5.1	1.4-5.4

Table 3.17: Physico- chemical characteristics of groundwater from bore well sources of Alappad coast, Kollam, Kerala, India, during each month of year 2012

2012	BW	Temp (^{0}C)	pH	Eh	EC (µS/cm)	TDS (mg/L)	TA (mg/L)	TH (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO$_3^-$ (mg/L)	Cl$^-$ (mg/L)	SO$_4^{3}$ (mg/L)	PO$_4^{3}$ (mg/L)	NO$_3^-$ (mg/L)	Fe (mg/L)	DO (mg/L)	BOD (mg/L)
Jan	$\bar{x} \pm \sigma$	30.50±0.17	7.15±0.15	-11±8	0.5±0.35	376.67±242.3	250.23±60.21	216.5±43.01	55.82±8	18.6±5.6	84.4±72	9.6±4.76	305.28±73.46	99.13±138.76	0.3±0	ND	ND	3.9±2.9	1.7±1.51	1.47±1.26
	CI	30.1-30.9	6.8-7.5	-30.9-8.9	-0.4-1.4	-225.3-978.6	100.7-399.8	109.7-323.4	35.9-75.7	4.7-32.6	-95-263.8	-2.2-21.4	122.8-487.8	-245.6-443.9	0.3	ND	ND	-3.3-11.2	-2.1-5.5	-1.7-4.6
Feb	$\bar{x} \pm \sigma$	28.73±0.06	7.38±0.1	-24.67±5.8	0.38±0.05	270.67±12.86	258.9±37.8	174.63±29.85	52.13±22.28	10.7±6.7	57.37±34.45	8.77±4.9	315.86±46.11	15.7±8.9	0.3±0	ND	ND	4.7±3.04	2.27±0.42	0.4±0
	CI	28.6-28.9	7.1-7.6	-39- -10.3	0.3-0.5	238.7-302.6	165-352.8	100.5-248.8	-3.2-107.5	-5.8-27.3	-28.2-143	-3.4-20.9	201.3-430.4	-4.6-36.1	0.3	ND	ND	-2.8-12.3	1.2-3.3	0.4
Mar	$\bar{x} \pm \sigma$	31.37±1.46	7.81±0.06	-47±3.6	0.31±0.08	196.33±39.53	243.42±34.9	210.05±51.92	56.6±6.73	16.6±16.6	32.9±30.9	10.7±6.7	296.97±42.57	10.6±3.2	0.2±0.17	ND	ND	4.67±2.6	2.93±0.84	0.4±0
	CI	27.7-35	7.7-8	-56--38	0.1-0.5	98.1-294.5	156.7-330	81-339	39.9-73.3	-24.7-57.9	-43.7-109.5	-5.9-27.3	191.2-402.7	2.6-18.5	-0.2-0.6	ND	ND	-1.8-11.1	0.8-5	0.4
Apr	$\bar{x} \pm \sigma$	31.33±1.1	7.37±0.25	-25±14.1	0.54±0.33	402.33±331.23	247.97±48.39	200.7±21.27	62.54±9.99	10.72±1	66.4±40	11.2±6.3	302.52±59.04	95.6±53.2	0.3±0	ND	ND	5.7±2	2.27±1.56	0.63±0.75
	CI	28.6-34.1	6.7-8	-60-10	-0.3-1.3	-420.6-1225.2	127.7-368.2	147.8-253.5	37.7-87.4	8.2-13.2	-33-165.9	-4.4-26.9	155.9-449.2	-36.5-227.7	0.3	ND	ND	0.8-10.7	-1.6-6.1	-1.2-2.5
May	$\bar{x} \pm \sigma$	31.30±0.92	7.1±0.2	-7.67±8.5	0.59±0.11	376.33±48.99	224.73±67.09	160.4±32.2	49.8±4.56	8.66±5.61	66.9±18	12.6±5.	274.17±81.85	65.13±46.45	0.53±0.23	ND	ND	6.1±1.9	1.6±0.2	0.5±0.4
	CI	29-33.6	6.6-7.6	-28.8-13.5	0.3-0.9	254.6-498	58-391.4	80.4-240.4	38.5-61.2	-5.3-22.6	22.2-111.6	0.1-25.1	477.5	-50.3-180.5	0-1.1	ND	ND	1.3-10.8	1.1-2.1	-0.5-1.5
Jun	$\bar{x} \pm \sigma$	29.97±0.67	6.93±0.15	0.67±6.5	0.33±0.15	338±15.52	232.47±61.49	162.06±10.2	47.54±11	10.46±4.6	48.4±28.9	8.23±5.9	283.6±75.02	43.9±37.86	0.3±0.06	ND	ND	6±2	1.93±1.07	0.1±0
	CI	28.3-31.6	6.6-7.3	-15.5-16.8	0-0.7	299.4-376.6	79.7-385.2	136.7-187.4	20-74.9	-0.9-21.8	-23.4-120.2	-6.4-22.9	97.2-470	-50-137.9	0.2-0.5	ND	ND	1-11	-0.7-4.6	0.1-0.1
Jul	$\bar{x} \pm \sigma$	31±1.21	6.77±0.84	12±46.03	3.68±5.81	3018.67±4861.4	183.48±87	134.13±30.8	40.15±4.7	8.17±6.8	64.4±43.5	9.87±4.76	223.85±106.15	25.9±20.07	1.37±1.24	ND	ND	3.8±2.4	2.07±1.8	0.2±0.17
	CI	28-34.0	4.7-8.9	-102.4-126.4	-10.8-18.1	-9058.7-15096	-32.7-399.6	57.5-210.8	28.6-51.7	-8.825.1	-43.6-172.5	-2-21.7	-39.9-487.6	-24-75.8	-1.7-4.5	ND	ND	-2.2-9.8	-2.4-6.5	-0.2-0.6
Aug	$\bar{x} \pm \sigma$	29.8±0.2	7.27±0.21	-17.67±11	0.65±0.27	427±189.85	225±86.6	163.14±36.1	38.59±5.12	16.13±5.6	89.03±35	8.03±4.4	274.5±105.7	71±57.37	0.63±0.15	ND	ND	5.4±3.14	1.77±0.75	0.4±0
	CI	29.3-30.3	6.7-7.8	-44-8.7	0-1.3	-44.7-898.7	9.8-440.2	73.4-252.9	25.9-51.3	2-30.2	2-176	-3-19	12-537.0	-71.5-213.5	0.3-1	ND	ND	-2.4-13.2	-0.1-3.6	0.4
Sep	$\bar{x} \pm \sigma$	29±0.44	7.13±0.12	-10±7.9	0.54±0.33	438±252.88	2254±3.3	132.7±22.9	31.84±13.92	12.85±5.15	45.97±28.7	6.7±4.96	274.5±52.83	13.9±7.32	0.33±0.06	ND	ND	5.13±3	2.03±1.69	0.7±0.7
	CI	27.9-30.1	6.8-7.4	-29.4-9.4	-0.3-1.3	-190.2-1066.2	117.4-332.6	75.9-189.5	-2.7-66.4	0-25.6	-25.4-117.3	-5.6-19	143.3-405.7	-4.3-32.1	0.2-0.5	ND	ND	-2.6-12.8	-2.2-6.2	-1-2.4
Oct	$\bar{x} \pm \sigma$	29.7±0.1	7.13±0.21	-8.33±10.3	0.48±0.15	395.33±72.29	217±35.5	159.8±19.5	23.9±3.23	24.2±5.03	49.2±21	8.15.1	264.74±43.3	47.17±15.68	0.30	ND	ND	4.6±2.6	2.37±1.85	0.17±0.06
	CI	29.5-29.9	6.6-7.7	-33.8-17.2	0.1-0.9	215.7-574.9	128.8-305.2	111.3-208.3	15.9-31.9	11.7-36.7	-3.2-101.6	-4.5-20.8	157.1-372.4	8.2-86.1	0.3	ND	ND	-1.9-11.1	-2.2-7.0	0-0.3
Nov	$\bar{x} \pm \sigma$	29.73±0.25	7.93±0.06	-65.67±9	0.5±0.24	395.33±168.67	201.5±71.03	153.34±43.27	36.43±6.96	15.1±6.65	58.7±44.3	6.1±4.7	245.8±86.7	39.6±46.4	0	ND	ND	5±1.9	2.67±1.69	0.33±0.12
	CI	29.1-30.4	7.8-8.1	-88.2- 43.1	-0.1-1.1	-23.7-814.4	25-378	45.8-260.8	19.1-53.7	-1.4-31.6	-51.3-168.6	-5.5-17.7	30.5-461.1	-75.7-154.9	0.0	ND	ND	0.3-9.7	-1.5-6.9	0-0.6
Dec	$\bar{x} \pm \sigma$	31.63±1.12	7±0.35	-2.67±17	0.72±0.56	467.67±254.21	216.97±58.54	213.64±10.85	78.4±8.9	4.28±2.84	86.2±88	7.9±4.	264.7±71.4	108.37±152.2	0.6±1.04	ND	ND	4.13±2.9	1.57±1.26	0.33±0.12
	CI	28.9-34.4	6.1-7.9	-45-39.7	-0.7-2.1	-163.9-1099.2	71.5-62.4	186.7-240.6	56.3-100.5	-2.8-11.3	-132.6-305.1	-2.2-18.0	87.3-442.1	-269.8-486.5	-2-3.2	ND	ND	-3.1-11.4	-1.6-4.7	0-0.6
Annual	$\bar{x} \pm \sigma$	30.34±0.8	7.25±0.3	-17.25±16.32	0.77±1.7	591.9±1414.3	227.22±60.3	173.4±31.86	47.8±10.1	13±7	62.5±44.9	9±5.2	277±73.5	53±67.7	0.4±0.5	ND	ND	4.9±2.6	2.1±1.33	0.47±0.5
	CI	29.8-30.8	7.1-7.4	-27.3--7.2	-0.3-1.8	-278.2-1461.9	190.2-264.3	153.8-193	41.6-54	8.7-17.3	34.9-90.1	5.8-12.2	232-322.4	11.3-94.7	0.1-0.7	ND	ND	3.3-6.5	1.3-2.9	0.2-0.8

3.7 Conclusion

This chapter of the thesis discusses the monthly variation in physico-chemical parameters. The mean values of each parameters analysed during each month of the year 2012 are compared with IS 10500: 2012 & WHO (2011) standards that are consolidated in table 3.15. Hill-Piper trilinear plots are used to find the hydrochemical facies of the study area and the prominent watertypes in each months from sources (Control well, dug wells and bore wells) separately. Different ionic ratios are used to interpret the major processes that control the hydrogeochemistry of the study area. Revelle's co-efficient is used to check the incidence instances of sea water intrusion.

The results of water quality study with respect to physico-chemical parameters suggest that annual mean of all parameters in both dug well and bore well strata are under permissible limit. The overall hydrochemical facies of the groundwater sources in the year 2012 is Ca^{2+}- Mg^{2+}- HCO_3^- type followed by Ca^{2+}- Na^+- HCO_3^- (mixed type). Water type in the study area falls under *temporary hardness water type* with non-dominant cation and bicarbonate anion type water. Groundwater from control well, dug wells and bore wells suggests the dominance of bicarbonate in the groundwater throughout the study period. The groundwater sources fall in the rock dominance field of in Gibbs plot revealing the specific nature of water predominated by dissolution of rock forming minerals. This is evidence that the mineral constituents of water are mainly contributed from the dissolution of rock through which water percolates. In the case of bore wells, in July 2012, high TDS value shifts to the evaporation dominant field of the Gibbs diagram which infers the mixing of sea water.

Ion exchange is the prominent process generally seen throughout the study area. But reverse ion exchange is observed in dug wells near to the proximity of sea, especially in station 18 (DW 15) where there is $Na^+/Cl^- <$ 1 in most of the months. In the case of bore wells, station 12 (BW 2) shows *reverse ion exchange* during April 2012. In Alappad coast, the interface between fresh water and groundwater is too small because of the geological position of this narrow islet between estuary in the east (and the navigational canal) and sea on the western side. A non-linear trend in sodium to chloride plot is observable for shallow and deep groundwater sources. This suggests that, both sodium and chloride not simultaneously increased or decreased throughout the study period. Revelle's co-efficient shows slight to moderate contamination with sea water in some sampling locations with R values > 1.0, indicating localised saline water intrusion in the study area irrespective of seasons.

The various plots for different molar ratios are evidence for the influence of silicate weathering in the study area. Plot for Ca^{2+}/Mg^{2+} molar ratio is greater than 1 and most of the water samples have $Ca^{2+}/Mg^{2+} >2$, as a result of dissolution of calcite as well as silicate minerals. In $Ca^{2+}+Mg^{2+}$ versus $HCO_3^-+SO_4^{2-}$ plot shows increase in the concentration of bicarbonate is due to weathering and dissolution of silicate containing rocks. This situation occurs during the dominance of *ion-exchange process* in the study area. In (Na^++K^+) versus total cations plot high ratios are plotted above the 1:2 line defines the significant contribution from silicate weathering. High concentration of Na^++K^+ may attributes to additional sources such as contamination as well as residence time of saline water. From total cations versus $(Ca^{2+}+Mg^{2+})$ plot, excess $Ca^{2+}$and Mg^{2+} from leaching of silicate weathering of rocks is significant compared to the chances of excess $Ca^{2+}$and Mg^{2+} from carbonate weathering of rocks. These pertinent observations suggest the hydrogeochemistry of the study area is controlled by silicate weathering of rocks.

Pearson's correlation matrix shows annual mean of pH for groundwater have strong negative correlation with Eh, EC bears a strong positive correlation with TDS and total hardness is positively correlated to calcium. In control well and dug wells, the annual mean of chloride is not correlated to any of the parameters. Whereas, in the case of samples from bore well strata, chloride is positively correlated with total hardness, calcium and sodium but negatively correlated with DO. In dug wells sodium (Na^+), potassium (K^+) and nitrate (NO_3^-) does not show correlation with any of the parameters analysed. In bore well strata, potassium, iron and BOD are not correlated to any of the physico-chemical parameters analysed during the study period.

ANOVA results shows that control well discloses significant difference between months of the year 2012 ($p<0.05$). November and December 2012 experienced significantly lower values ($p<0.0$). Parameters also differ significantly between them ($p<0.001$). TDS is significantly higher than all the rest followed by HCO_3^-. Eh is significantly lower compared to all other, followed by Mg^{2+}, SO_4^{2-}, PO_4^{3-}, Iron, DO and BOD. In the case of dug well, there is no significant difference between months of 2012 with respect to the parameter values ($p<0.05$). Parameters differ significantly between them ($p<0.001$). TDS is significantly higher than all others. Concentrations of SO_4^{2-}, and TH, Eh, Temperature, pH, EC, DO, BOD, PO_4^{3-}, Fe and NO_3^- are significantly lower than all others ($p<0.001$). ANOVA results of water quality parameters between different months of BW strata in 2012, registered a significant difference between parameters ($p<0.001$). January and December 2012, showed significantly higher values for the parameters and March and April, 2012 registered significantly lower values ($p<0.001$). Parameters differ significantly between them ($p<0.001$). TDS is significantly higher an all the months followed by HCO_3^-, TA and TH. Significantly lower values were observed in Eh, EC, TA, BOD, PO_4^{3-} and SO_4^{2-}. There is significant difference between wells ($p<0.05$). BW showed significantly higher values followed by DW and CW ($p<0.05$). Parameters also exhibited a significant difference between them ($P<0.001$). TDS is significantly higher among all the parameters, followed by TA, TH and CaH. ($p<0.001$). Significantly lower parameter values were registered by Eh, followed by PO_4^{3-}, NO_3^-, EC, BOD and SO_4^{2-}.

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Chapter 4

WATER QUALITY INDEX, IRRIGATION WATER QUALITY AND CORROSION INDICES OF GROUNDWATER OF DUG WELLS AND BORE WELLS IN ALAPPAD COAST DURING THE YEAR 2012

4.1 Introduction

The major work presented in the following section of the thesis comprises of evaluation of groundwater quality in multiple aspects derived from the results of physico-chemical parameters. This includes water quality index (WQI) for assessing water for domestic purposes, irrigation water quality parameters to check the suitability of groundwater for irrigation practices and corrosion indices to utilise the groundwater for industrial purposes[1-4].

4.2 Water Quality Index (WQI)

Water quality index is one of the most effective tools to communicate information on the quality of water. It becomes an important parameter for the assessment and management of water sources for human consumption[5]. WQI identifies the composite influence of different water quality parameters. The Water Quality Index (WQI) is calculated using the Weighted Arithmetic Index method and the parameters used are pH, EC, total dissolved solids (TDS), total hardness (TH), Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-},Cl^{-} & SO_4^{2-}.

Table 4.1: Monthly variation of water quality index (SI) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	Parameters					
	CW		DW		BW	
	WQI	Water Quality	WQI	Water Quality	WQI	Water Quality
Jan 2012	32.5	G	35.2±20	G	35.7±18	G
Feb 2012	39.5	G	41.2±22	G	30.6±7	G
Mar 2012	42.3	G	43.8±23	G	32.7±7	G
Apr 2012	37.1	G	38.8±16	G	40.3±13	G
May 2012	38.7	G	43.8±26	G	40.9±1	G
Jun 2012	28.7	G	33.9±20	G	24±9	E
Jul 2012	28.8	G	39.7±33	G	185.8±275	UDP
Aug 2012	33.6	G	38.6±20	G	42.2±10	G
Sep 2012	30.6	G	35±16	G	34±14	G
Oct 2012	40.7	G	49.9±46	G	33±6	G
Nov 2012	43.4	G	45.3±34	G	39±11	G
Dec 2012	42.0	G	52±44	P	43.4±25	G
$\bar{x} \pm \sigma$	36.5±5.4	G	41.4±28	G	48.5±80	G
μ	36.5±3.3	G	41.4±17.5	G	48.5±49.3	G
CI	33.1-39.8	G	24-58.9	E-P	-0.9-97.8	UDP

E-Excellent G-Good P-Poor UDP-Unfit for Drinking Purpose

The water quality index of control well in all months fall in *Good* (25-50) category, having **Grade B**, annual mean being 36.5±5.4, with a confidence interval CI, 33.1-39.8, at 95% significant level. The dug wells also show WQI value between 25-50 inferring water is *Good* for human consumption with respect to the physico-chemical parameters taken under consideration for calculating WQI in all months except in December 2012. In December water degraded to poor quality with a WQI of 52±44 (Grade C). The annual mean of WQI for dug wells is 41.4±28, with a confidence interval of 24-58.9, where it shows *Excellent to Poor* range, at 95% level of significance.

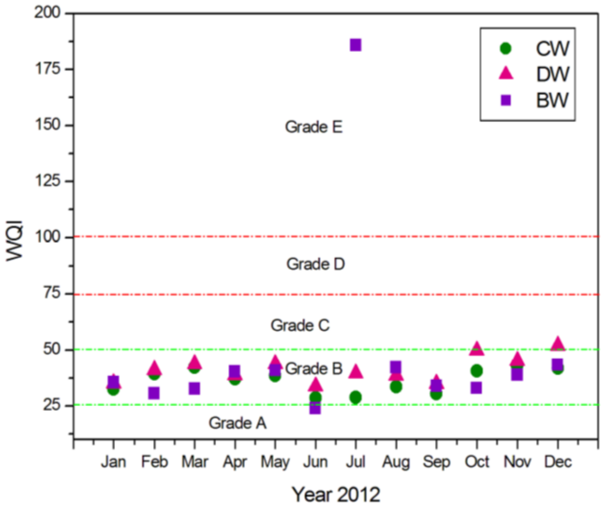

Figure 4.1: Variation in water quality index (WQI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during 2012

From the graph (Figure 4.1) it is clear that the bore wells falls in the range 25-50 in most of the months confirming *Good water quality* with **Grade B.** In June 2012 water seem to be *Excellent quality* with a monthly mean of 24±9 (**Grade A**). Contradiction to this, in July 2012 water degraded to a WQI of 185.8±275, which is *Unfit for drinking purposes* (**Grade E**), due to high TDS in the water samples collected during that period. The annual mean of WQI for bore wells during the year 2012 is 48.5±80, however the confidence interval shows the water is UDP without conventional treatment.

4.3 Irrigation Water Quality

The water quality for irrigation is essential for the extent of vegetable cover, maintenance of soil productivity and protection of environment. Irrigation water with excessive amount of dissolved ions adversely affects plants as well as soil, both physically and chemically[6]. The composition and constituents of dissolved salts in groundwater determines the suitability of water for irrigation[7]. According to this, irrigation suitability of groundwater is verified using sodium adsorption ratio (SAR), sodium percent (Na %), permeability index (PI), Kelley's index (KI), magnesium ratio (MR), residual sodium carbonate (RSC), and chloro-alkalinity indices (CAI-1 & CAI-2). USSL and Wilcox diagrams illustrate the relationships between electrical conductivity (EC) with SAR and Na% respectively.

4.3.1 Sodium Adsorption Ratio (SAR)

Sodium is a very important irrigation water parameter especially in coastal areas as sodium from seawater can contaminate the groundwater aquifers[8]. Sodium adsorption ratio is the level to which sodium adsorbed to the soil by replacing calcium and magnesium[9]. Increased SAR value of the soil is an indication of alkaline soil profile growth and poor water percolation capacity of soil[10]. SAR is calculated using the following equation:

$$\mathbf{SAR} = \frac{\mathbf{Na^{+}}}{\sqrt{\frac{\mathbf{Ca^{2+}} + \mathbf{Mg^{2+}}}{\mathbf{2}}}}$$

Based on SAR[7,11], groundwater quality is classified into four classes. SAR <10 is considered as *Excellent* water quality and comes under class S1. SAR value from 10 to 18 is also *Good* in quality and falls in class S2 category. Class S3 and S4 category water have fairly more sodium concentration with SAR value 19 to 26 (*Doubtful quality*) and above 26 (*Unsuitable quality*) respectively.

Table 4.2: Monthly variation of sodium adsorption ratio (SAR) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	SAR	Class	SAR	Class	SAR	Class
Jan 2012	2.5	S1	2.1±1.5	S1	2.4±1.9	S1
Feb 2012	2.8	S1	1.9±1.3	S1	1.9±1.2	S1
Mar 2012	2.6	S1	2.6±1.7	S1	1.1±1.1	S1
Apr 2012	2.2	S1	1.9±1.1	S1	2.1±1.3	S1
May 2012	1.9	S1	1.6±1.2	S1	2.3±0.6	S1
Jun 2012	1.4	S1	1.8±1.1	S1	1.6±1.0	S1
Jul 2012	1.4	S1	2.3±2.2	S1	2.5±1.6	S1
Aug 2012	1.7	S1	2.0±1.7	S1	3.1±1.6	S1
Sep 2012	1.6	S1	1.9±1.4	S1	1.8±1.2	S1
Oct 2012	2.3	S1	2.1±2.0	S1	1.7±0.8	S1
Nov 2012	2.0	S1	2.7±2.4	S1	2.3±2.0	S1
Dec 2012	1.6	S1	2.6±2.3	S1	2.6±2.6	S1
$\bar{x} \pm \sigma$	1.99±0.5	S1	2.1±1.7	S1	2.11±1.5	S1
μ	1.99±0.31		2.12±1.05		2.11±0.92	
CI	1.68-2.3	S1	1.07-3.17	S1	1.19-3.03	S1

Class S1-Excellent

All groundwater sources in the Alappad study area comes under *excellent* groundwater quality with respect to SAR. The monthly SAR values of control well, dug wells and bore wells throughout the study period is found to be less than 10. The annual mean of SAR in control well (1.99±0.5) is less compared to dug well (1.07-3.17) and bore well (1.19-3.03) strata.

4.3.1.1 USSL diagram

The US salinity Laboratory diagram (USSL) helps to rate the irrigation water by plotting SAR against electrical conductivity in micro siemen/cm[12]. According to sodium hazard criteria, water is classified into four categories, namely *low sodium* (**S1**), *medium sodium* (**S2**), *high* (**S3**) and *very high* (**S4**) *sodium water* whereas salinity hazard divides water into *low saline* (**C1**:< 250 µS/cm), *medium saline* (**C2**: 250 – 750 µS/cm), *high saline* (**C3**: 750 – 2250 µS/cm) and *very high saline water* (**C4**: 2250 – 5000 µS/cm). The USSL diagram consists of 16 zones based on the sodium hazard (SAR) and salinity hazard (EC) combination. The degree of suitability of groundwater for irrigation can be assessed depending up on which of these zones the groundwater samples belongs to[13] and from this, the water is categorized into *good, moderate and bad water quality*.

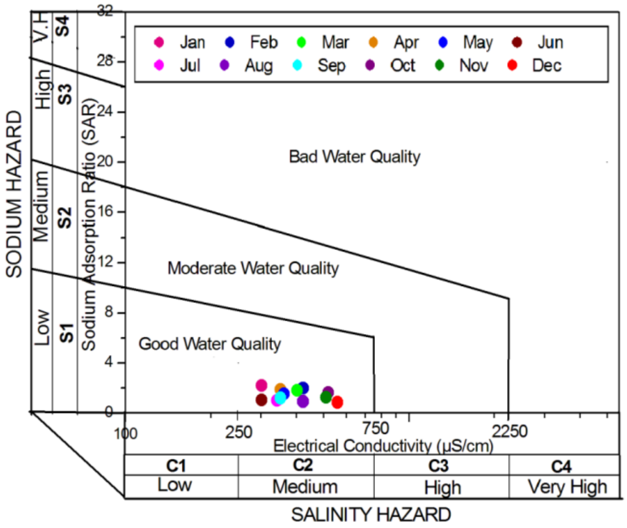

Figure 4.2: USSL Diagram for groundwater from control well (CW) of Alappad coast, Kollam, Kerala, India during the year 2012.

From the figure 4.2, it is clear that in the case of control well all the months have SAR<10 and EC between 250 µS/cm to 750 µS/cm. Since all points fall in **C2S1** category of USSL plot, it confirms good quality water with *medium saline and low sodium* water. Shallow dug wells in the study period shows *medium saline with low sodium hazard* (**C2S1**) from January to September 2012 and again in November 2012. But during October and December 2012 a slight increase in salinity hazard leads to shift the water sources to *high salinity and low sodium* (**C3S1**) category with moderate water quality. Water having high salinity hazard (C4) is not suitable for irrigation unless the soil is permeable enough to facilitate leaching.

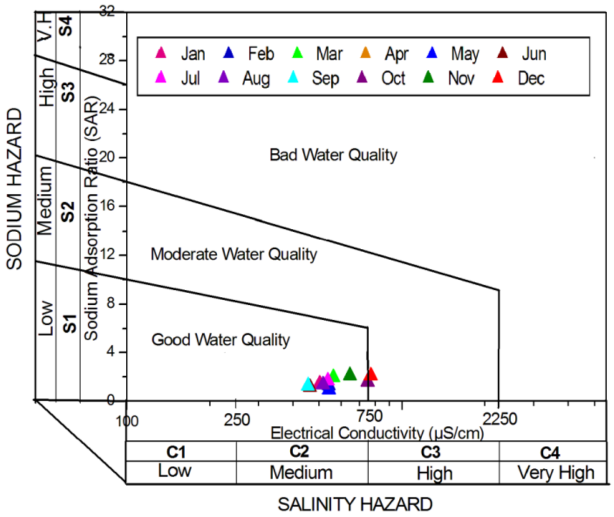

Figure 4.3: USSL Diagram for groundwater from of dug wells (DW) of Alappad coast, Kollam, Kerala, India during the year 2012.

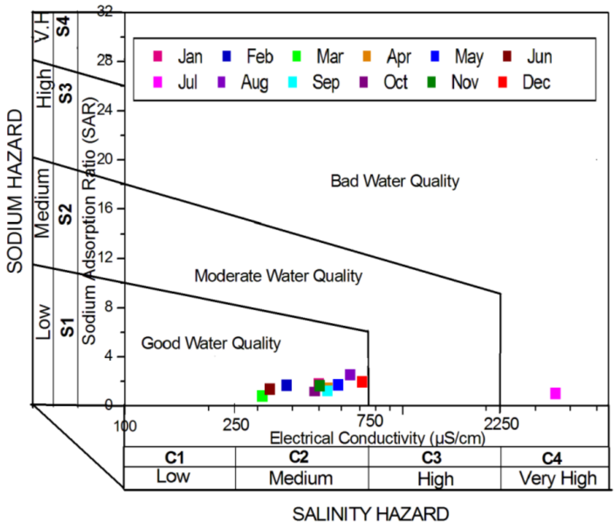

Figure 4.4: USSL Diagram for groundwater from bore wells (BW) of Alappad coast, Kollam, Kerala, India during the year 2012.

The groundwater samples from bore wells have good water quality, except in the month of July 2012 with *very high salinity hazard and low sodium water* (**C4S1**). The salinity hazard may be associated with very high dissolved constituents during monsoon dilution. In all other months the water quality falls in *medium saline with low sodium water* (**C2S1**). The overall irrigation water quality of groundwater in the study region with respect to SAR is suitable for irrigation with moderate leaching requirements, without any distinct salinity control. Low sodium water is mostly free from exchangeable sodium in harmful level.

4.3.2 Sodium Percent (Na%)

Sodium concentration is important in classifying irrigation water because sodium reacts with soil to reduce its permeability. When groundwater containing high sodium percentage (doubtful or unsuitable category) interact with soil it leads to osmotic effects on soil–plant system. High concentration of sodium ions displaces the calcium and magnesium ions in clay particle by adsorbing into it. This base-exchange process of Na in water for Ca and Mg in soil reduces permeability[14]. Sodium in irrigation water usually expressed in terms of percent sodium (Na%) and it is determined using the following formula[21],

$$\mathbf{Na\%} = \frac{\mathbf{Na^{+} + K^{+}}}{\mathbf{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}}} \times \mathbf{100}$$

Based on percentage sodium, groundwater is classified into five categories: excellent **(<20%)**, good **(20-40%)**, permissible **(40-60%)**, doubtful **(60-80%)** & unsuitable **(>80%)**.

Table 4.3: Monthly variation of sodium percent (Na%) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	Na%	**Water Quality**	**Na%**	**Water Quality**	**Na%**	**Water Quality**
Jan 2012	54.3	P	40.4±14	P	41.8±19.8	P
Feb 2012	60.0	P	40.5±16.3	P	41.2±19.7	P
Mar 2012	54.8	P	48.4±14.5	P	27.3±20.8	G
Apr 2012	52.9	P	44.4±11.1	P	41.3±17.8	P
May 2012	52.9	P	38.8±12.4	G	49.8±7.6	P
Jun 2012	43.1	P	41.6±11.8	P	38.8±16.2	G
Jul 2012	38.6	P	44.6±12.8	P	49.5±22.3	P
Aug 2012	42.8	P	41.2±12.3	P	54.6±13	P
Sep 2012	40.9	P	41.5±11.4	P	42.4±21.9	P
Oct 2012	54.3	P	42.9±16.7	P	41.2±12.8	P
Nov 2012	46.7	P	49.4±18.8	P	43.3±26.1	P
Dec 2012	38.9	G	45.8±17.7	P	40.4±25.8	P
$\bar{x} \pm \sigma$	48.4±7.4	P	43.3±14.4	P	42.63±19.4	P
μ	48.4±4.54		43.3±8.85		42.63±11.92	
CI	43.84-52.91	P	34.45-52.15	G-P	30.71-54.55	G-P

E- Excellent *G-Good* *D-Doubtful* *P-Permissible*

From the Figure 4.5 it is clear that control well shows mostly *permissible* water quality for irrigation being sodium percent less than 60% throughout the study period. In February 2012, the concentration reaches up to 60.3%, but in rest of the months percentage sodium is limited to below 55% with minimum concentration *good category* of 38.9% in December 2012. The annual mean of percent sodium is 48.4±7.4%, with a confidence interval of 43.8 - 52.9% (Permissible range) at 95% significant level.

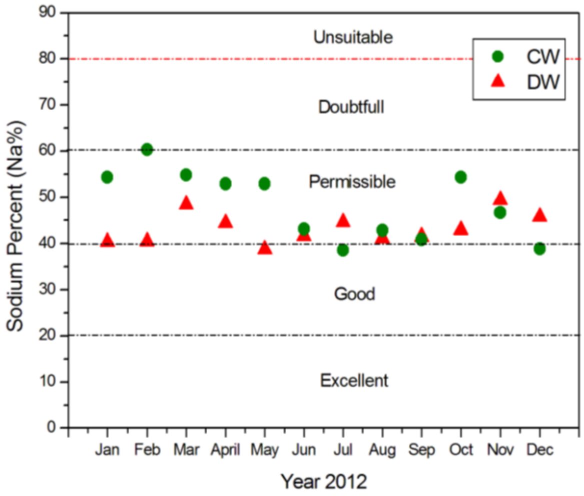

Figure 4.5: Monthly variation in mean of sodium percent (Na%) of groundwater from control well (CW) and dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012

The shallow dug well sources exhibits *permissible* water quality with annual mean of 43.3±14.4% with in a confidence interval of 34.45% - 52.15% (*good to permissible*) at 95% significant level. During May 2012, the sodium percent falls to *good category* with a monthly mean of 38.8%.

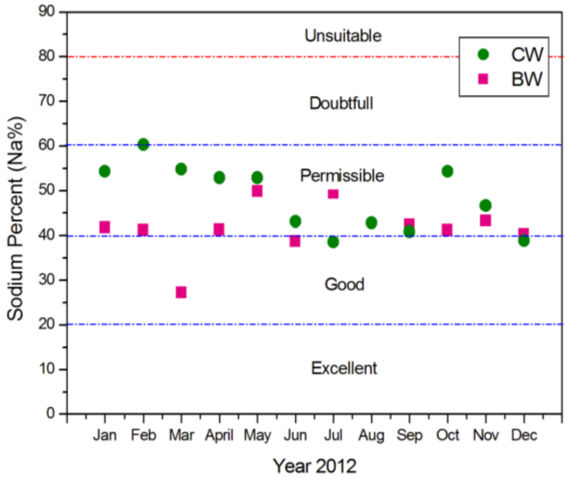

Figure 4.6: Monthly variation in mean of sodium percent (Na%) of groundwater from control well (CW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The deep bore wells in the study area shows wide range of variation between stations and months even though the monthly mean falls in *permissible category* (Figure 4.6). In January and February 2012, bore wells are under *permissible category*, but in March 2012, sodium percent becomes *good* for irrigation. It maintains *permissible* quality in April and May 2012, after that upgrades to good quality in June 2012. From July 2012 onwards, Na% in water from bore wells remained under *permissible quality*. The overall Na% of bore well water during the year 2012 belongs to *permissible category* with annual mean of 42.63±19.4%, but the confidence interval at 95% significant level shows *good to permissible* water quality (30.7-54.6%).

4.3.2.1 Wilcox diagram

The relation between Na% (sodium percent) and EC is shown in Wilcox diagram[15].

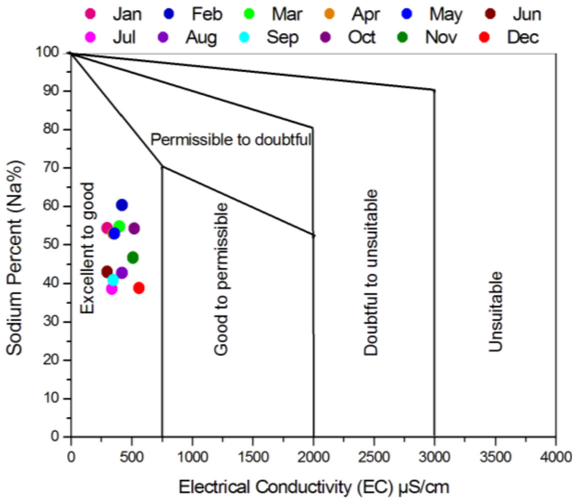

Figure 4.7: Wilcox diagram for groundwater quality of control well (CW) of Alappad coast, Kollam, Kerala, India during year 2012

According to Wilcox diagram based on the combined effect of percentage sodium and electrical conductivity, water is divided into five zones- Excellent to good, *good to permissible, permissible to doubtful, doubtful to unsuitable and unsuitable* quality of water.

Water from the control well has Na% up to 60% and EC is less than 750 µS/cm. So all the water samples fall in *excellent to good* field in the Wilcox diagram throughout the study period. The Na% in dug wells are below 60% throughout the year 2012. But electrical conductivity shows a slight increase beyond 750 µS/cm in October and December 2012. The rest of the months fall in *excellent to good category*, whereas in October and December 2012, water from the dug wells drop to *good to permissible* for irrigation. Water from the deep bore wells show Na% below 60% for all the months in the year 2012. Electrical conductivity is also favourable for *excellent to good* range throughout the study period except in July 2012, where a severe hike in the EC is observed and the water drops to *unsuitable* for irrigation purposes.

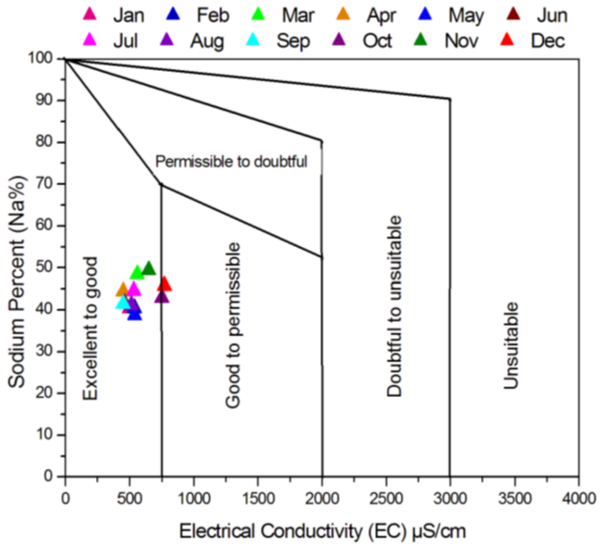

Figure 4.8: Wilcox diagram for groundwater quality of dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012

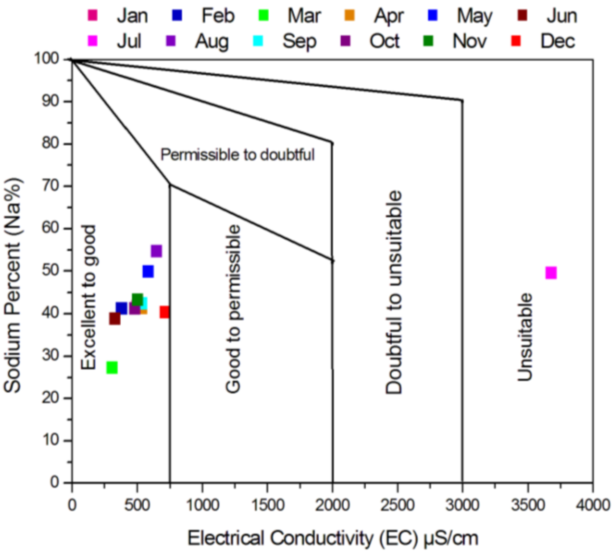

Figure 4.9: Wilcox diagram for groundwater quality of bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

4.3.3 Permeability Index (PI)

The permeability of soil is affected by sodium, calcium, magnesium and bicarbonate concentrations existing in the water used for irrigation purposes[16]. Using these parameters, PI is calculated from the following equation[17].

$$\mathbf{PI} = \frac{\mathbf{Na^{+}} + \sqrt{\mathbf{HCO_3^{-}}}}{\mathbf{Na^{+}} + \mathbf{Ca^{2+}} + \mathbf{Mg^{2+}}} \times \mathbf{100}$$

According to permeability index, irrigation water quality is classified into three classes. The *Class I* possess 75% or more of maximum permeability and *Class II* consists of more than 25% of permeability which are suitable for irrigation. The *Class III* have only 25%

of maximum permeability and it is considered as unsuitable for irrigation purposes.

Table 4.4: Monthly variation of permeability index (PI) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	PI	**Water Quality**	**PI**	**Water Quality**	**PI**	**Water Quality**
Jan 2012	83.9	Class I	76.5±14	Class I	72.7±9.3	Class II
Feb 2012	91.4	Class I	75.5±17.9	Class I	78.2±12.9	Class I
Mar 2012	83.2	Class I	79.3±13.4	Class I	63.7±19.3	Class II
Apr 2012	84.4	Class I	82.4±18.6	Class I	72.5±9.5	Class II
May 2012	94.1	Class I	77±13.8	Class I	82.4±11.5	Class I
Jun 2012	85.1	Class I	78.4±14.6	Class I	78.4±6.2	Class I
Jul 2012	69.9	Class II	80.6±15.5	Class I	85±20.5	Class I
Aug 2012	74.6	Class II	77.2±11.5	Class I	83.5±12.1	Class I
Sep 2012	71.7	Class II	79.6±16.9	Class I	86.7±15.9	Class I
Oct 2012	84.8	Class I	80.7±21.4	Class I	78.5±7.2	Class I
Nov 2012	76.6	Class I	87.9±15.4	Class I	78.4±16.6	Class I
Dec 2012	68.7	Class II	77±15.2	Class I	69±14.2	Class II
$\bar{x} \pm \sigma$	80.7±8.3	Class I-II	79.3±15.9	Class I	77.4±13.7	Class I
μ	80.7±5.10		79.3±9.8		77.4±8.4	
CI	75.6-85.8	Class I	69.6-89.1	Class I-II	69-85.8	Class I-II

Class I & II-Safe for Irrigation

From the Table 4.4 it is clear that control well has maximum permeability of 75% or more in most of the months. The annual mean of permeability index falls in *Class I* (80.7±8.3%), that is safe for irrigation purposes with the confidence interval 75.6% - 85.8% maximum permeability at 95% level of significance.

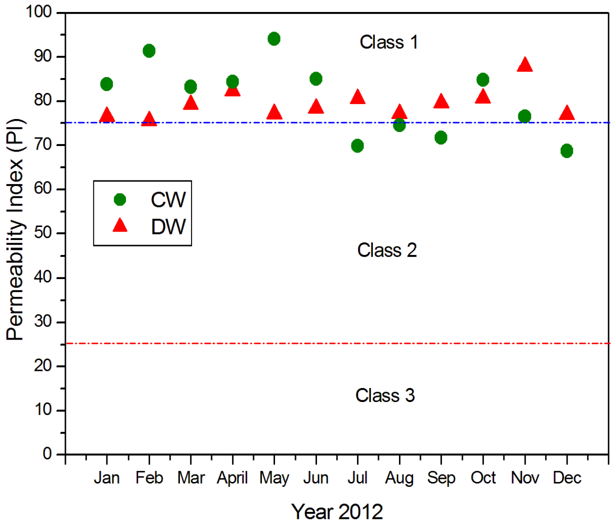

Figure 4.10: Monthly variation in mean permeability index (PI) of groundwater from control well (CW) and dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012

The water from shallow dug wells maintain a monthly mean of more than 75% permeability index throughout the study period. The station wise variations in each month leads to a maximum permeability of Class I and Class II categories, both are suitable for irrigation. The annual mean of permeability index is 77.4±13.7% (Class II), with a confidence interval of 69% - 85.8% (Class I to II), at 95% level of significance.

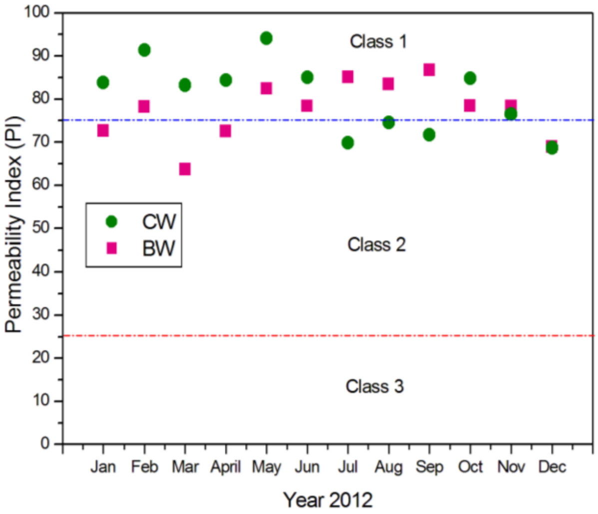

Figure 4.11: Monthly variation in mean permeability index (PI) of groundwater from control well (CW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

In January, March, April and December 2012, the bore wells show a monthly mean of permeability index less than 75% that comes in *Class II.* In all other months the water comes under *Class I*, with 75% permeability. The annual mean of permeability index for bore wells in the year 2012 is 77.4±13.7% *(Class I)*, with a confidence interval of 69 - 85.8% permeability *(Class I & Class II)* at 95% significant level.

4.3.4 Kelley's Index (KI)

Kelley's index is the concentration of sodium measured against sum of calcium and magnesium. The irrigation water is classified into two categories based on KI. The Kelley's Index<1 indicates suitability of water for agricultural use whereas KI>1, water is unsuitable for irrigation.

$$\mathbf{KI} = \frac{\mathbf{Na^{+}}}{\mathbf{Ca^{2+}} + \mathbf{Mg^{2+}}}$$

Table 4.5: Monthly variation of Kelley's Index (KI) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	KI	**Water Quality**	**KI**	**Water Quality**	**KI**	**Water Quality**
Jan 2012	1.1	US	0.7±0.5	S	0.8±0.6	S
Feb 2012	1.4	US	0.7±0.5	S	0.8±0.5	S
Mar 2012	1.1	US	1.0±0.7	US	0.4±0.4	S
Apr 2012	1.0	US	0.8±0.4	S	0.7±0.5	S
May 2012	0.9	S	0.6±0.4	S	0.9±0.3	S
Jun 2012	0.6	S	0.7±0.4	S	0.6±0.4	S
Jul 2012	0.6	S	0.9±0.5	S	1.1±0.7	US
Aug 2012	0.7	S	0.7±0.5	S	1.3±0.8	US
Sep 2012	0.6	S	0.7±0.4	S	0.8±0.6	S
Oct 2012	1.1	US	1.0±0.9	S	0.7±0.3	S
Nov 2012	0.8	S	1.3±1.3	S	1.0±1.0	US
Dec 2012	0.6	S	1.1±1.1	S	0.9±0.9	S
$\bar{x} \pm \sigma$	0.86±0.3	S-US	0.86±0.7	S	0.83±0.6	S
μ	0.86±0.2		0.86±0.4		0.83±0.4	
CI	0.7-1	S-US	0.4-1.3	S-US	0.5-1.2	S-US

S-Suitable *US-Unsuitable*

On the basis of Kelley's index the water from control wells is unsuitable for irrigation from the month of January to April 2012, being KI > 1.0. After that from May 2012, the water shows a decrease in KI, to suitable range for irrigation till September 2012. Again the water becomes unsuitable in terms of KI (1.1) in October 2012, but regains it suitability water quality in November (0.8) and December 2012 (0.6). Kelley's index shows an annual mean of 0.86±0.2 *(suitable)*, with a confidence interval of 0.7 – 1.0 at 95% significant level, which is inferred as most suitable for irrigation. The annual mean of KI is 0.86±0.7 for water from dug wells, which is considered as *suitable category*. The confidence interval of KI is 0.5-1.2 (suitable to unsuitable range), at 95% level of significance.

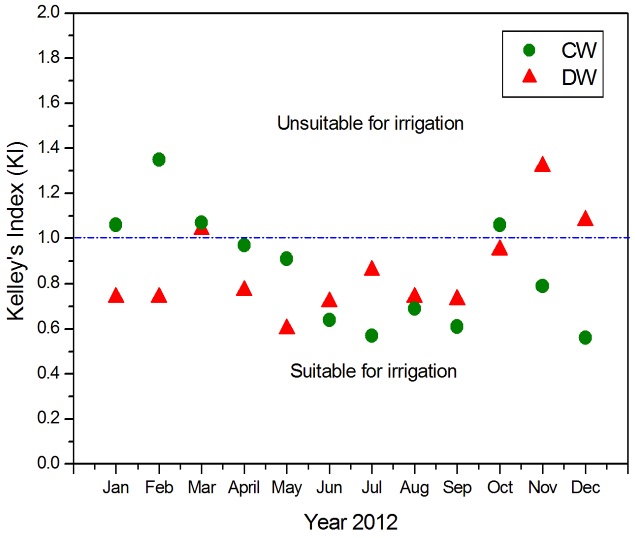

Figure 4.12: Monthly variation in mean Kelley's index (KI) of groundwater from control well (CW) and dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012

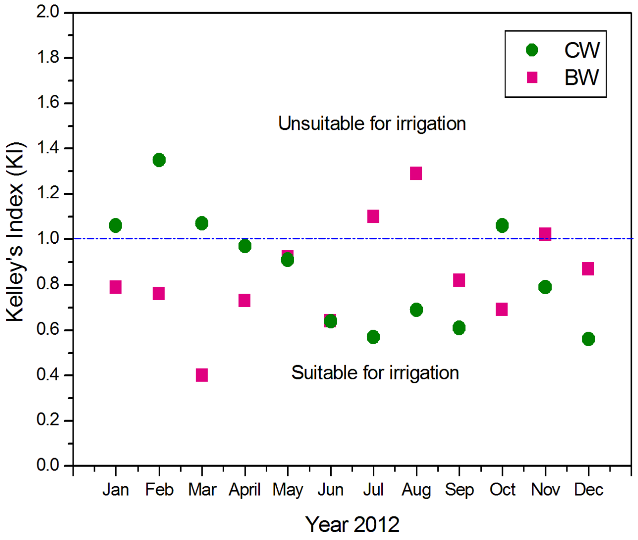

Figure 4.13: Monthly variation in mean Kelley's index (KI) of groundwater from control well (CW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The bore wells shows water has KI > 1 in July, August and November 2012 shifting groundwater to *unsuitable* for irrigation purposes during these months. The annual mean is 0.83±0.6, with a confidence interval of 0.5 - 1.2 *(suitable to unsuitable range)* at 95% level of significance.

4.3.5 Magnesium Adsorption Ratio (MAR)

Usually calcium and magnesium in most waters preserves a state of equilibrium. Groundwater evolved from rocks containing dolomite and basalt may contain more magnesium than calcium[18]. Plants growing in soil having excess concentration of magnesium develop coppery colour in the margins of leaves which later spreads over the surface finally leads to defoliation of leaf. It is known that presence of excess amount of magnesium reduces the availability of potassium in soil[19,20]. The Magnesium Adsorption Ratio (MAR) is calculated using following formula[21].

$$\mathbf{MAR} = \frac{\mathbf{Mg^{2+}}}{\mathbf{Ca^{2+} + Mg^{2+}}} \times \mathbf{100}$$

Magnesium hazard, MAR>50% is considered as unsuitable for irrigation purposes. If the ratio less (MAR<50%) means, water is suitable for irrigation.

Table 4.6: Monthly variation of magnesium adsorption ratio (MAR) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	MH	Water Quality	MH	Water Quality	MH	Water Quality
Jan 2012	26.2	S	29.5±9.9	S	35.1±3.5	S
Feb 2012	3.5	S	27.0±16.6	S	27.7±22.2	S
Mar 2012	28.5	S	27.2±4.5	S	28.6±24.5	S
Apr 2012	20.5	S	23.3±6.4	S	22.4±4.2	S
May 2012	20.8	S	25.8±12.5	S	21.1±9.9	S
Jun 2012	22.4	S	35.0±20.7	S	27.1±13	S
Jul 2012	21.1	S	32.7±19.9	S	22.6±17.8	S
Aug 2012	20.1	S	34.1±11.8	S	40.1±5.4	S
Sep 2012	28.6	S	31.9±12.3	S	41.2±20.3	S
Oct 2012	65.7	US	64.2±8.0	US	62.2±6.9	US
Nov 2012	31.5	S	48.0±20.5	S	39.2±8.4	S
Dec 2012	39.2	S	30.6±17.1	S	8.5±6	S
$\bar{x} \pm \sigma$	27.4±14.8	S	34.1±14.4	S	31.3±3.4	S
μ	27.4±9.1		34.1±8.9		31.3±2.1	
CI	18.26-36.45	S	25.3-43	S	29.20-33.44	S

S-Suitable *US-Unsuitable*

The magnesium adsorption ratio for control well shows that water is *suitable for irrigation* in all the months during the study period in the year 2012 except in October 2012, where it exceeds 50%. The annual mean of magnesium adsorption ratio is 27.4±14.8%, with a confidence interval of 18.3 - 36.5% at 95% significant limit that infers the suitability of water for irrigation purposes.

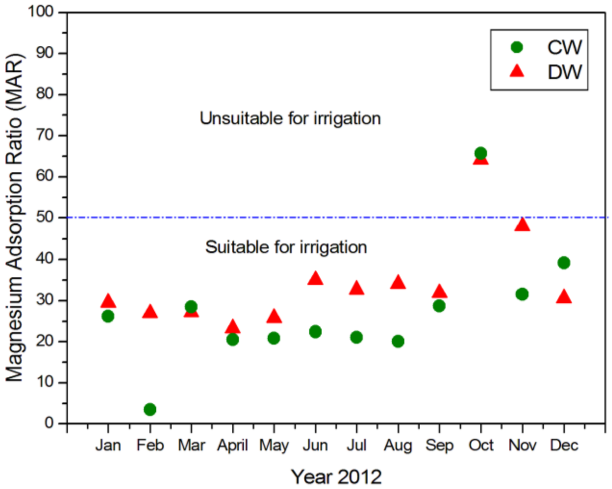

Figure 4.14: Monthly variation in mean magnesium adsorption ratio (MAR) of groundwater from control well (CW) and dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012.

In the case of dug well strata, all the months except October 2012, have magnesium adsorption ratio less than 50%. The annual mean of magnesium adsorption ratio is favourable for irrigation (34.1±14.4%), with a confidence interval of 25.3 - 43% at 95% level of significance.

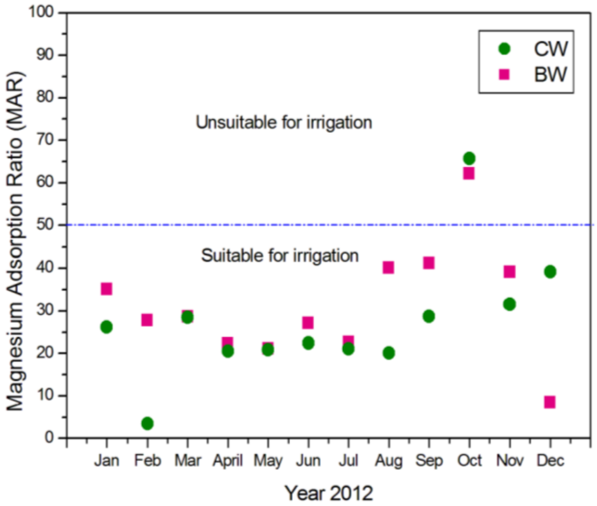

Figure 4.15: Monthly variation in mean magnesium adsorption ratio (MAR) of groundwater from control well (CW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012.

As in the case of shallow dug wells in the study area, deep bore well groundwater sources also exceeds the safe limit of magnesium adsorption ratio for irrigation during October 2012 with a monthly mean of 62.2±6.9 % (*unsuitable*). The annual mean MAR of bore wells have 31.3±3.4% with confidence interval, CI of 29.2 - 33.4% (95% significant level), water is considered *suitable for irrigation* purposes.

4.3.6 Residual Sodium Carbonate (RSC)

Residual sodium carbonate is very important irrigation water quality parameter especially in groundwater containing higher concentrations of calcium, magnesium and bicarbonates or carbonates. High RSC values of groundwater samples are indications of increased adsorption of sodium in the soil[7,22,23].

$$\mathbf{RSC} = \left(\mathbf{CO_3^{2-}} + \mathbf{HCO_3^{-}}\right) - (\mathbf{Ca^{2+}} + \mathbf{Mg^{2+}})$$

If the sum of carbonates is excess than the sum of calcium and magnesium, then there may be a risk of complete precipitation of calcium and magnesium[24]. RSC less than 1.25 meq/L is considered as suitable (safe) for irrigation purposes whereas RSC from 1.25 meq/L to 2.5 meq/L is recommended as marginally suitable and values greater than 2.5 meq/L is reported as unsuitable for irrigation[25].

Table 4.7: Monthly variation of residual sodium carbonate (RSC) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	RSC	**Water Quality**	**RSC**	**Water Quality**	**RSC**	**Water Quality**
Jan 2012	0.8	S	0.7±1.7	S	0.7±1.9	S
Feb 2012	0.7	S	0.2±0.7	S	1.7±0.7	MS
Mar 2012	0.8	S	0.6±1.0	S	0.7±1.5	S
Apr 2012	0.6	S	0.6±0.7	S	0.9±0.6	S
May 2012	1.5	MS	0.4±1.0	S	1.3±1.8	MS
Jun 2012	0.9	S	0.3±1.5	S	1.4±1.0	MS
Jul 2012	-0.6	S	0.1±1.7	S	1±2.3	S
Aug 2012	0.0	S	0.1±1.1	S	1.2±1.9	S
Sep 2012	-0.2	S	0.3±1.4	S	1.8±1.1	MS
Oct 2012	0.4	S	0.4±1.3	S	1.1±0.4	S
Nov 2012	0.1	S	1.2±1.7	S	1±1.0	S
Dec 2012	-0.1	S	0.5±1.8	S	0.1±1.4	S
$\bar{x} \pm \sigma$	0.41±0.6	S	0.45±1.4	S	1.1±0.4	S
μ	0.41±0.36		0.45±0.84		1.1±0.24	
CI	0.06–0.77	S	-0.39 –1.28	S-MS	0.83–1.32	S–MS

S- Suitable *MS-Marginally Suitable* *US-Unsuitable*

Control well shows residual sodium carbonate concentration less than 1.25 meq/L in all months having good water quality *(suitable category)* except in May 2012, where the water becomes *marginally suitable*, with an increase in RSC to 1.5 meq/L. The annual mean of RSC in control well is 0.41±0.6 meq/L, with confidence interval 0.06 – 0.77 meq/L *(suitable)* at 95% level of significance.

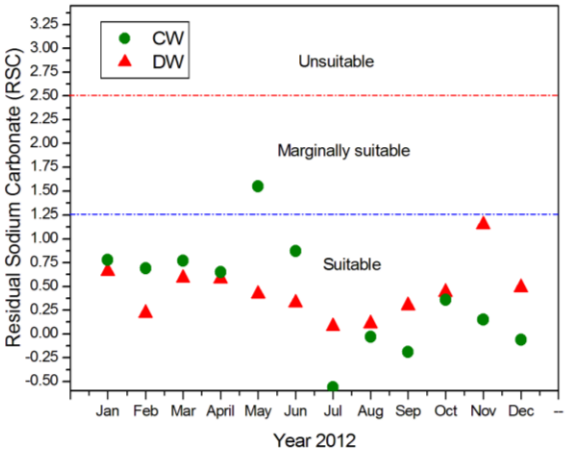

Figure 4.16: Monthly variation in mean of residual sodium chloride (RSC) of groundwater from control well (CW) and dug wells (DW) of Alappad coast, Kollam, Kerala, India during year 2012

The monthly mean of RSC in groundwater of shallow dug well strata shows, water is *suitable* throughout the year 2012 with annual mean of 0.45±1.4 meq/L. But the confidence interval infers a range of -0.39 to 1.28 meq/L with *suitable to marginally suitable category* at 95% level of significance.

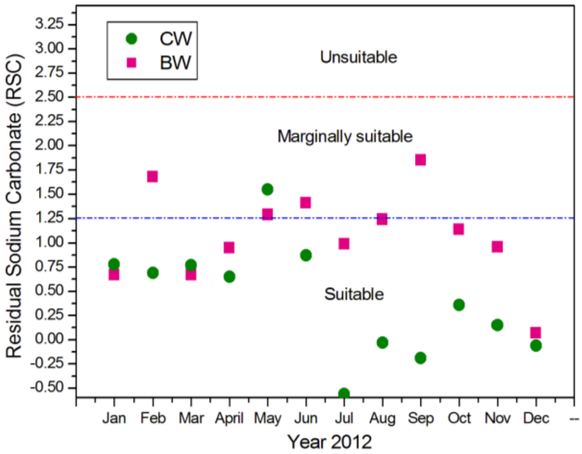

Figure 4.17: Monthly variation in mean of residual sodium chloride (RSC) of groundwater from control well (CW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The bore wells have a different profile compared to the shallow groundwater sources in the study period. In January 2012, the deep groundwater sources have RSC value *suitable* for irrigation with monthly mean 0.7±1.9 meq/L. During February 2012, the RSC value exceeds the safe limit to *marginally suitable* level (1.7±0.7 meq/L) and followed by safe range in March and April 2012. But again in May and June 2012 water quality degraded to *marginally suitable* for irrigation. Groundwater in July 2012 and August 2012 maintains RSC within *safe* limit but in September 2012, the water exceeds this limit with monthly mean of 1.8±1.1 meq/L *(marginally suitable*). From October to December 2012, RSC in water from deep bore well sources are safe for irrigation .The annual mean of RSC in water from bore wells is 1.1±0.4 meq/L, but in the range *suitable to marginally suitable* for irrigation within the confidence interval of 0.83 - 1.32 meq/L, at 95% level of significance.

4.3.7 Chloro-Alkalinity Indices-1 & 2 (CAI-1 & CAI-2)

Groundwater with a base-exchange reaction in which the alkaline earths have been exchanged for Na^+ ions ($HCO_3^- > Ca^{2+}+Mg^{2+}$) may be referred to as base-exchange-softened water, and that in which the Na^+ ions have been exchanged for the alkaline earths ($(Ca^{2+}+Mg^{2+}) > HCO_3^-$) may be referred to as base-exchange-hardened water[26]. CAI 1& 2 are calculated using the following formula proposed by Scholler[27].

$$\mathbf{CAI\ 1 = [Cl^- - (Na^+ + K^+)]/Cl^-}$$

$$\mathbf{CAI\ 2 = [Cl^- - (Na^+ + K^+)]/(SO_4^{2-} + HCO_3^- + CO_3^{2-} + NO_3^-)}$$

Chloro-alkalinity indices may be positive or negative. A positive CAI indicates chloro-alkalinity equilibrium state where $Na^+ + K^+$ in the water is get exchanged with Ca^{2+} and Mg^{2+} in the rock forming aquifer. Whereas negative CAI refers to chloro-alkalinity disequilibrium that signifies the exchange of Ca^{2+} and Mg^{2+} in water with $Na^+ + K^+$ of rocks[14,20,28].

Table 4.8: Monthly variation of chloro-alkalinity index 1 (CAI-1) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	CAI-1	Water Quality	CAI-1	Water Quality	CAI-1	Water Quality
Jan 2012	-1.5	CAD	-0.6±0.6	CAD	-2.5±4.0	CAD
Feb 2012	-1.0	CAD	-0.8±0.6	CAD	-8.3±9.4	CAD
Mar 2012	-1.3	CAD	-1.1±0.8	CAD	-6.3±8.4	CAD
Apr 2012	-1.3	CAD	-1.1±1.3	CAD	-0.2±0.6	CAD
May 2012	-27.0	CAD	-3.4±7.3	CAD	-1.5±1.7	CAD
Jun 2012	-9.2	CAD	-1.5±2.5	CAD	-1.5±1.2	CAD
Jul 2012	-0.2	CAD	-0.8±0.7	CAD	-6.2±8.2	CAD
Aug 2012	-0.2	CAD	-0.6±0.7	CAD	-5.3±8.3	CAD
Sep 2012	-0.4	CAD	-1±1.6	CAD	-7.2±7.5	CAD
Oct 2012	-0.9	CAD	-1.8±3.2	CAD	-1±1.2	CAD
Nov 2012	-0.8	CAD	-0.8±1.3	CAD	-3±3.9	CAD
Dec 2012	-0.8	CAD	-1±1.0	CAD	-1.6±2.7	CAD
$\bar{x} \pm \sigma$	-3.7±7.7	CAD	-1.2±2.6	CAD	-3.72±5.7	CAD
μ	-3.7±4.8		-1.2±1.6		-3.72±3.5	
CI	-8.47- 1.0	CAD-CAE	-2.81-0.35	CAD-CAE	-7.24- -0.2	CAD

CAD-Chloro-alkalinity Disequilibrium   CAE- Chloro-alkalinity Equilibrium

The chloro-alkalinity indices-1 of control well shows negative index (*chloro-alkalinity disequilibrium*), with annual mean -3.7±7.7meq/L. But the confidence interval indicates a range of 8.47 - 1.0 meq/L, at 95% level of significance, suggesting ion exchange reaction in positive direction also occurs to some extend along with the negative path. The annual mean values of CAI 1 in groundwater from dug well strata is -1.2±2.6 meq/L and bore well strata is -3.72±5.7 meq/L proposing negative schoeller index with confirming ion-exchange of $Ca^{2+}+Mg^{2+}$ in water with $Na^{+}+K^{+}$ in aquifer material. But in the case of dug well strata the confidence interval, CI ranges from *chloro-alkalinity disequilibrium* to *chloro-alkalinity equilibrium* (-2.81-0.35 meq/L) where the upper limit of the range is positive indicating ion-exchange of $Na^{+}+K^{+}$ in the water with $Ca^{2+}+Mg^{2+}$ from aquifer.

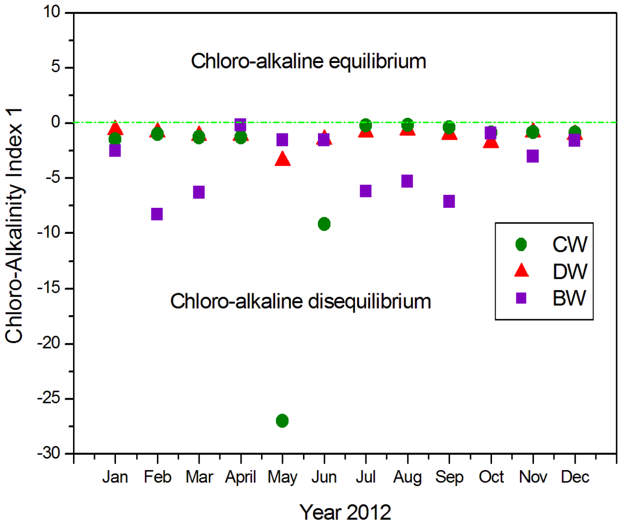

Figure 4.18: Monthly variation in mean of chloro-alkalinity index-1 (CAI-1) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Table 4.9: Monthly variation of chloro-alkalinity index 2 (CAI-2) of groundwater from control well (CW), dug well (DW) and bore well (BW) sources of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	CAI-2	Water Quality	CAI-2	Water Quality	CAI-2	Water Quality
Jan 2012	-0.6	CAD	-0.2±0.3	CAD	-0.2±0.3	CAD
Feb 2012	-0.6	CAD	-0.3±0.2	CAD	-0.4±0.3	CAD
Mar 2012	-0.5	CAD	-0.5±0.5	CAD	-0.3±0.3	CAD
Apr 2012	-0.5	CAD	-0.3±0.3	CAD	-0.1±0.3	CAD
May 2012	-0.6	CAD	-0.2±0.4	CAD	-0.3±0.2	CAD
Jun 2012	-0.5	CAD	-0.2±0.4	CAD	-0.2±0.2	CAD
Jul 2012	-0.1	CAD	-0.3±0.2	CAD	-0.7±0.7	CAD
Aug 2012	-0.1	CAD	-0.1±0.5	CAD	-0.5±0.2	CAD
Sep 2012	-0.2	CAD	-0.3±0.4	CAD	-0.4±0.3	CAD
Oct 2012	-0.5	CAD	-0.3±0.3	CAD	-0.2±0.3	CAD
Nov 2012	-0.4	CAD	-0.3±0.3	CAD	-0.4±0.3	CAD
Dec 2012	-0.3	CAD	-0.5±0.8	CAD	-0.2±0.2	CAD
$\bar{x} \pm \sigma$	-0.4±0.2	CAD	-0.27±1.4	CAD	-0.33±0.3	CAD
μ	-0.4±0.11		-0.27±0.88		-0.27±0.21	
CI	-0.52– -0.29	CAD	-1.16– 0.6	CAD–CAE	-0.53– -0.12	CAD

CAD-Chloro-alkalinity Disequilibrium

The control well shows negative schoeller index value, indicating chloro-alkalinity disequilibrium. Here calcium and magnesium from the groundwater is exchanged with sodium and potassium from aquifer material. The annual mean of -0.4±0.2 meq/L with confidence interval of ¯0.52-¯0.29 meq/L at 95% level of significance *(chloro-alkalinity disequilibrium)*. In groundwater samples from dug well strata, the annual mean is -0.27±1.4 meq/L (*chloro-alkalinity* dis*equilibrium*) but the confidence interval, CI shows the range extends to positive CAI 2 also (-1.16- 0.6 meq/L at 95% level of significance) suggesting both ion exchange (*chloro-alkalinity equilibrium*) and reverse ion exchange (*chloro-alkalinity disequilibrium*) are reported from shallow dug well sources of the study area.

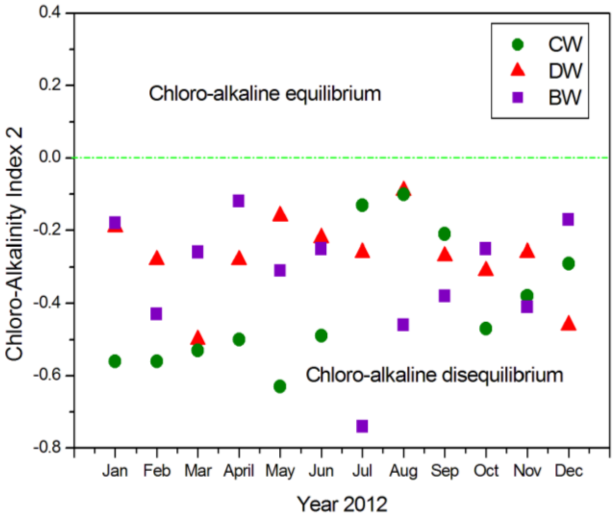

Figure 4.19: Monthly variation in mean of chloro-alkalinity index-2 (CAI-2) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

For bore well strata, CAI 2 is negative throughout the year 2012, with annual mean of -0.33±0.3 meq/L and confidence interval also limits to *chloro-alkalinity disequilibrium*, ranging from -0.53 to -0.12 meq/L at 95% level of significance.

4.4 Corrosion Indices

Corrosion is the ability of water to cause incrustation of metals and damage the water supply systems due to certain factors such as pH, TDS, alkalinity, calcium hardness, HCO_3^-, Cl^-, and SO_4^{2-} in inappropriate level. It is very essential to check the corrosive properties for predicting the industrial suitability of water[13]. The indices used for predicting the corrosive behaviour of groundwater are Langelier Saturation Index (LSI), Ryznar Stability Index (RSI), Aggressiveness Index (AI) and Larson-Skold index.

4.4.1 Langelier Saturation Index (LSI)

Langelier Saturation Index (LSI) is used to predict the tendencies of a water to precipitate or dissolve calcium carbonate, the main parameter for determining the corrosivity of water. According to Langelier[29,30] the presence of excess amount of free CO_2 is the major factor contributing corrosive property of water, in addition to low pH. As a result, low alkalinity conditions accompanied with free CO_2 accelerate corrosion behaviour of natural water. Usually calcium and magnesium are detained with bicarbonate in solution if CO_2 is sufficient and prevent its decomposition into carbonates.

Langelier Saturation Index is calculated using the measured pH of the water and pH at saturation (pHs) using four water quality parameters namely TDS, temperature, calcium hardness as $CaCO_3$ and alkalinity. The difference between the measured pH and calculated pH (ie. pHs) give LSI of a given water sample[31,32].

The LSI value ranges from –3 to +3. The positive values of LSI indicate that the water is super saturated with $CaCO_3$ and scale formation is possible on the metal surface and of corrosion will be reduced or inhibited. A negative value of LSI specifies the water is under saturated dissolving $CaCO_3$ scales and water is considered as corrosive. If the LSI is 0, water is said to be in equilibrium state where scale formation is neither encouraged nor discouraged[33].

$$\mathbf{LSI = pH - pH_s} \quad \text{..} (1)$$

$$\mathbf{pH_s = (9.3 + A + B) - (C + D)} \quad \text{..} (2)$$

Where pH = actual pH of water

pHs = pH of saturation for $CaCO_3$

A = [Log_{10} (TDS) -1)/10], TDS in ppm

B = [-13.12 × Log_{10} (T + 273)) + 34.55], Temperature, T in °C

C = [Log_{10} (Calcium hardness) - 0.4], Calcium hardness in ppm (as $CaCO_3$)

D = Log_{10} (Alkalinity), alkalinity in ppm (as $CaCO_3$).

Table 4.10: Monthly variation Langelier saturation index (LSI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	LSI	**Tendency of water**	**LSI**	**Tendency of water**	**LSI**	**Tendency of water**
Jan 2012	0.0	BP	0.3±0.4	SSFC	-0.2±0.2	SCNSF
Feb 2012	0.1	SSFC	0.2±0.5	SSFC	0.0±0.3	BP
Mar 2012	0.4	SSFC	0.2±0.5	SSFC	0.5±0.1	SSFC
Apr 2012	0.2	SSFC	0.1±0.6	SSFC	0.1±0.4	SSFC
May 2012	0.1	SSFC	0.1±0.5	SSFC	-0.3±0.3	SCNSF
Jun 2012	-0.2	SCNSF	-0.1±0.5	SCNSF	-0.5±0.3	SCNSF
Jul 2012	-0.1	SCNSF	-0.1±0.5	SCNSF	-0.1±0.2	SCNSF
Aug 2012	0.1	SSFC	0.1±0.6	SSFC	-0.3±0.4	SCNSF
Sep 2012	-0.1	SCNSF	0.0±0.5	BP	-0.5±0.4	SCNSF
Oct 2012	-0.6	SCNSF	-0.3±0.5	SCNSF	-0.6±0.3	SCNSF
Nov 2012	0.4	SSFC	-0.2±0.6	SCNSF	0.3±0.2	SSFC
Dec 2012	0.0	BP	0.2±0.8	SSFC	-0.2±0.4	SCNSF
$\bar{x} \pm \sigma$	0.01±0.3	SSFC	0.03±0.5	SSFC	-0.1±0.3	SCNSF
μ	0.01±0.2		0.03±0.3		-0.1±0.2	
CI	-0.2 -0.2	SCNSF-SSFC	-0.3-0.4	SCNSF-SSFC	-0.3-0	SCNSF-BP

IC- Intolerable corrosion; SC- Serious corrosion; SCNSF- Slightly corrosive but non scale forming;
BP- Balanced but pitting; SSFC-Slightly scale forming but corrosive;
SFNC- Scale forming and non corrosive

The LSI of control well in January 2012 is at equilibrium or saturated condition and from February 2012 onwards till May 2012, LSI is between 0 to 0.5. This positive LSI supposes water is supersaturated with $CaCO_3$, leading to the deposition of scales on the surface of metals. But this calcium carbonate scale deposition is not sufficient to prevent corrosion hence tendency of water is *slightly scale forming but corrosive* (SSFC). During monsoon months of June and July 2012 water becomes *slightly corrosive but non scale forming* (SCNSF). In August 2012, LSI shifted to *slightly scale forming but corrosive* (SSFC) and tend to be in equilibrium with balanced *but pitting* (BP) nature. October 2012. LSI become positive with *slightly scale forming but corrosive* (SSFC) nature in November 2012 and finally reaches at equilibrium (LSI=0) in December 2012. The annual mean of LSI of control well is 0.01±0.3, indicating water exhibits *slightly corrosive but non scale forming to slightly scale forming but corrosive* (SCNSF-SSFC) nature.

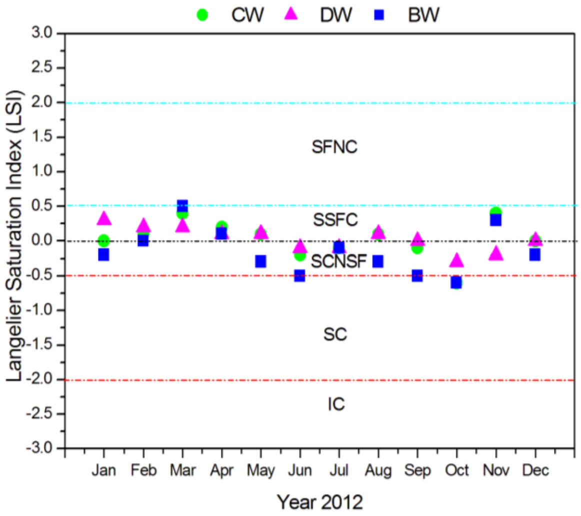

Figure 4.20: Monthly variation in mean of Langelier saturation index (LSI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The dug wells have a lower limit of *slightly corrosive but non scale forming* (SCNSF) nature throughout the study period, assuming water has a basically corrosive nature. But from January 2012 to May 2012 the upper limit of LSI is 0.7, leading to *scale forming and non-corrosive* (SFNC) behaviour of water. In June-July period, the upper range of LSI is narrowed down to *slightly scale forming but corrosive* (SSFC). August 2012 shows slight increase in scaling nature of water but remained *slightly scale forming but corrosive* (SSFC). In September 2012 water remained in *balanced but pitting* (BP). During October and November 2012, LSI is negative, as dissolving of calcium carbonate scale occurs and water is *slightly corrosive but non scale forming* (SCNSF). In December 2012 the water becomes *slightly scale forming but corrosive* (SSFC). The annual mean of LSI for shallow dug wells is -0.1±0.3, with confidence interval, CI -0.3 to 0.4 at 95% level of significance. Hence overall corrosion behaviour of water remains *slightly corrosive but non scale forming* to *slightly scale forming but corrosive* (SCNSF-SSFC).

The bore wells in the study depicts a wide range of behaviour in terms of corrosion tendency and scale formation. In January 2012 bore wells are *slightly corrosive but non scale forming* (SCNSF) which becomes balanced but pitting (BP) in February 2012. During March and April 2012, monthly mean of LSI shifts to positive with *slightly scale forming but corrosive* (SSFC) water. But from May 2012 onwards LSI turned into negative and remained *slightly corrosive but non scale forming* (SCNSF) till October 2012. In November 2012, LSI become *slightly scale forming but corrosive* (SSFC) but later become *slightly corrosive but non scale forming* (SCNSF) in December 2012. The annual mean of LSI for bore wells is -0.1±0.3, with confidence interval -0.3-0.4 at 95% level of significance, confirming water is *slightly corrosive but non scale forming* to *slightly scale forming but corrosive* (SCNSF-SSFC) nature.

4.4.2 Ryznar Stability Index (RSI)

Ryznar Stability Index (RSI) is an empirical index developed by Ryznar in 1944 that is used to predict the scaling tendency of water. This index works on the assumption that the water with scale forming properties can control the rate of corrosion while non-scaling water are considered as corrosive[34]. RSI is generally used for flowing water systems such as flowing water through pipe system, whereas LSI is used mostly for standing water such as storage water or reservoirs. Hence the combined use of these two indices provide adequate information to improve the accuracy in predicting scale forming or corrosion tendencies of water. This helps to reduce the cost of maintenance of distribution systems[35].

$$\mathbf{RSI = 2pH_s - pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The control well RSI falls in 7.0 to 9.0 range showing dissolving scale formation and corrosive nature of soil. In most of the months control well shows intense dissolving of scale which leads to *heavy corrosion* (HC). The annual mean of RSI is 7.7±0.4, with a confidence interval, CI of 7.4-7.9, at 95% significant level.

Table 4.11: Monthly variation Ryzner stability index (RSI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	RSI	Tendency of water	RSI	Tendency of water	RSI	Tendency of water
Jan 2012	7.6	HC	7.2±0.7	CS	7.5±0.2	HC
Feb 2012	7.6	HC	7.3±1.1	CS	7.4±0.5	CS
Mar 2012	7.1	CS	7.5±1.1	HC	6.7±0.2	LSC
Apr 2012	7.5	HC	7.5±1.0	HC	7.1±0.6	CS
May 2012	7.6	HC	7.4±0.7	CS	7.7±0.5	HC
Jun 2012	7.9	HC	7.9±0.9	HC	7.9±0.5	HC
Jul 2012	7.9	HC	7.8±1.0	HC	7.5±0.4	HC
Aug 2012	7.5	HC	7.6±1.0	HC	7.8±0.6	HC
Sep 2012	7.8	HC	7.6±0.9	HC	8.2±0.7	HC
Oct 2012	8.7	HC	8.3±0.9	HC	8.4±0.3	HC
Nov 2012	7.3	CS	8.1±1.0	HC	7.3±0.4	CS
Dec 2012	7.6	HC	7.6±1.1	HC	7.4±0.5	CS
$\bar{x} \pm \sigma$	7.7±0.4	HC	7.7±1.0	HC	7.6±0.5	HC
μ	7.7±0.2		7.7±0.6		7.6±0.3	
CI	7.4-7.9	CS- HC	7.1-8.3	CS- HC	7.3-7.9	CS- HC

LSC- Little Scale Forming *CS-Corrosion Significant* *HC-Heavy Corrosion*

From the graph (Figure 4.21), RSI of monthly means of dug wells also falls above 7.0, showing a corrosive nature throughout the study period. In January, February and April 2012 RSI of water is in between 7 to 7.5 reporting *corrosion significant* (CS) nature of water. In all other months during the year 2012 RSI > 7.5 indicating water exhibited *heavy corrosion* (HC) behaviour. The annual mean of RSI for dug wells is 7.7±1.0 with confidence interval, CI 7.1-8.3 at 95% level of significance, inferring RSI of water is *corrosion significant* to *heavy corrosion* in nature and has the potential to damage the water supply systems.

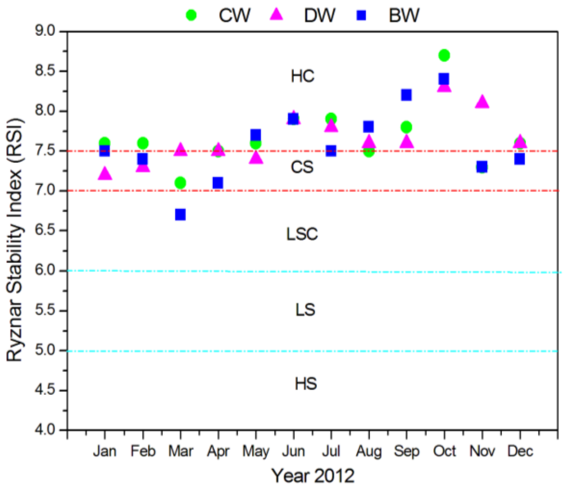

Figure 4.21: Monthly variation in mean of Ryzner stability index (RSI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Ryzner index for monthly mean of bore wells reports *little scale forming to heavy corrosion* status of water (Figure 4.21). However annual mean of RSI in bore wells is 7.6±0.5, as the water behaviour varies from *corrosion significant* (CS) *to heavy corrosion* (HC), with a confidence interval of 7.3-7.9, at 95% level of significance.

4.4.3 Aggressive Index (AI)

The Aggressive Index (AI) is an empirical formula developed for assessing the aggressiveness of water supply that leads to the exfoliation of asbestos from pipes[36]. Aggressiveness index is comparatively simple and less accurate index for corrosion calculated from pH, alkalinity and calcium hardness excluding temperature and dissolved solids. Aggressiveness index as RSI consists of only positive values and classifies water into three classes, namely non-aggressive, moderately aggressive and highly aggressive.

$$\mathbf{AI = pH + \log_{10} Alkalinity + \log_{10} Calcium\ Hardness} \quad .....(4)$$

Table 4.12: Monthly variation of aggressiveness index (AI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	**CW**		**DW**		**BW**	
	AI	**Tendency of water**	**AI**	**Tendency of water**	**AI**	**Tendency of water**
Jan 2012	11.9	MA	12.2±0.4	NA	11.7±0.1	MA
Feb 2012	12.0	NA	12.1±0.6	NA	11.9±0.3	MA
Mar 2012	12.3	NA	12.1±0.6	NA	12.3±0.1	NA
Apr 2012	12.0	NA	12.0±0.6	NA	11.9±0.4	MA
May 2012	11.9	MA	12.0±0.5	NA	11.5±0.3	MA
Jun 2012	11.7	MA	11.7±0.5	MA	11.4±0.3	MA
Jul 2012	11.7	MA	11.8±0.6	MA	11.0±1.0	MA
Aug 2012	12.0	NA	12.0±0.6	NA	11.6±0.4	MA
Sep 2012	11.7	MA	11.9±0.5	MA	11.3±0.4	MA
Oct 2012	11.3	MA	11.6±0.5	MA	11.2±0.3	MA
Nov 2012	12.2	NA	11.7±0.6	MA	12.2±0.2	NA
Dec 2012	11.8	MA	11.9±0.6	MA	11.6±0.4	MA
$\bar{x} \pm \sigma$	11.9±0.3	MA	11.9±0.5	MA	11.6±0.4	MA
μ	11.9±0.2		11.9±0.3		11.6±0.3	
CI	11.7-12	MA-NA	11.6-12.2	MA- NA	11.4-11.9	MA

MA- Moderately Aggressive *NA- Non-Aggressive*

The aggressiveness index of control well reveals that, groundwater comes in *moderate aggressive* to *non-aggressive* (MA-NA) nature. The annual mean of aggressiveness index of control well is 11.9±0.3, with a confidence interval of 11.7 – 12, at 95% confidence level. All the dug well sources comes in moderately aggressive to non-aggressive classes, with an annual mean of 11.6±0.4 and confidence interval of 11.6 - 12.2, at 95% significant level.

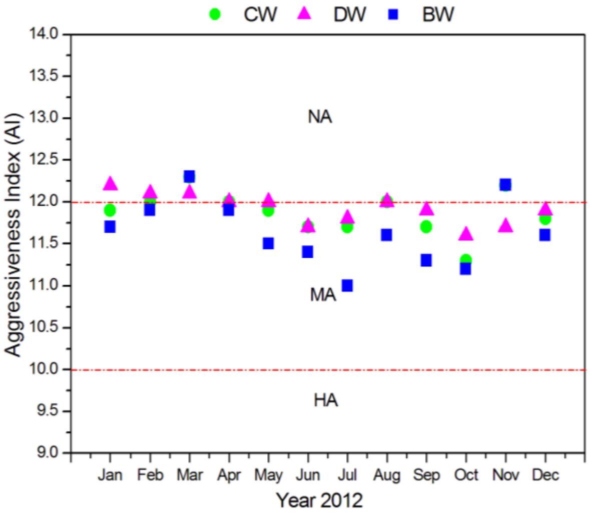

Figure 4.22: Monthly variation in mean of aggressiveness index (AI) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The bore wells show a *moderately aggressive* (MA) behaviour in January and February 2012, which shifts to *non-aggressive* (NA) in March 2012. It display *moderately aggressive* (MA) behaviour from April to October 2012, but becomes *moderately aggressive* (MA) nature in November 2012. In December 2012 water reported to be *moderately aggressive* (MA). The annual mean of AI for water from bore wells falls in *moderately aggressive* to *non-aggressive* (11.6±0.4) but the confidence interval is 11.4-11.9 revealing water quality is *moderately aggressive* at 95% significant level.

4.4.4 Larson-Skold Index

Larson-Skold index is also known as Larson ratio. Unlike all the above mention corrosion indices (LSI, RSI & AI), Larson ratio considers corrosion formed due to anions in the water samples. This index is proposed considering the role of chloride and sulphate in pitting of pips made of mild steel[37]. According to this, concentrations of chloride ion and sulphate ion alone are not responsible for pitting but also the concentration of bicarbonate also has to consider. If the concentration of chloride and sulphate ions are low and may not took part in the corrosive property of water, sometimes low bicarbonate concentration can induce corrosion by increasing the concentration of iron in water. While reports suggest the high concentration of bicarbonate assumed to be noncorrosive towards iron[38].

Table 4.13: Monthly variation of Larson-Skold index (L-S) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

Period Month/Year 2012	CW		DW		BW	
	L-S	**Tendency of water**	**L-S**	**Tendency of water**	**L-S**	**Tendency of water**
Jan 2012	0.4	NC	0.4±0.4	NC	0.7±1.0	NC
Feb 2012	0.6	NC	0.4±0.3	NC	0.1±0.1	NC
Mar 2012	0.4	NC	0.6±0.5	NC	0.1±0	NC
Apr 2012	0.4	NC	0.4±0.2	NC	0.5±0.2	NC
May 2012	0.0	NC	0.4±0.5	NC	0.4±0.4	NC
Jun 2012	0.1	NC	0.5±0.3	NC	0.3±0.2	NC
Jul 2012	0.7	NC	0.8±1.7	SC	0.3±0.3	NC
Aug 2012	0.7	NC	0.8±1.2	SC	0.6±0.5	NC
Sep 2012	0.5	NC	0.5±0.4	NC	0.1±0.1	NC
Oct 2012	0.6	NC	0.4±0.4	NC	0.3±0.1	NC
Nov 2012	0.5	NC	0.5±0.3	NC	0.4±0.5	NC
Dec 2012	0.4	NC	0.5±0.4	NC	0.9±1.4	SC
$\bar{x} \pm \sigma$	0.5±0.2	NC	0.5±0.7	NC	0.4±0.5	NC
μ	0.5±0.1		0.5±0.4		0.4±0.3	
CI	0.3-0.6	NC	0.1-1.0	NC- SC	0-0.7	NC

NC-Non Corrosive *SC-Slightly Corrosive* *HC-Highly Corrosive*

Larson-Skold index for control well water samples is within the range of 0 to 0.8 (Figure 4.23). Here high concentration of HCO_3^- prevents water from becoming corrosive. The concentration of chlorides and sulphates probably will not interfere with the nature film formation. Hence the water is *Non-corrosive* (NC). The annual mean of Larson-Skold index for water from control well is 0.5±0.2, with in the confidence interval of, CI 0.3 – 0.6, at 95% significant level.

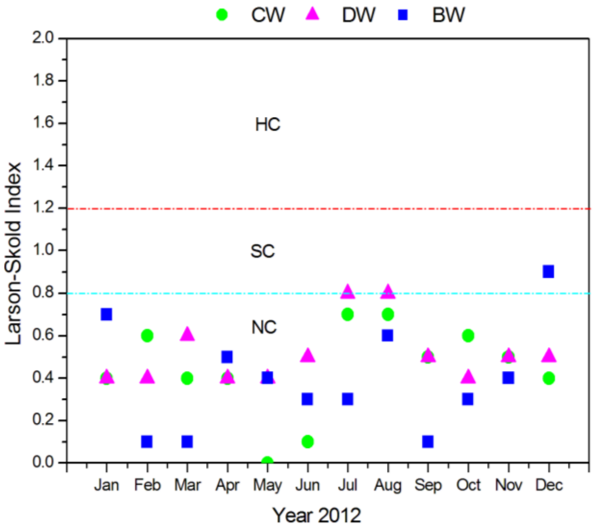

Figure 4.23: Monthly variation in mean of Larson-Skold index (L-S) of groundwater from control well (CW), dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during year 2012

The dug wells from January to June 2012 and September to December are *Non-corrosive* (NC). During July to August period comparatively high concentration and variation of chloride and sulphate interfere with natural film formation or scale forming tendency of water making it s*lightly corrosive* (SC). The annual mean for dug wells is 0.4±0.5, but the confidence interval at 95% significance level is 0.1-1.0 making water *non corrosive* to *slightly corrosive* (NC-SC).

The bore wells in most of the months are *non-corrosive* (NC). An increase in chloride with relatively lower concentration of bicarbonate leads to the tendency of water towards corrosion and water becomes *slightly corrosive* (SC) during December 2012. Bore wells has annual mean of 0.4±0.5, covering *non-corrosive* to *slightly corrosive* (NC - SC) range. However the confidence interval (0 - 0.7) suggest water is generally *non-corrosive* (NC) in nature at 95% level of significance.

4.5 Trace metal study

Inductively coupled plasma/mass spectrometry (ICP/MS) is used to determine the concentration of various trace elements in the groundwater sources. Natural environmental factors like lithology of the aquifer, quality of recharging waters, rock-water interaction in the aquifer as well as anthropogenic activities greatly influence the extent of trace element content in groundwater by polluting delicate system and changing the physico-chemical characters[57]. The availability of these metals in groundwater is very significant as it is directly linked to food chain. The increase in concentration of these trace metals can cause serious issues to living organisms. The things will be worst for human beings as we occupy the apex of trophic structure and any harmful pollutants entire into the food chain increase in concentration many times in the successive trophic levels due to biomagnification. The trace metals such as Lithium (Li), Aluminium (Al), Vanadium (V), Chromium (Cr), Manganese (Mn), Nickel (Ni), Cobalt (Co), Copper (Cu), Zinc (Zn), Gallium (Ga), Arsenic (As), Selinium (Se), Rubidium (Rb), Strontium (Sr), Silver (Ag), Cadmium (Cd), Indium (In), Cesium (Cs), Barium (Ba), Lead (Pb) and Bismuth (Bi) are analysed for the groundwater sources of Alappad coast in December 2012 and the results are tabulated in the table below (Table 4.14) which includes the standard permissible limits of these trace metals recommended by BIS and WHO. It is found that the concentration of all the trace elements are very low in all the dug wells and bore wells analysed and remained within the limit of BIS and WHO standards.

Table 4.14: Trace element analysis of groundwater from dug wells (DW) and bore wells (BW) of Alappad coast, Kollam, Kerala, India during the month of December 2012

Trace Metals	DW1	DW2	DW3	DW4	DW5	DW6	DW7	DW8	DW9	DW10	DW11	DW12	DW13	DW14	DW15	BW1	BW2	BW3	DW $(\bar{x} \pm \sigma)$	BW $(\bar{x} \pm \sigma)$	BIS (2012)	WHO (2011)
Li (µg/l)	1.2	0.3	0.6	5.9	1.3	0.3	0.2	1.1	1	6.2	10	7.3	1.4	3.6	0.3	5.6	2.8	3.3	2.7±3	3.9±1		
Al (µg/l)	18	19.8	27.6	14.1	14.5	15.2	41.6	16.1	36.9	28.7	23.1	35.6	12.4	58.4	112.5	24.5	91.1	25.3	31.6±26	47±38	200	100
V (µg/l)	1.7	2.7	2.2	0.2	0.6	1.1	0.5	2	2.9	1.6	2.9	5	4.2	0.8	1.1	0.4	0.4	6.4	2.0±1	2.4±3		
Cr (µg/l)	11.7	1.4	0.6	0.3	0.7	0.7	0.3	0.6	0.5	0.5	4.6	1.2	1.4	0.7	0.6	0.4	0.5	0.4	1.7±3	0.4±0	50	50
Mn (µg/l)	8.1	6.7	8.5	18.7	8	21.7	4.5	5.1	4.5	5.5	2.4	3.3	24.6	8.3	6.2	30.3	37.6	169.6	9.1±7	79.2±78	500	400
Ni (µg/l)	1	0.7	1.8	1	2	0.6	2	1.2	0.7	0.9	1	0.8	4.2	3	3	5.2	4.1	119.5	1.6±1	42.9±66	20	70
Co (µg/l)	0.1	0	0.1	0	0.1	0.1	0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0	0.1	0.1	0.2	0.1±0	0.1±0		
Cu (µg/l)	2.4	2.5	4.9	1.6	6.3	1.3	1.8	2.1	4	2.7	5.3	4.3	3.2	5.7	2.9	1.4	1.4	3.8	3.4±2	2.2±1	1500	2000
Zn (µg/l)	21.3	7.4	15	3.7	6.5	4	2.7	5.6	2.5	4.4	23.3	36.2	7.2	15.2	4.3	6.2	4.2	21.7	10.6±10	10.7±10	15000	
Ga (µg/l)	4.3	2.2	2.4	5.1	6	1.9	6.5	3.3	4.1	2.3	1.9	3.5	2.3	2.9	8.1	16.4	12.2	13.1	3.8±2	13.9±2		
As (µg/l)	0.7	1.9	2.1	0.7	1.2	1.1	0.2	0.8	1.6	5.5	1.4	4.5	2.8	1.8	0.3	0	0.1	0.2	1.8±1	0.1±0	50	10
Se (µg/l)	6.2	4.9	3.9	4.1	3.9	3.6	3.2	4.4	4.2	4.3	4.8	4.6	4.3	4.1	4.4	3.9	3.7	4	4.3±1	3.9±0	10	40
Rb (µg/l)	7.9	6.1	7.3	10.3	2.5	5	3.7	21.4	19.6	6.6	10.9	21.7	9	4.3	4.1	10.8	8.6	17.6	9.4±6	12.3±5		
Sr (µg/l)	277.1	83.8	247.7	451.6	272.7	248.8	39	227	430	710.8	1374.6	421.2	555.7	568.1	57.8	653.5	492.5	849.3	397.7±334	665.1±179		
Ag (µg/l)	0.7	1	0.3	0.1	0.7	0.3	0.9	0.4	12	0.2	0.3	0.3	0.5	0.5	0.7	1.2	0.6	1.5	1.3±3	1.1±0	100	
Cd (µg/l)	0.1	0.1	0.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.1±0	0.1±0	3	
Ba (µg/l)	24.4	12.7	13.7	29.1	33.1	12	38.7	20.7	22.4	13.4	10.8	17.3	11.7	14.8	37.7	99.4	69.2	86.1	20.8±10	84.9±15	700	700
Pb (µg/l)	0.4	0.4	1.6	0.2	0.5	0.3	0.4	0.2	0.3	0.7	0.4	0.8	0.5	0.5	0.4	0.8	0.7	0.5	0.5±0	0.7±0	50	10

4.6 Total Carbon Analysis

Total organic carbon analyser is a best alternative for conventional COD and BOD analysis of water. The BOD analysis need five days incubation period where as COD test generate harmful waste products including mercury, hexavalent chromium, sulphuric acids, silver and other toxic materials depending up on the method adopted[39]. TOC analysis is both less time consuming and potentially more precise than the COD test[40].

Total carbon in groundwater include sum of total inorganic and total organic carbon. Total organic carbon is usually used as an indicator of organic matter present in water. Organic carbon derived from natural sources consists of decomposition of plants and animals where as other sources of organic carbon are resultant from anthropogenic activities[41].

In drinking water the organic carbon should be controlled in order to prevent the growth of microbial organisms that make the water unfit for consumption[42]. The inorganic carbon includes of carbonates, bicarbonates and dissolved carbon dioxide[43]. The solubility of metals such as zinc and copper are influenced by the pH and inorganic content of groundwater. Solubility of both these metals decreases with increase in pH but concentration of zinc carbonate decreases with increase in carbonate species, whereas concentration of copper increases with increase in carbonate species in water[42]. Total organic carbon analyser determines the total carbon (TC) and total inorganic carbon (TIC) in a water sample. Total organic carbon is determined by subtracting TIC from TC.

Table 4.15: Total carbon (TC), total inorganic carbon (TIC) & total organic carbon (TOC) of groundwater from dug well sources of Alappad coast, Kollam, Kerala, India, during December 2012.

Station	TC (mg/L)	TIC (mg/L)	TOC (mg/L)
DW1	40.4	36.1	4.3
DW2	37.3	33.7	3.6
DW3	40.5	22.6	17.9
DW4	49.8	39.3	10.5
DW5	42.9	38.9	4
DW6	31.6	27	4.6
DW7	46.4	40.4	6
DW8	45.4	40.7	4.7
DW9	40.9	37.3	3.6
DW10	49.5	46.1	3.4
DW11	46.8	42.4	4.4
DW12	42.5	24.1	18.4
DW13	54.8	39.8	15
DW14	59.1	46.9	12.2
DW15	15.6	9.5	6.1
$\bar{x} \pm \sigma$	42.9±10.2	35.0±10.1	7.9±5.4

The carbon analysis in shallow dug well sources revels that majority of carbon in the water are inorganic carbon. Average total carbon in the study area is 42.9±10.2 mg/L and inorganic carbon makes an average contribution of 35.0±10.1 mg/L. A small amount of total organic carbon is observed in the study area with an average of 7.9±5.4 mg/L. The station DW3, DW12 and DW 13 shows a slight increase in organic carbon concentration of 17.9 mg/L, 18.4 mg/L and 15 mg/L respectively.

Table 4.16: Total carbon (TC), total inorganic carbon (TIC) & total organic carbon (TOC) in groundwater from bore well sources of Alappad coast, Kollam, Kerala, India, during December 2012.

Station	TC (mg/L)	TIC (mg/L)	TOC (mg/L)
BW1	48.1	45.1	3
BW2	50.8	48.2	2.6
BW3	38.5	36.7	1.8
$\bar{x} \pm \sigma$	45.8±6.5	43.3±6.0	2.5±0.6

The total organic carbon in deep bore well sources is 45.8±6.5 mg/L and inorganic carbon gives substantial contribution of 43.3±6.0 mg/L. The total organic carbon input is negligible, 2.5±0.6 mg/L, inferring no harmful organic pollutant is present in water.

4.7 Designated Best Use

Designated best use of water means identifying the highest quality of the water in terms of water quality requirements for specific use recommended by Central Pollution Control Board (CPCB)[44]. According to this water sources can be classified into 5 classes (A, B, C, D and E) subjected to the quality of water for particular usage of water body. Class A includes all water bodies used for drinking without any conventional treatment but after disinfection. Water sources that are used for outdoor bathing comes in class B. Drinking water sources after conventional treatment and disinfection are included in class C and propagation of wild life and fisheries is termed in class D. Class E comprises of those water bodies which are used in irrigation, industrial cooling and controlled waste disposal.

The parameters used to assess the designated best use of a water source for drinking, irrigation and industrial purposes are pH, dissolved oxygen (DO), biological oxygen demand (BOD), total coliforms organism (MPN), electrical conductivity (EC), sodium adsorption ratio (SAR) and boron. SAR and boron concentration of groundwater are analysed to evaluate the irrigation suitability prescribed by CPCB. In December 2012 MPN and boron are analysed in order to classify the groundwater according to the designated best use developed by CPCB.

Water quality parameters of individual groundwater sources of December 2012 to find the designated best use (DBU). Here the pH of all water sources are between 6.5 to 8 and EC below 2250 µS/cm, both are under prescribed limit. The dissolved oxygen (DO) should be 5 mg/L or more for Class A and 4 mg/L or more for other classes (Class B, C & D). No water sources have DO range above 6 mg/l, implying the water sources are unfit for drinking purposes without conventional treatment but after disinfection. In water samples from DW4, DW6, DW7, BW1, BW2 and BW3, DO <4 mg/l, which make this water sources are unfit for drinking and outdoor bathing purposes. The BOD in DW10, DW11, DW12, DW13 and DW 14 < 2 mg/L, making theses water sources also unfit for Class A, B, C & D. Presence of E coli in DW 1, DW 2 and DW 11 makes it strictly unfit for human consumption and can be used directly for irrigation, industrial cooling and controlled waste disposal (Class E) only.

Table 4.17: Classification of water from shallow and deep groundwater sources of Alappad coast, Kollam, Kerala, India based on designated best use by CPCB during the period December 2012.

Station No:	Type	MPN/ 100ml	E. Coli	pH	EC µS/cm	DO mg/l	BOD mg/l	SAR	Boron	Class
1	DW1	4	Present	7.5	560	5.4	0.6	1.6	0.76	Class E
2	DW2	23	Present	7.5	320	5.8	0.6	1.5	0.80	Class E
3	DW3	Nil	Absent	7.4	210	4.9	0.6	0.7	0.79	Class B,C&E
4	DW4	Nil	Absent	7.8	340	3.3	1.2	0.7	0.77	Class C & E
5	DW5	Nil	Absent	7.4	390	4.5	0.6	1.1	0.80	Class B,C&E
6	DW6	Nil	Absent	6.9	680	3.9	0.6	4.3	0.76	Class C & E
7	DW7	Nil	Absent	7.7	430	2.5	1.2	1.6	0.87	Class C & E
8	DW8	Nil	Absent	7.4	3310	4.7	0.6	6.9	0.69	Class B & C
9	DW9	Nil	Absent	7.7	430	4.5	1.2	1.3	0.77	Class B,C& E
10	DW10	Nil	Absent	7.9	620	4.9	2.4	1.7	0.83	Class B,C& E
11	BW1	Nil	Absent	7.2	440	1.4	0.4	1.9	0.78	Class C & E
12	BW2	Nil	Absent	7.2	350	2.9	0.4	0.4	0.63	Class C & E
13	BW3	Nil	Absent	6.6	1360	0.4	0.2	5.4	0.81	Class C
14	DW11	9	Present	7.9	1100	4.9	4.8	3.0	0.80	Below E
15	DW12	Nil	Absent	7.9	470	4.7	2.4	2.8	0.77	Class C& E
16	DW13	Nil	Absent	7.9	1150	4.5	2.4	3.6	0.82	Class B & C
17	DW14	Nil	Absent	8	1430	4.5	4.8	8.3	0.89	Class C
18	DW15	Nil	Absent	8	120	6.8	4.8	0.6	0.74	Class C & E

From the Table 4.17, it is clear that water sources DW3, DW5, DW9 and DW10 can be used for outdoor bathing (Organised) (Class B), drinking source after conventional treatment and disinfection (Class C) and irrigation, industrial cooling and controlled waste disposal (Class E). Irrigation water quality parameters EC, SAR and boron are evaluated in order to check the suitability for irrigation, industrial cooling and controlled waste disposal and confirms that all are under permissible limit except for EC in DW 8, BW 3, DW 11, DW 13 and DW 14 due to high EC level. Groundwater from DW 4, DW 6, DW 7, BW 1, BW 2, DW 12 and DW 15 comes under class C and class E, which can be used for drinking purposes after conventional treatment and disinfection and irrigation, industrial cooling and controlled waste disposal. Groundwater from DW 14 does not meet any of the criteria (below class E) and proper treatment is required prior to any usage.

4.8 Analysis of Variance (ANOVA Test)

Hypothesis V:

Is there any significant difference in WQI between CW, DW & BW and between months of 2012

Table 4.18: Results of ANOVA test for the comparison of Water Quality Index for control well (CW), dug wells (DW) and bore wells (BW) in various months of 2012.

Source	SS	df	ms	F	p- value
Total	22473.2164	35			
Between wells	869.1539	2	434.5770	0.635	p>0.05
Between Months	6621.0097	11	601.9100	0.884	p>0.05
Residual	14983.0528	22	681.0479		

Inferences

WQI does not differ significantly between wells and between months ($p>0.05$).

4.9 Conclusion

This chapter of the thesis discusses the monthly variation of water quality index (WQI), irrigation water quality parameters and corrosion indices of shallow and deep groundwater sources along the study area in the year 2012. Trace element analysis, total organic carbon analysis and designated best use are done to find the overall groundwater quality in multiple aspects.

Overall WQI indicates groundwater is not suitable for direct drinking purposes, unless subjected to conventional treatments followed by disinfection. According to statistical analysis (ANOVA), WQI does not differ significantly between wells and between months.

Irrigation water quality parameters showed most of the groundwater is suitable for irrigation. According to USSL diagram, groundwater from control well falls in medium salinity –low sodium (**Class C2S1**) water, that have recognised as *good quality water* for irrigation and this can be used without any salinity control. Water from dug well sources mostly comes under medium salinity –low sodium (**Class C2S1**). Only in October and December 2012, due to a slight increase in electrical conductivity, water falls in high salinity- low sodium category (**Class C3S1**) which is considered as *moderate water quality*. Prolonged use of this water may be detrimental to crops. Water from deep aquifers (bore well strata) comes in medium salinity –low sodium (**Class C2S1**) except in July 2012, where an abrupt increase in EC is reported and become very high salinity but low sodium water (**Class C4S1**). Water with very high salinity hazard (C4) is usually not suitable for irrigation but under exceptional situations this water can be used for salt tolerant crops in permeable soil with sufficient drainage so that leaching can be possible.

Langelier Saturation Index for control wells in most of the months are positive with annual mean being 0.01±0.3, indicating water is *slightly scale forming but corrosive* (SSFC) nature. Here deposition of $CaCO_3$ scales on the surface of metals is not sufficient to inhibit corrosion tendency of groundwater. The annual mean of LSI for shallow dug wells is -0.1±0.3, with confidence interval, CI -0.3–0.4 (95% level of significance), confirming water quality ranges from *slightly corrosive but non scale forming* to *slightly scale forming but corrosive* (SCNSF-SSFC). In bore well strata also LSI of groundwater shows *slightly corrosive but non scale forming* to *slightly scale forming but corrosive* (SCNSF-SSFC) nature with annual mean -0.1±0.3 with confidence interval -0.3–0.4 at 95% significant level.

Ryznar Stability Index (RSI) of water from control well displays intense scale dissolving tendency in most of the months in the year 2012 which leads to *heavy corrosion* (HC). The annual mean of RSI for water from control well is 7.7±0.4, with a confidence interval, CI of 7.4–7.9, at 95% level of significance. The annual mean of RSI for dug wells is 7.7±1.0 with confidence interval, CI 7.1-8.3 (95% level of significance) and annual mean for groundwater from bore wells is 7.6±0.5 with a confidence interval of 7.3–7.9, at 95% level of significance. These all shows RSI of water ranges from *corrosion significant* to *heavy corrosion* inferring has the potential to damage the water supply systems.

The aggressiveness index of groundwater from different sources of the study area also proposes water is moderately aggressive. Larson Skold index for finding the role of chloride and sulphate in the promotion of corrosive nature of water reveals that being in very low concentration, sulphate have not contributed in corrosion formation. But chloride have contributed to the corrosive nature of water in very few dug wells during July and August 2012 and in bore wells during December 2012 where bicarbonate concentration is relatively low to inhibit corrosion. However, the annual mean of Larson Skold index for groundwater from all the strata suggests that chloride and sulphate have not influenced the promotion of corrosive activity of groundwater in the study area during the year 2012. From all the corrosion indices it can be concluded that even though water has a tendency of scaling formation, it is not sufficient to inhibit corrosion; hence water is aggressive in nature.

Trace elements analysed are well within the safe standard limits proposed by BIS and WHO standards. The presence of E. coli was reported in few dug wells, which are unfit for drinking purposes. TOC analysis proven total organic concentration is very low level in all the groundwater sources. According to Designated Best Use (DBU) proposed by Central Pollution Control Board (CPCB), India, most of the shallow and deep groundwater sources in the study area are suitable for drinking only after proper treatment of certain biological water quality parameters.

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Chapter 5

TEMPORAL VARIATIONS IN OVERALL QUALITY OF GROUNDWATER OF DUG WELLS IN ALAPPAD COAST, INTERMITTENTLY DURING THE PERIOD 2001 TO 2017

5.1 Introduction

This chapter discusses the temporal variations of groundwater quality of shallow dug wells of Alappad coast for a period of 2001 to 2017. This study have special significance as this region is hit by 26th Decenber 2004 Indian Ocean Tsunami and the analysis of groundwater for this long period from way back 2001 to 2017 give insight into the natural processes involved in the hydrogeochemistry of this barrier island[1-6]. In the preceeding chapter 3 and 4 variation of water quality parameters throughout the year 2012 is discussed to have a perception on the groundwater hydrogeochemistry and quality of the shallow dug well sources of the region. This study is continued for next 5 years during December of 2013, 2014, 2015, 2016 & 2017. This data is compared with the reported data of 2001[7] as a primary reference for pre-tsunami water quality available and post-tsunami water quality data available during the entire 12 months in the year 2005 and December 2008[8]. The major findings of the study includes temporal variations in physico-chemical parameters analysed, hydrochemical facies and water type, variations in water quality index, irrigation water quality and suitability of the groundwater for industrial purposes. The major objective of this chapter is to evaluate the overall water quality of shallow groundwater resources of Alappad region.

The variation of water quality including physico-chemical, water quality index (WQI), irrigation water quality and corrosion indices of dug wells (DW) over the year 2001 to 2017 presented as a function of days starting from April 2001to December 2017. Results are plotted as a function of days 2001 (sampling day expressed as 0), January 2005 to December 2005 (1460-1790 days), 2008 (2890 days), January 2012 to December 2012 (3980-4310 days), 2013 (4675 days), 2014 (5040 days), 2015 (5405 days), 2016 (5770 days) and 2017 (6135) in all representing graphs and tables.

5.2 Physico-chemical Parameters

The physico-chemical parameter analysed includes pH, Eh, EC, TDS, alkalinity, total hardness, calcium, magnesium, sodium, potassium, bicarbonates, chloride, sulphate, phosphate, nitrate, total iron, DO and BOD.

5.2.1 pH

The pH of dug wells during 2001 is 7.6±0.6, with a confidence interval (CI) of 6.6-8.6, at 95% significant level. This indicates that the pH covers slightly acidic to alkaline range. In 2005 post tsunami study reveals the pH of shallow groundwater sources shrink to a range of 7.5-7.9; annual mean being 7.7±0.4 (BIS standard 6.5 – 8.5). From the monthly variation it can be seen that pH reflects slight alkaline behaviour. In 2008 the mean pH of dug wells is 7.5±0.4, which displays near neutral situation. In the year

2012, the annual mean of pH is 7.8±0.37, with confidence interval, 7.6 to 8.1 shows increase in the alkaline nature. The results of the succeeding years analysis reveal the mean of pH during 2013 is 7.8±0.3, while a decrease in pH is observed in 2014 (7.4±0.3). In 2005, water turned alkaline range with a mean of 8.0±0.2, but later falls to 7.3±0.3 in 2016 and 7.6±0.3 in 2017. pH analysed over the last 16 years intermittently disclose that the pH of shallow dug well sources are within the limit 6.5 to 8.5, prescribed by WHO^9 and BIS standards. This indicate there is a stable hydrogeochemistry is prevailing.

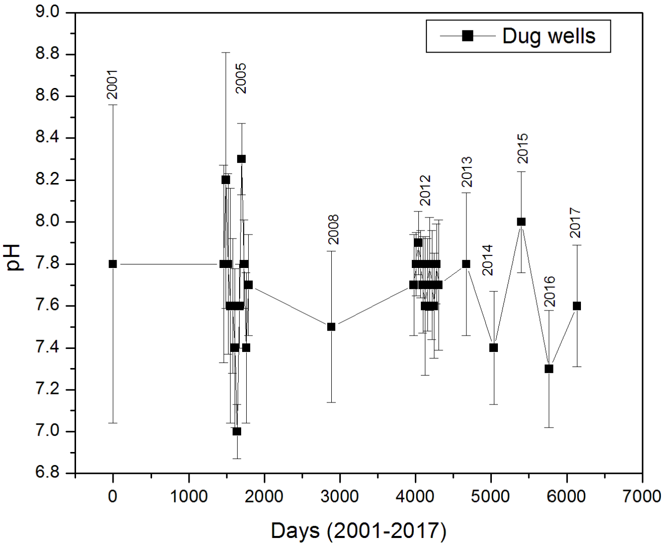

Figure 5.1: Temporal variation of pH of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

pH of the water has prior importance as it is very much related to all the water quality related requirements such as the drinking water purposes, irrigation related problems, corrosion prevention etc.

5.2.2 Eh (Redox Potential)

Redox potential is used to determine the oxidation-reduction condition of water. It is useful to determination of Eh of water samples are significant as the fate of certain pollutants are depends on the redox conditions in groundwater[9]. It is known that under certain flow and redox conditions, riparian zones along waterways (T- S canal) have demonstrated a natural ability to intercept and denitrify NO_3^- in shallow groundwater[10,11]. From the graph (Figure 5.2), it is clear that, the water is under reduced state in the entire study period, except in July and August 2005. The annual mean of Eh in the year 2005 is -32±20.5, with a confidence interval of -44.7 to -19.5, at 95% significant limit. In 2008 Eh become -39.3 ±8.8 mV.

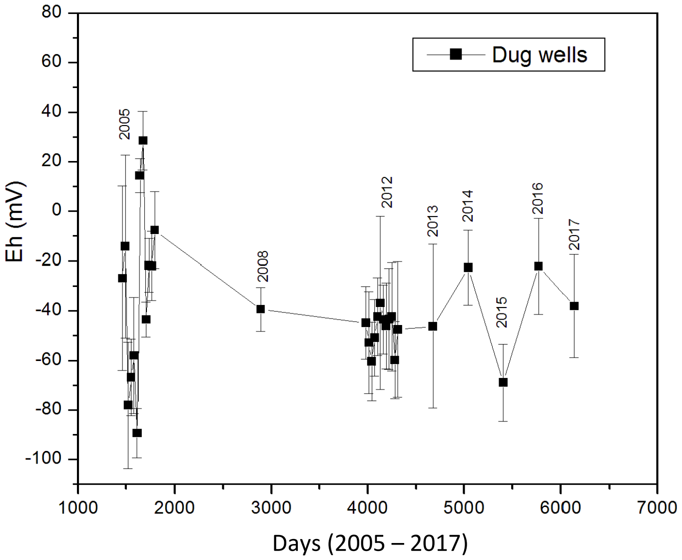

Figure 5.2: Temporal variation of Eh of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

During 2012, the Eh range from -35.1 to -60.1 with annual mean of -48±20 mV. In the subsequent years, Eh are -46.3±33 mV (2013), -22.7±15.1 mV (2014), -69±15.6 mV (2015), -22.1±19.3 mV (2016) and -38.1±20.8 mV (2017).

5.2.3 Electrical Conductivity (EC)

Electrical conductivity of water samples give insight into properties of water such as salinity, TDS and to some extent mixing of sea water with freshwater. The 2001 data shows a low saline behaviour with a mean of 0.36±0.08 mS/cm. There is a huge hike in EC just after Indian Ocean Tsunami occurred on 26 December 2004 and this increased EC continued throughout the year 2005. In January, 2005 EC is reported as 7.03±7.93 mS/cm which is for an extremely high salinity causes huge damage to the natural ecosystem. A decrease of EC to 4.25±4.53 mS/cm is occurred in February 2005, but an exceptional hike of 9.26±14.12 mS/cm make water too saline that is similar to brine in March 2005. Afterwards, a gradual decrease in EC is witnessed, with minimum EC of the year 2005, 0.79±0.32 mS/cm is reported in October 2005. But during November (2.53±1.57 mS/cm) and December 2005 (2.32±1.53 mS/cm) water turned to high saline nature. The annual mean of EC in the year 2005 is 3.5±5.2 mS/cm, with a confidence interval of 0.3 mS/cm - 6.7 mS/cm, at 95% significant level. In 2008 EC had been within medium saline range with a monthly mean of 0.83±1.09 mS/cm.

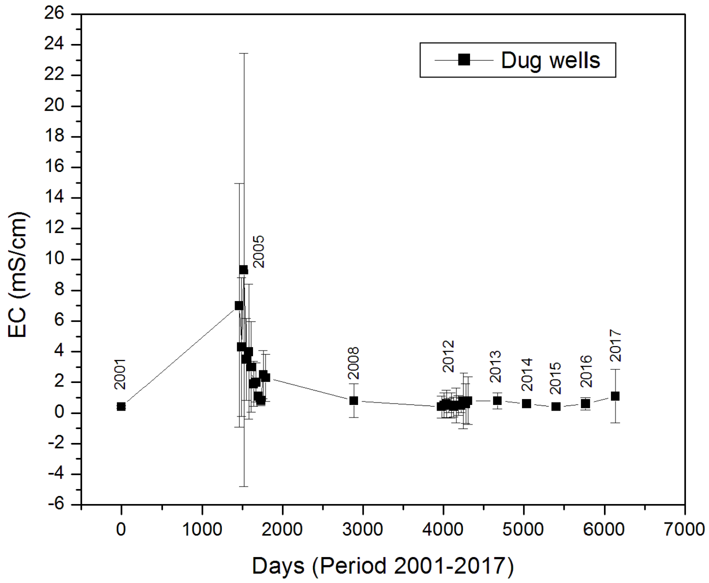

Figure 5.3: Temporal variation of electrical conductivity (EC) for groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017

In 2012, electrical conductivity is < 0.65 mS/cm, falling in low salinity class, except in October and December 2012, where the EC increased to a medium salinity level. The annual mean of EC in 2012 is 0.55±0.52 mS/cm, fall in low saline to medium saline type, with a confidence interval of 0.23– 0.87 mS/cm, at 95% significant level. The EC of the following period of analysis are 0.8±0.5 mS/cm (2013), 0.6±0.3 mS/cm (2014), 0.4±0.2 mS/cm (2015), 0.6±0.4 mS/cm (2016) and 1.1±1.8 mS/cm (2017). The study on electrical conductivity of shallow dug wells in Alappad coast reveals there is a huge impact of tsunami event on dug wells during the entire year 2005 which over the course of time reduced to an acceptable limit.

5.2.4 Total Dissolved Solids (TDS)

Total dissolved solids of groundwater differ according to the geological settings as the mineral constituents of the aquifer contribute differently depend on the solubility[12]. Total dissolved solids are closely related to electrical conductivity of water, hence they followed a similar trend generally over the period during the year 2005 to 2017.

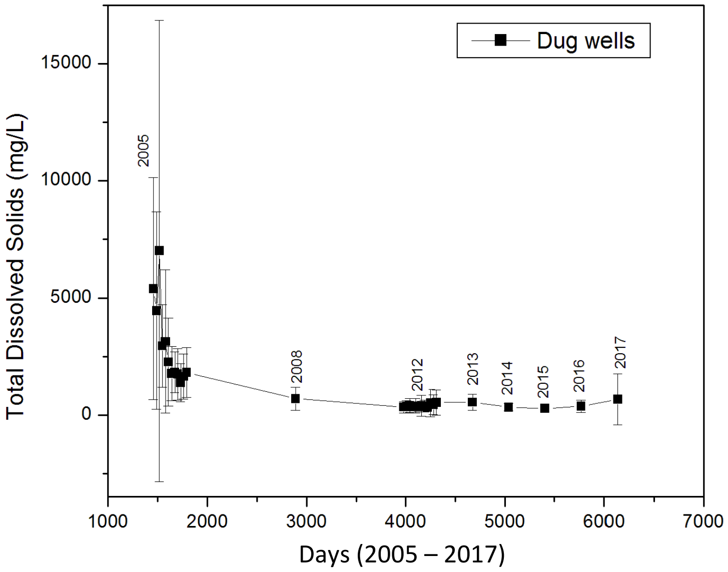

Figure 5.4: Temporal variation of total dissolved solids (TDS) of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

In the early months of 2005, TDS is very high about 5393.5±4736.8 mg/L (January 2005) and 4449.4±4209.5 (February 2005). This situation becomes more worse in March when the TDS become 6998.0±9847.9 mg/L. This alarming increase in TDS is attributed to the most catastrophic tsunami event occurred in December 2004.Contamination of openwells by debris intruded by scrolling tsunami waves might have brought this. From

April, 2005 onwards a gradual decrease in TDS is observed with lowest content 1374.2±818.3 mg/L, reported in October 2005. But a slight increase in TDS value is noted in November 2005, and reached 1814.8±1067.8 mg/L in December 2005. The annual mean of TDS in the year 2005 is 2948.5±3643.7 mg/L, with a confidence interval of 707.0 mg/L - 5190.0 mg/L at 95% significant limit. In 2008 TDS falls to 697.3±494.1 mg/L.

In the year 2012 TDS is observed to be < 500 mg/L, which is below the acceptable limit recommended by BIS and WHO. But a slight increase in TDS is noticed in October and December 2012, with a monthly mean of 508.9±581.4 mg/L and 531.7±539.9 mg/L respectively. The annual mean of TDS during this 2012 period is 396.8±350.4 mg/L, with a confidence interval of 181.2 - 612.3 mg/L, at 95% level of significance. In the following years of analysis TDS is reported as 545.7±341.3 mg/L (2013), 335.0±166.7 mg/L (2014), 284.9±125.8 mg/L (2015), 376.2±253.7 mg/L (2016) and 670.5±1083.9 mg/L (2017).

5.2.5 Alkalinity

Alkalinity of the shallow groundwater resources in January 2005 is 312.4±255.7 mg/L. It is increased to 326.6±168.6 mg/L in March 2005. It is decreased to 271.5±154.8 mg/L in April 2005 and in the subsequent three months, alkalinity is between 260 -300 mg/L range. A slight increase in concentration of alkalinity is observed in August 2005 (321.4±161.3 mg/L) and reduced to 263.0±141.0 mg/L in September 2005. This pattern of increase and decrease of alkalinity is also observed in October (318.7±163.8 mg/L), November (295.1±134.1 mg/L) and December (332.8±190.7 mg/L) during 2005. However, the alkalinity concentration in the year 2005 is greater than the acceptable limit of 200 mg/L, recommended by BIS but within the permissible level of 600 mg/L if there is no alternative sources are available. The annual mean is reported to be 301.9±177.8mg/L, with a confidence interval of 192.5 - 411.3 mg/l at 95% significant level. In December 2008 is greatly reduced to 31.3±11.3 mg/L.

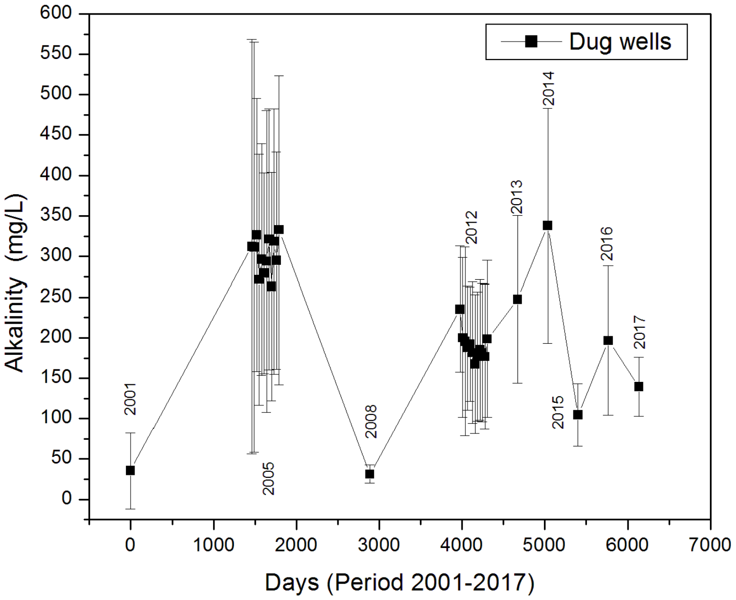

Figure 5.5: Temporal variation of alkalinity of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017

In the year 2012, the concentrations of alkalinity of dug wells are high but within the permissible limit of 200 mg/L for all the 12 months of analysis. The annual mean is reported to be 189.73±88.4 mg/L. During December 2013 alkalinity is increases to 247.3±103.5 mg/L and it is further increased to 338.1±145.0 mg/L. The concentration of alkalinity is decreased to 104.5±38.6 mg/L (2015), 196.3±92.2 mg/L (2016) and 139.5±36.2 mg/L (2017) in the month of December.

5.2.6 Total Hardness

Total hardness in April 2001 is found to be 79.50±49.16 mg/L for shallow dug wells of the study area. In January 2005 a hike in the concentration of total hardness is witnessed with a monthly mean of 930.0±803.9 mg/L in January 2005. In February 2005 it is reduced to 580.6±620.7 mg/L but sudden hike of 1435.0±1626.0 mg/l is noticed in March 2005. Afterwards, total hardness gradually decreased to reach a concentration of 260.5±112.9 mg/L in October 2005. An increase is observed in November 2005 (346.1±195.4 mg/L) and December 2005 (371.9±203.8 mg/L). The annual mean of total hardness during the year 2005 is, 557.9±596.9 mg/L, with a confidence interval of 190.7 - 925.1 mg/L, at 95% significant level. The total hardness concentration of water in December 2008 is 174.1±102.9 mg/L

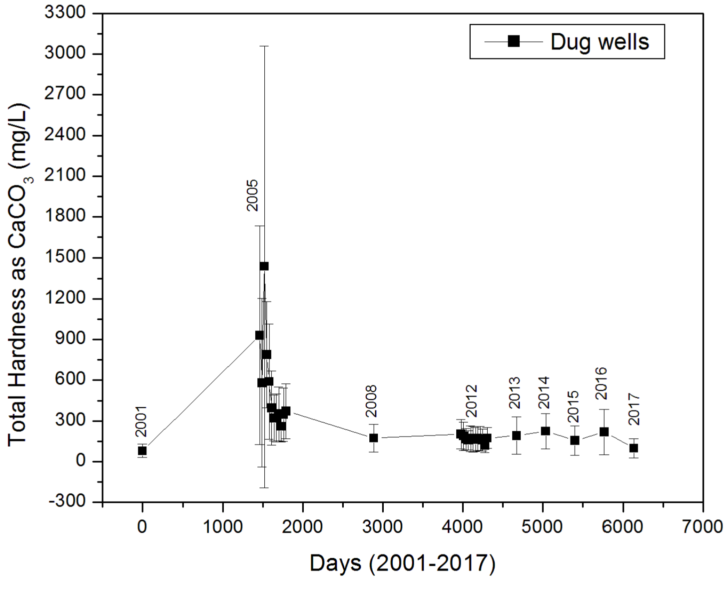

Figure 5.6: Temporal variation of total hardness (TH) of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In the year 2012, January 2012 experienced 202.2±106.7 mg/L but gradually decreased to the acceptable limit below 200 mg/L. the annual mean of total hardness is 167.3±86.9 mg/L, with a confidence interval of 113.8 mg/L - 220.7 mg/L, at 95% significant level. During the subsequent analysis the total hardness is observed to be 191.7±137.9 (December 2013), 224.0±130.9 (December 2014), 155.5±106.6 (December 2015), 218.4±167.4 (December 2016) and 98.6±70.6 mg/L (December 2017).

5.2.7 Calcium

The calcium content in water from shallow groundwater sources during April 2001 is reported as 23.00±19.34 mg/L. This is very much below the acceptable limit of 75 mg/L prescribed by BIS and WHO standards. During the year 2005, January reported a calcium concentration of 202.0±231.9 mg/L and then reduced to 146.0±179.4 mg/L in February. Along with the increase in total hardness calcium also has a hike of 414.5±618.5 mg/L in March 2005 that is far beyond the acceptable and permissible limit of calcium concentration recommended by BIS and WHO standard. In April 2005, calcium concentration reduced to 84.2±44.3 mg/L and again increased to 178.5±140.7 mg/L in May 2005. From June 2005 onwards, concentration of calcium in dug wells gradually decreased and come to 95.5±50.7 mg/L in December 2005. The annual mean of calcium concentration in shallow dug wells in the year 2005 is 131.4±204.9 mg/L.

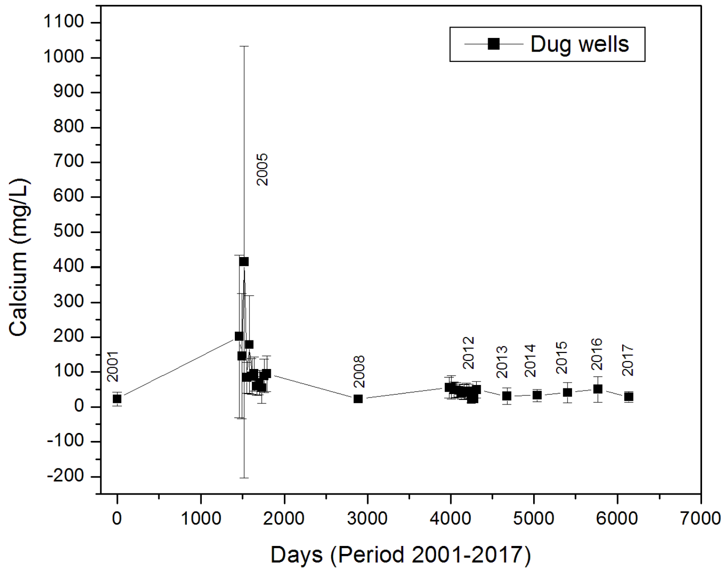

Figure 5.7: Temporal variation of calcium of groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In December 2008, calcium concentration is reduced to 23±7mg/L. During the year 2012, water shows a calcium concentration < 50 mg/L throughout the analysis. The annual mean being 43.5±22.0 mg/L, with a confidence interval of 30.0 - 57.0 mg/L, at 95% significant limit. The calcium concentration in all the other years analysis are very low in December 2013 (31.2±23.4 mg/L), December 2014 (33.2±17.6 mg/L), December 2015 (41.0±28.9 mg/L), December 2016 (50.8±36.7 mg/L) and December 2017 (28.8±14.9 mg/L).

5.2.8 Magnesium

The Mg concentration of DW strata in 2001 is 5±3mg/L. In post tsunami year 2005 study data reveal that the Mg of shallow groundwater sources is 55.1±46.2 mg/L, with a confidence interval of 26.7 mg/L -

83.5 mg/L. A hike in the concentration of magnesium to 102.0±85.1 mg/L is noticeable in the month of January due to the tsunami event. After that the concentration decreased to 51.8±51.9 mg/L and 95.7±68.4 mg/L in February and March 2005 respectively. An increase in concentration is reported in 138.6±75.8 mg/L during April 2005. However, the magnesium concentration is reduced to less than 50 mg/L in the rest of the months in 2005.

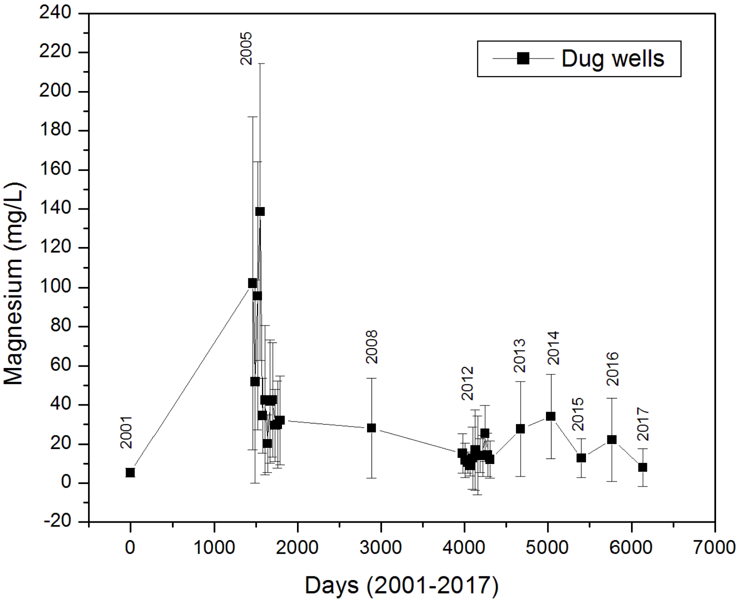

Figure 5.8: Temporal variation of magnesium in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

During 2008, magnesium concentration found to be 28.1±25.5 mg/L. In the year 2012, concentration of magnesium is even reduced to less than 30 mg/L throughout the year inferring it is under acceptable limit of less than 30 mg/L. In the subsequent years water is reported to have magnesium concentration of 27.6±24.2 mg/L (December 2013), 34.1±21.6 mg/L

(December 2014), 12.8±10.0 mg/L (December 2015), 22.1±21.4 mg/L (December 2016) and 7.9±9.8 mg/L (December 2017).

5.2.9 Sodium

The Na^+ conccentration of the dug well strata in 2001 is 39±8.3mg/L. Post tsunami study data in the year 2005 reveals that the Na^+ of shallow groundwater sources has an annual mean of 519.5±927.6 mg/L. A huge concentration of sodium (1009±1155 mg/L) is reported as a result of tsunami waves and increased to 1367.8±2425.4 mg/L in March 2005. A decrease in concentration of sodium along with other ions is observed in the subsequent months. Finally in December 2005 sodium concentration reaches a monthly mean of 268.8±202.4 mg/L. The year 2008, sodium is reduced to 105.3±120.3 mg/L.

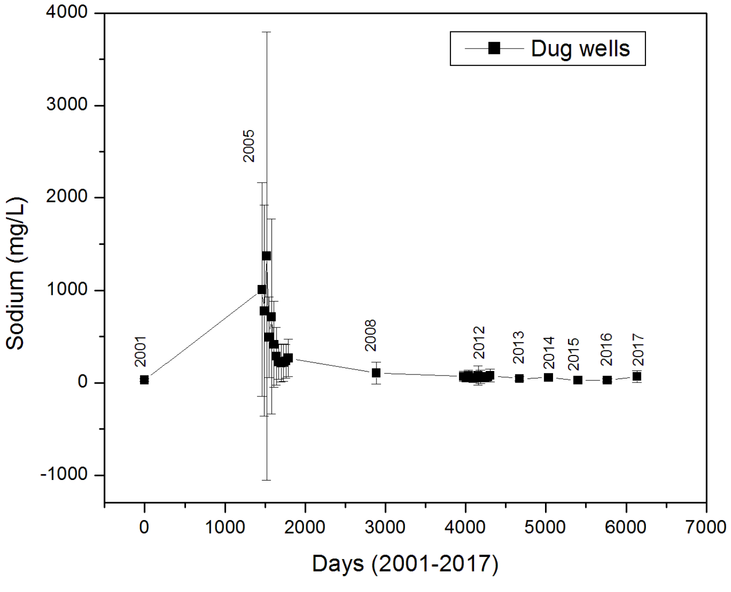

Figure 5.9: Temporal variation of sodium in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In the year 2012 a sharp decrease in concentration of sodium is noticeable from the preceding period of analysis. The Na^+ in each month in 2012 is less than 80 mg/L, being annual mean of 64.3±59.3 mg/L. The results of the subsequent years analysis reported a monthly mean of 44.2±22.8 mg/L (2013), 56.6±30.0 mg/L (2014), 27.9±14.8 mg/L (2015), 28.5±16.8 mg/L (2016) and 68.9±63.7mg/L (2017). Thus the data generated over the last 16 years reveal that the Na^+ concentration of DW strata is much higher in the year 2005 but analysis done in last preceding 6 years indicates water restored it's situation pertained in 2001 with respect to sodium concentration.

5.2.10 Potassium

The potassium concentration in dug wells during pre-tsunami period of 2001 is 6.3±6mg/L. The concentration of potassium for the first three months and May in the year 2005 is in the range 20 to 50 mg/L. This increase in potassium can be attributed to mixing of sea water with the fresh water sources during tsunami. After May 2005, concentration gradually decreased with a minimum concentration of 10.9±5.7 mg/L in November 2005, but again in December 2005, potassium concentration remained 15.3±7.2 mg/L. The annual mean of potassium during the year 2005 is 19.5±3 mg/L which is beyond the acceptable limit of 12 mg/L by WHO standard.

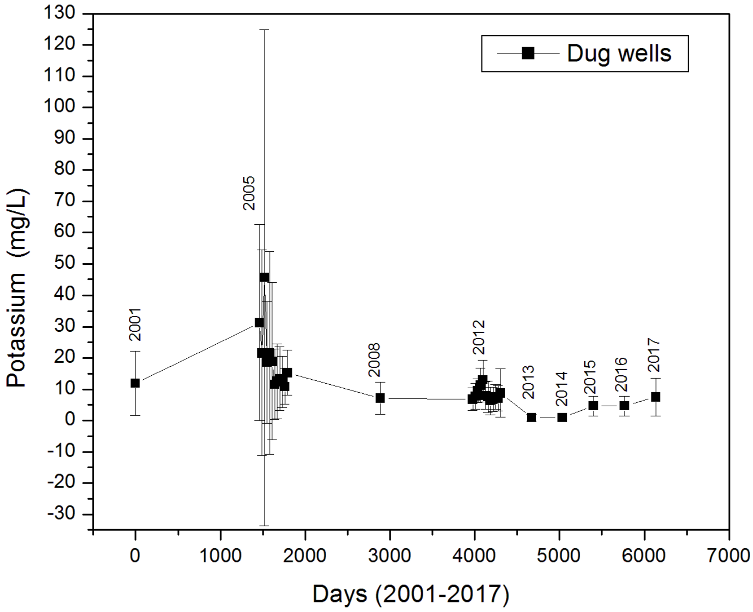

Figure 5.10: Temporal variation of potassium in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In December 2008, the concentration of potassium become 7.1±5.2 mg/L. The continuous analysis done in the year 2012 reported an annual mean of 8.4±4.9 mg/L, with a confidence interval of 5.4 - 11.4 mg/L, at 95% significant level. During the recurrent analysis during the years 2013 to 2017, the potassium concentrations are reported 0.9±1.1 mg/L (2013), 0.9±0.5 mg/L (2014), 4.7±3.2 mg/L (2015), 4.7±3.2 mg/L (2016) and 7.5±6.1 mg/L, it is noticed that from December 2008 onwards, water maintained an acceptable range of potassium concentration till December 2017.

5.2.11 Bicarbonate

Bicarbonate in groundwater is mainly evolved from the weathering and dissolution of carbonate and silicate minerals due to carbonic acid[13]. It is also contributed from biological origins such as humus in the presence of CO_2 and combines with rainwater[14]. In April 2001, bicarbonate concentration in the dug wells of study area is 42.7±58.0 mg/L. From the Figure 5.11, it is clear that, there is high bicarbonate level and no much variation in bicarbonate between months in 2005. During the year 2005, annual mean of bicarbonate is found to be 368.3±216.9 mg/L, with a confidence interval of 234.9 - 501.7 mg/L, at 95% significant level. The acceptable limit of bicarbonate in drinking water by WHO standards is 500 mg/L.

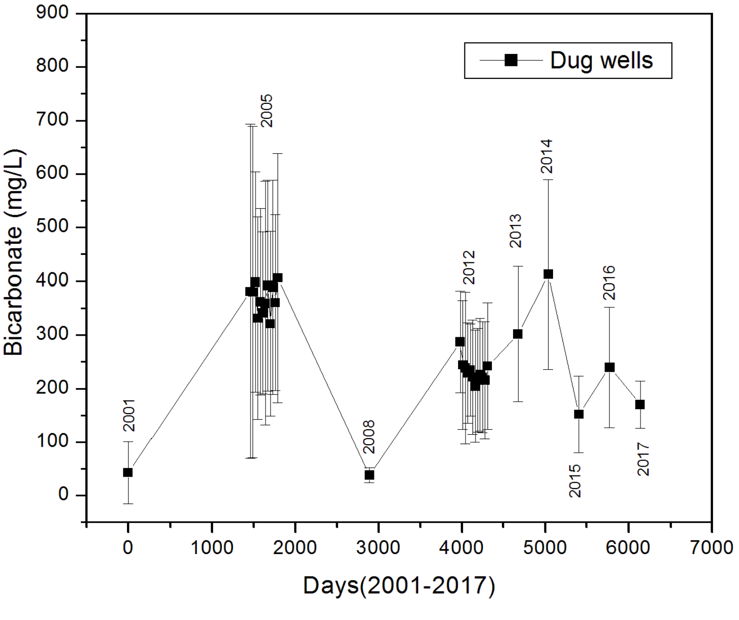

Figure 5.11: Temporal variation of bicarbonate in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In December2008, the concentration of bicarbonate falls near to pre-tsunami range (38.1±13.7 mg/L). The continuous analysis of dug wells during the year 2012 conveyed an annual mean of 231.5±107.9 mg/L, which is lower compared to bicarbonate concentration in the year 2005. In the subsequent year concentrations of bicarbonate are 301.7±126.2 mg/L (2013), 412.5±176.9 mg/L (2014), 151.5±71.9 mg/L (2015), 239.5±112.5/L (2016) and 170.2±44.2 mg/L (2017). The data generated over the last 17 years reveals that, the HCO_3^- of DW strata are within the maximum permissible limit of 500mg/L.

5.2.12 Chloride

Chloride is a dominant ion in sea water and under normal conditions it is very low in fresh water. High concentration in chloride ions in fresh water act as an indicator of sea water intrusion as well as organic pollution due to sewage waste. In April 2001, mean of chloride concentration in the shallow groundwater sources are 53.3±15.0 mg/L. During 2005, due to flooding of sea water as a result of tsunami, January to May 2005 gives chloride concentration greater than 1000 mg/L. A very high concentration reported in March 2005 with a monthly mean of 2646.0±4314.5 mg/L. When monsoon started chloride is deceased to 872.4±1013.8 mg/L and is reduced to a minimum of 360.7±344.0 mg/L in October 2005. However in December 2005, chloride concentration remained 451.1±407.5 mg/L. The mean of chloride concentration in 2005 is 993.8±1618.4 mg/L and the unusually high standard deviation is due to the wide spatial and temporal variation of chloride in the study area after tsunami.

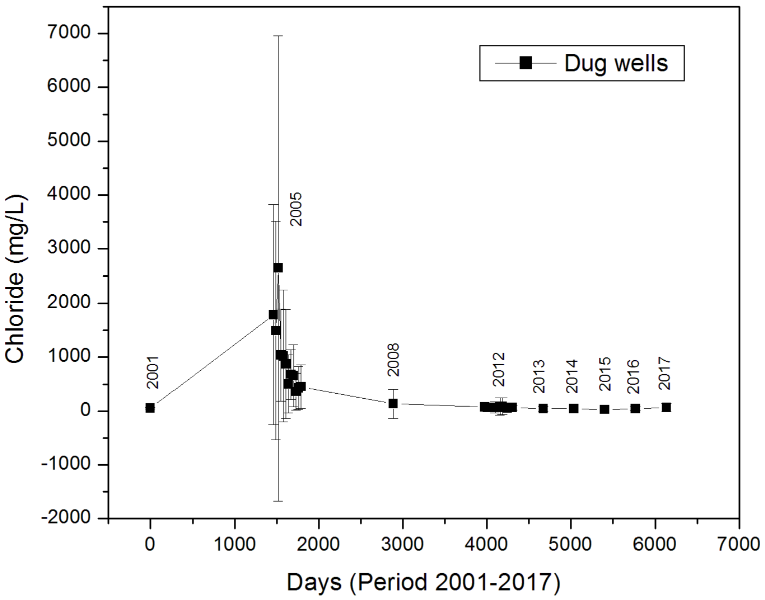

Figure 5.12: Temporal variation of chloride in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017

A noticeable decrease in chloride concentration is seen in December 2008, when compared to 2005 data with a monthly mean of 135.7±269.3 mg/L. During 2012, the monthly means of chloride concentration is found to be lower than 100 mg/L, with an annual mean of 65.5±83.6 mg/L. In the following years of analysis, the monthly means of chloride is found to be 46.0±47.6 mg/L (2013), 41.4±31.3 mg/L (2014), 27.9±30.2 (2015), 41.4±33.4 mg/L (2016) and 63.2±78.5 mg/L (2017).

5.2.13 Sulphate

Sulphate is present in groundwater as soluble salts of calcium, magnesium and sodium[15]. It may vary according to seasons, especially in rainy season when infiltration and percolation causes the recharge of groundwater[16]. High sulphate content in drinking water (>400 mg/L) along with sodium and magnesium may leads to health risks like gastrointestinal irritations[17].

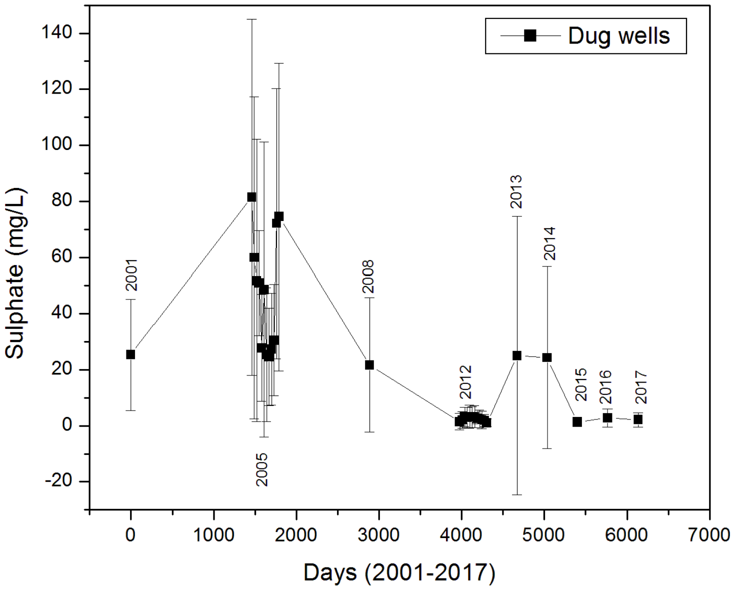

Figure 5.13: Temporal variation of sulphate in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017

The concentration of sulphate in April 2001 25.4±19.8 mg/L. In the year 2005, 81.5±63.5 mg/L is reported in January just after two weeks of tsunami event. From February 2005 onwards, the sulphate concentration gradually decrease and reached a minimum monthly concentration of 24.6±17.5 mg/L in August 2005 and finally in December 74.5±54.8 mg/L. The annual mean of sulphate concentration in the year 2005 is 47.9±41.2 mg/L with a confidence interval of 22.6 - 73.2mg/L, at 95% significant level. In December 2008, sulphate is reduced 21.7±24.0 mg/L. During the year 2012, sulphate in dug wells of the study area reached very negligible concentration with an annual mean of 2.5±3.1 mg/L. In the follow up analysis from December 2013 to 2017, the monthly mean of sulphate concentration is noted as 25.0±49.7 mg/L (2013), 24.3±32.5 mg/L (2014), 1.4±1.6 mg/L (2015), 2.8±3.2 mg/L (2016) and 2.2±2.5 mg/L (2017) WHO.

5.2.14 Phosphate

Phosphate, an essential macro-nutrient of natural waters, in shallow groundwater occurs mainly as a result of agricultural run-off. Phosphate is considered as immobile in soil as a result of strong phosphorous binding capacity of mineral soils. This restricts the vertical movement of phosphate through the soil to the groundwater aquifers[18,19]. Thus further inhibits, the possibility of leaching of phosphate to deeper groundwater[20].

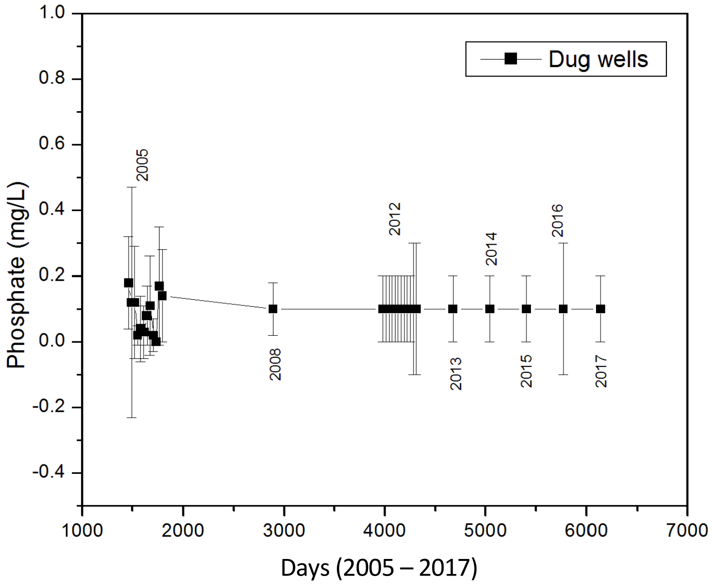

Figure 5.14: Temporal variation of phosphate in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

Phosphorus in solution present in the form of orthophosphate, PO_4^{3-}. In the year 2005, phosphate concentrations in shallow dug wells are very low with an annual mean of 0.1±0.2 mg/L. In 2008 December phosphate concentration is observed to be 0.1±0.1 mg/L. During the year 2012 also concentration of phosphate is found to be very negligible with an annual mean of 0.1±0.1 mg/L and same trend is followed from December 2013 to 2017.

5.2.15 Nitrate

Presence of nitrate content in groundwater is mostly due to leaching and infiltration of excess amount of nitrogen containing fertilizers added to soil. The second possibility may be the evaporation and transpiration of rainwater which wash-off atmospheric nitrogen which eventually reaches the shallow aquifers. Increased concentration of nitrate in drinking water causes serious threat to infants as it cause Blue-baby syndrome or methemoglobinemia. It also adversely affects livestocks especially in ruminant animals.

During the post tsunami period January 2005, nitrate concentration is 2.9±1.2 mg/L and in February 2005,it increased to 3.5±2.1 mg/L. The concentration gradually decreased in the subsequence months and reaches a minimum concentration of 0.26±0.2 mg/L in November 2005. The annual mean of nitrate in dug wells during the year 2005 is 1.1±0.8 mg/L. In December 2008, the concentration of nitrate is1.4±1.0 mg/L.

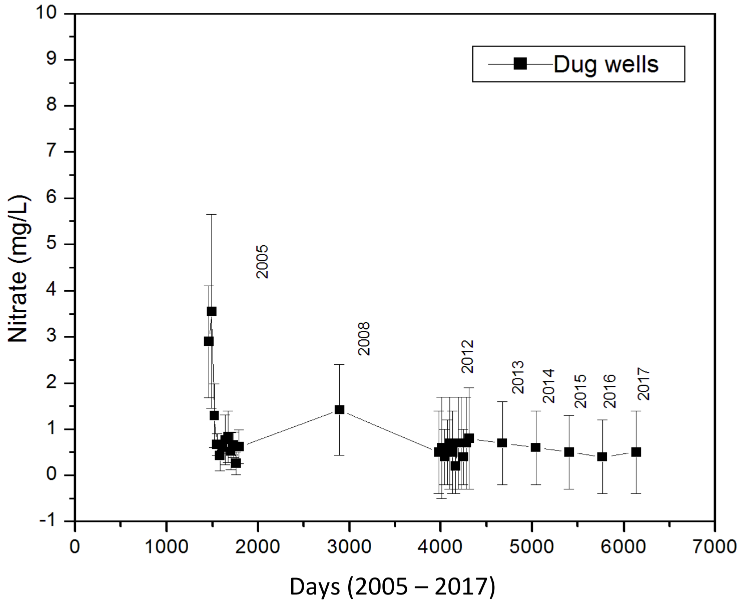

Figure 5.15: Temporal variation of nitrate in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

The annual mean of nitrate in the year 2012 is 0.56±0.9 mg/L and in the succeeding years, the concentration is 0.7±0.9 mg/L (2013), 0.6±0.8 mg/L (2014), 0.5±0.8 mg/L (2015), 0.4±0.8 mg/L (2016) and 0.5±0.9 mg/L (2017). So it is inferred that the nitrate concentration is very low in the study region throughout the period under investigation.

5.2.16 Iron

High concentration of iron in groundwater leads to an unpleasant metallic taste with a discoloured appearance[21]. Permissible limit of iron according to WHO is < 0.3 ppm for drinking water. After the catastrophic 26th December 2004 Indian Ocean Tsunami, the concentration of iron in shallow groundwater is 0.74±0.4 mg/L in January 2005, which is increased to 0.84±0.5 mg/L in February 2005. From March 2005 onwards, the concentration decreased to the permissible level of < 0.3 mg/L and reaches to 0.06±0.05 mg/L in December 2005.The annual mean of iron concentration in the year 2005 is 0.2±0.2 mg/L. In December 2008, monthly mean of iron is 0.17±0.1 mg/L. In the year 2012, annual mean of iron concentration is 0.06±0.1 mg/L and in the subsequent years, iron is assessed in December month only which reported 0.02±0.1 mg/L (2013), 0.02±0.08 mg/L (2014), 0.15±0.2 mg/L (2015), 0.08±0.2 mg/L (2016) and 0.11±0.2 (2017).

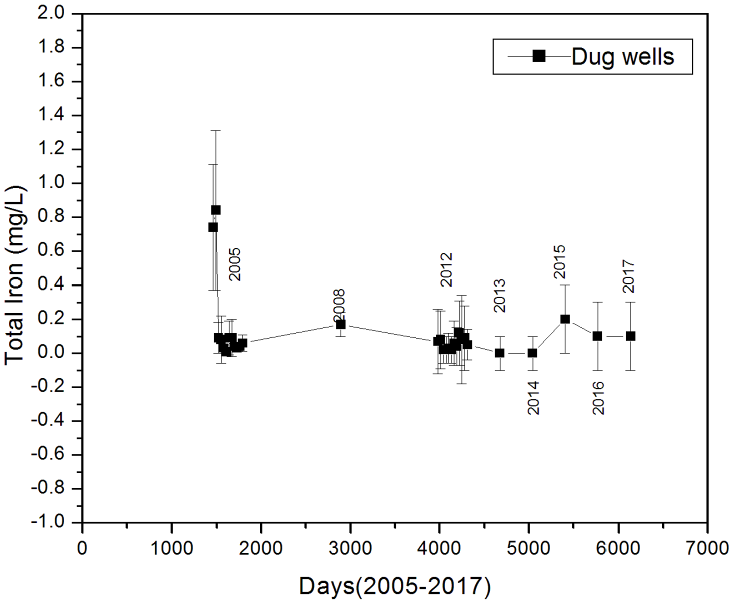

Figure 5.16: Temporal variation of iron in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

5.2.17 Dissolved Oxygen (DO)

Dissolved oxygen in the study area shows more or less same trend all along the study period from 2005 to 2017. The annual mean of DO in 2005 is 4.5±2.3 mg/L, with a confidence interval of 3.1 - 5.9 mg/L, at 95% significant level. In December 2008, water shows a good quality in terms of DO level at 6.6±3.2 mg/L.

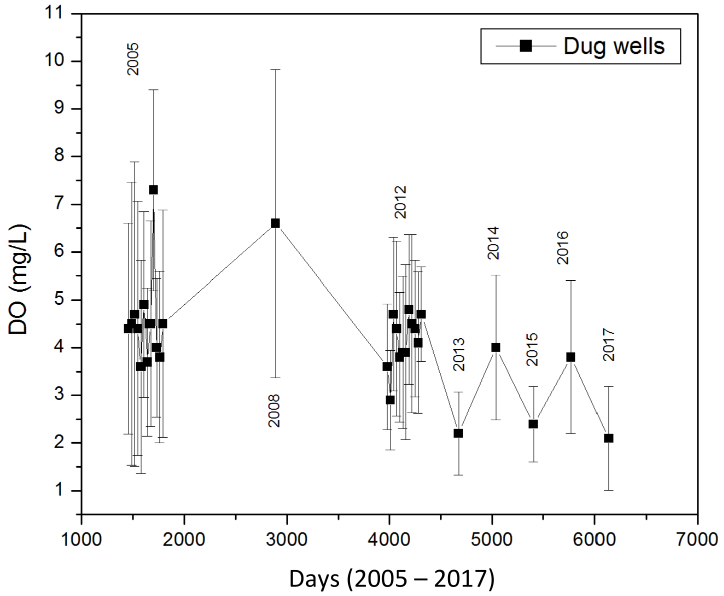

Figure 5.17: Temporal variation of dissolved oxygen (DO) in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

In the year 2012, an annual mean of 4.1±1.5 mg/L is reported for DO, with a confidence interval of 3.2 - 5.1 mg/L, at 95% significant level. The DO levels in subsequent years are 2.2±0.9 mg/L (2013), 4.0±1.5 mg/L (2014), 2.4±0.8 mg/L (2015), 3.8±1.6 mg/L (2016) and 2.1±1.1 mg/L (2017).

5.2.18 Biological Oxygen Demand (BOD)

The BOD level in the year 2005 have wide variation with a minimum monthly mean of 4.2±1.2 m/L in July 2005 and maximum reaching a monthly mean of 20.7±11.6 mg/L in August 2005. The annual mean of BOD in the year 2005 is 8.8±5.3 mg/L, with 5.5 - 12mg/L confidence interval at 95% significant level. In December 2008, water have a high BOD level of 9.2±5.4 mg/L. The annual mean of BOD level in the year 2012 is 3.4±3.2, with a confidence interval of 1.4 - 5.4 mg/L, at 95% significant level. In the subsequent years the BOD concentration are 2.7±1.9 mg/L (2013), 3.0±2.1 mg/L (2014), 2.4±1.7 mg/L (2015), 2.7±2.0 mg/L (2016) and 5.6±3.0 mg/L (2017).

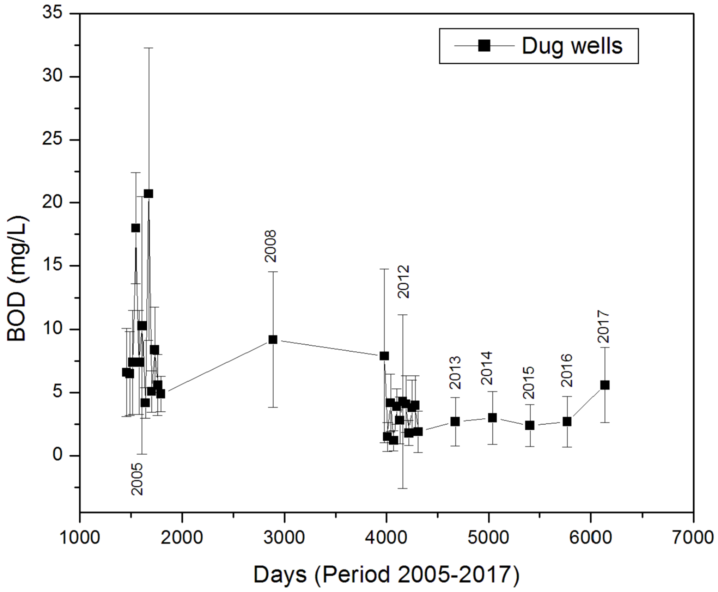

Figure 5.18: Temporal variation of biological oxygen demand (BOD) in groundwater from shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017

Central Pollution Control Board – (CPCB), Govt.of India recommended 2 mg/L or less of BOD for drinking water source without conventional treatment but with disinfection and 3 mg/L or less BOD for drinking water after conventional treatment followed by disinfection. Throughout the study period, the level of BOD is more than 2-3 mg/L. This indicate the shallow dug wells need more conventional treatments and disinfection prior to any use.

5.3 Hydrochemical Facies

Hill-Piper-Trilinear plots (Figure 5.19) give significant observation on water type characters based on cation and anion ratio[22]. In April 2001, the water comes in saline water type with a hydrochemical facies of Na^{+}-K^{+}-Cl^{-} -SO_4^{2-}.

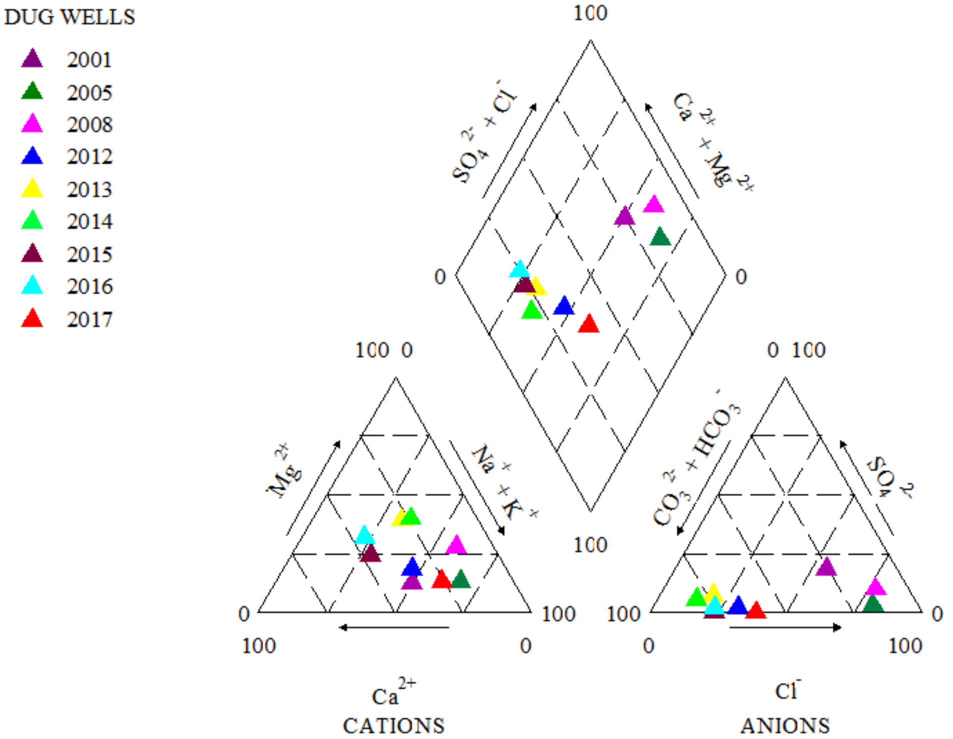

Figure 5.19: Hill-Piper trilinear plot for groundwater from dug wells along the Alappad coast, Kollam, Kerala, India during the period 2001 to 2017.

After tsunami event, the water type of shallow dug well sources in Alappad coast belongs to category *saline water type* with hydrochemical facies Na^{+}-K^{+}-Cl^{-} -SO_4^{2-} in December 2005 and 2008 being the data in the diamond are placed in the position signifies the instance of saline intrusion (right corner). This groundwater sources can be classified as Na^++ K^+ and Cl^- dominant type. In the year 2012, the annual mean of various cation and anion concentrations fall in the water type moves marginally towards *temporary hardness water type* with non-dominant cations and bicarbonate anion type water. The hydrochemical facies of the mean of dug well sources in the year 2012 are Ca^{2+}-Mg^{2+}-HCO_3^-· It is seen from the cation and anion triangles the order of dominant ions are Na^++K^+ (47%) > Ca^{2+} (35%)> Mg^{2+} (18%) and HCO_3^- (70%) > Cl^- (29%) > SO_4^{2-} (1%).

From year 2013 to 2016 the water type occupies a left corner of the Hill-Piper diamond plot, which is *temporary hardness water type* region. The hydrochemical facies of the mean of dug well sources from December 2013 to December 2016 are Ca^{2+}-Mg^{2+}-HCO_3^-. In 2013 the cation triangle of piper plot bears Na^++K^+ (32%) > Mg^{2+} (40%) > Ca^{2+} (28%) and in the anion triangle HCO_3^-(73%) > Cl^-(20%) > SO_4^{2-}(7%) are observed. In 2014, the ions are Na^++K^+ (35%)> Mg^{2+} (40%) > (25%) Ca^{2+} in cation triangle and from the anion triangle HCO_3^- (80%) > Cl^- (15%) > SO_4^{2-} (5%) are observed. During December 2015, water have cation and anion concentration in the order Ca^{2+} (45%) > Na^++K^+ (30%) >Mg^{2+} (25%) and HCO_3 (78%) > Cl^- (21%) >SO_4^{2-} (1%). In December 2016 the sequence of the abundance of major cations and anions are in the order Ca^{2+} (45%) > Mg^{2+} (31%) > Na^++K^+ (24%) and HCO_3^- (78%) > Cl^- (21%) > SO_4^{2-} (1%). In December 2017, water displayed a mixed behaviour, where no prominent hydrochemical facies can identify. But from anion-cation triangles it is belonged to Na^++ K^+ dominant cation to Cl^- anion water type.

5.4 Gibb’s Diagram

Gibb’s diagrams the groundwater from shallow dug wells for a period from 2001 to 2017 clearly shows the pre-tsunami data (April 2001) falls in the rock dominant field of the Gibb’s plot. This reveled the controlling factor of groundwater chemistry is from dissociation of rock forming minerals. During the post-tsunami period in the year 2005 and December 2008 water is plotted in the evaporation dominant field of the Gibb’s plot, as the groundwater chemistry of shallow dug wells after tsunami is disturbed by mixing of sea water with fresh water, leading to high concentration of sodium in groundwater. The water plotted in the evaporation dominant field have sodium rich, high salinity end member. In the year 2012 and the subsequent years (December 2013 to December 2017) all the water sources are plotted in the rock dominant field, indicating the water is calcium rich and is medium saline in nature. The mineral composition of water in the shallow dug wells are contributed from dissolved salts from rocks and soil.

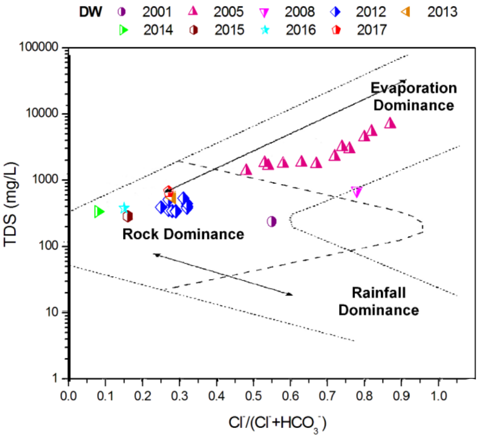

Figure 5.20: Gibb’s a for groundwater from shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

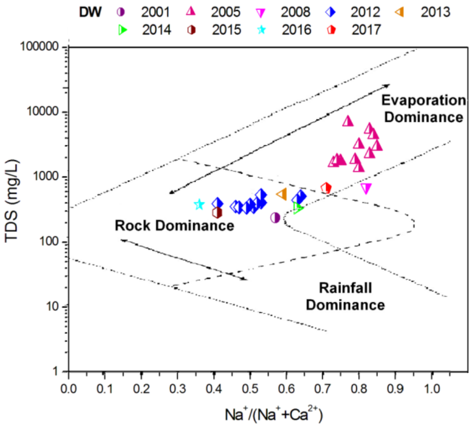

Figure 5.21: Gibb’s b for groundwater from shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

5.5 Water Quality Index (WQI)

The water quality index of groundwater in pre-tsunamic situation (April 2001) comes in *good category* (**Grade B**), suitable for drinking purposes. But in the year 2005, WQI > 100, which means water is *unfit for human consumption*, due to high concentration of chemical constituents in the water as an after effected of the catastrophic 26th December 2004 Indian Ocean Tsunami. During the this period groundwater in most of the dug wells deteriorated to Grade E.

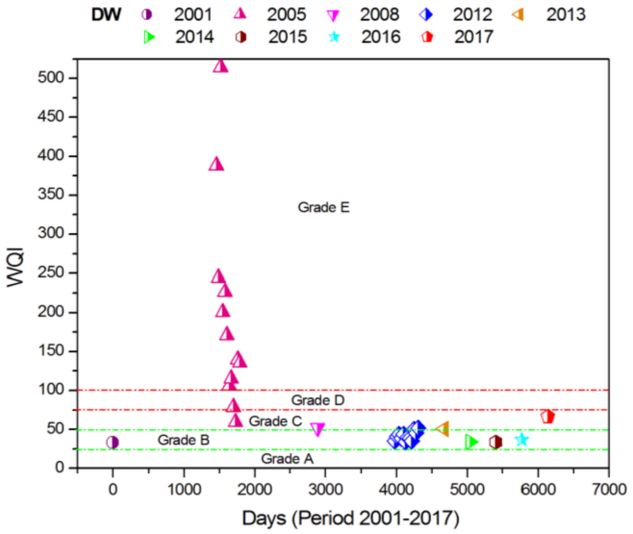

Figure 5.22: Temporal variation in water quality index (WQI) of groundwater from shallow dug well (DW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

In December 2008, the WQI is reported as 52.1, water remaining in *poor quality* (**Grade C**) that is not safe for drinking purposes. During 2012, the water quality improved to **Grade B**, with *good water quality* in most of the months except in December 2012. During December 2012, degraded to **Grade C** considered as *poor water quality*, as the WQI of groundwater increased to 52. December 2013 also show *poor water quality*, with WQI 50.7, but in December 2014, December 2015 and December 2016, WQI comes in **Grade B**, as the groundwater maintained a *good quality*. In December 2017, WQI of groundwater is 66.5, making it poor quality and falls in **Grade C**. The temporal variation in WQI over the years with respective grades are given in the Table 5.1.

Table 5.1: Temporal variation in water quality index (WQI) of groundwater from shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Year/Month	WQI	Water Quality	Grade
Apr 2001	33	Good	B
Jan 2005	388.5	Unfit	E
Feb 2005	244.5	Unfit	E
Mar 2005	514.3	Unfit	E
Apr 2005	200.8	Unfit	E
May 2005	226.4	Unfit	E
Jun 2005	171.2	Unfit	E
Jul 2005	106	Unfit	E
Aug 2005	115.4	Unfit	E
Sep 2005	78.9	Very Poor	D
Oct 2005	59.7	Poor	C
Nov 2005	139.7	Unfit	E
Dec 2005	136	Unfit	E
Dec 2008	52.1	Poor	C
Jan 2012	35.2	Good	B
Feb 2012	41.2	Good	B
Mar 2012	43.8	Good	B
Apr 2012	38.8	Good	B
May 2012	43.8	Good	B
Jun 2012	33.9	Good	B
Jul 2012	39.7	Good	B
Aug 2012	38.6	Good	B
Sep 2012	35	Good	B
Oct 2012	49.9	Good	B
Nov 2012	45.3	Good	B
Dec 2012	52	Poor	C
Dec 2013	50.7	Poor	C
Dec 2014	34.1	Good	B
Dec 2015	33.8	Good	B
Dec 2016	36.7	Good	B
Dec 2017	66.5	Poor	C

**Unfit- Unfit for human consumption*

A - Excellent B- Good C- Poor D- Very poor E- Unfit for human consumption

5.6 Irrigation water quality parameters

Irrigation parameters include sodium adsorption ratio, sodium percent, permeability index, Kelley's index, magnesium hazard and residual sodium carbonate are evaluated to find the overall water quality with respect to suitability for irrigation from 2001 to 2017.

5.6.1 Sodium Adsorption Raito (SAR)

Sodium adsorption ratio (SAR) is a measure of sodium in the water sample against calcium and magnesium ions. In the coastal aquifers occasional salt water intrusion leads to high sodium concentration, which in turn have the tendency to replace Ca^{2+} or Mg^{2+} present in the soil or aquifer material.

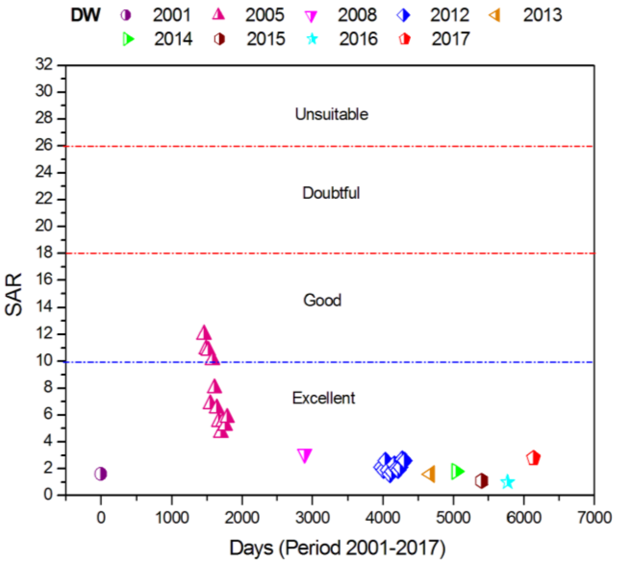

Figure 5.23: Temporal variation of sodium adsorption ratio (SAR) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In 2001, SAR is 1.2 and comes in *excellent class*. After tsunami from January 2005 to March 2005 and again in May 2005, SAR is between 10 -18, so the water quality during this period falls in *good class*. From June 2005 onwards water is having SAR < 10 for all the studied months including year 2012, December 2013, 2014, 2015, 2016 and 2017 indicating water is of *excellent quality* in terms of sodium adsorption ratio (Figure 5. 23).

5.6.1.1 USSL Diagram

USSL diagram divides groundwater sources with respect to SAR and electrical conductivity (EC) totally into 16 subclasses. In this diagram groundwater comes under C1S1 indicates, water having *low salinity with low sodium hazard* and C2S1 class means water *medium salinity and low sodium hazard.* Both the classes are good for irrigation.

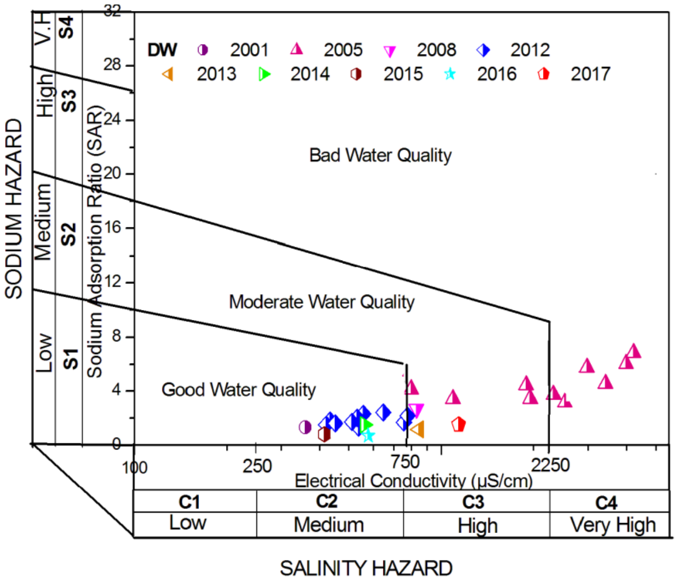

Figure 5.24: USSL diagram of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Water with *low sodium hazard and high salinity hazard* falls in C3S1 and C3S2 class consist of *high salinity with medium sodium* water, equally comes under moderate water quality. The C4S1 type water having *very high salinity hazard and low sodium hazard* and all other subclasses (C1S3, C1S4, C2S3, C2S4, C3S3, C3S4, C4S3 & C4S4) comes under bad water quality that is unfit for irrigation. From the figure 5.17, it is clear that, the groundwater during 2001 and most of the months in the year 2012, December 2014, December 2015 and December 2016 falls in C2S1 class (good water quality). After 26th December 2004 Indian Ocean Tsunami, most of the dug wells have high EC, hence it is spread in C3S2 (moderate water quality) and C4S2 classes (bad water quality).

5.6.2 Sodium Percent (Na%)

Shallow groundwater sources in April 2001 have 52.7% of sodium percent that comes under *permissible* class for irrigation purposes. Even though tsunami hit this barrier island badly, the Na% during the year 2005 falls in *permissible limit* (40% -60%), except in March 2005, where a slight increase (61%) in sodium percent is observed. In the year 2012, all the 11 months of sampling reported Na% between 40% to 60 %, inferring water have Na% below *permissible* limit and in May 2012, Na% dropped to 38.8%, that includes under *good water quality.* From December 2013 to December 2016, water have Na% between 20% - 40%, indicating *good category*, where as in December 2017 Na% increased to 57% and falls in *permissible category.*

Table 5.2: Temporal variation of sodium adsorption ratio (SAR) and sodium percent (Na%) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Year/Month	SAR	Inference	% Na	Inference
Apr 2001	1.6	E	52.7	P
Jan 2005	12.0	G	59.2	P
Feb 2005	10.9	G	60.9	D
Mar 2005	10.8	G	43.9	P
Apr 2005	6.8	E	50.4	P
May 2005	10.1	G	56.6	P
Jun 2005	8.0	E	57.7	P
Jul 2005	6.5	E	57.1	P
Aug 2005	5.5	E	57.6	P
Sep 2005	4.7	E	52.2	P
Oct 2005	5.5	E	58.6	P
Nov 2005	5.2	E	57.6	P
Dec 2005	5.8	E	59.7	P
Dec 2008	3.1	E	51.9	P
Jan 2012	2.1	E	40.4	P
Feb 2012	1.9	E	40.5	P
Mar 2012	2.6	E	48.4	P
Apr 2012	1.9	E	44.4	P
May 2012	1.6	E	38.8	G
Jun 2012	1.8	E	41.7	P
Jul 2012	2.3	E	44.6	P
Aug 2012	2.0	E	41.2	P
Sep 2012	1.9	E	41.5	P
Oct 2012	2.1	E	42.9	P
Nov 2012	2.7	E	49.5	P
Dec 2012	2.6	E	45.8	P
Dec 2013	1.6	E	39.0	G
Dec 2014	1.8	E	37.9	G
Dec 2015	1.1	E	33.9	G
Dec 2016	1.0	E	26.6	G
Dec 2017	2.8	E	56.9	P

E - Excellent G - Good P - Permissible D - Doubtful

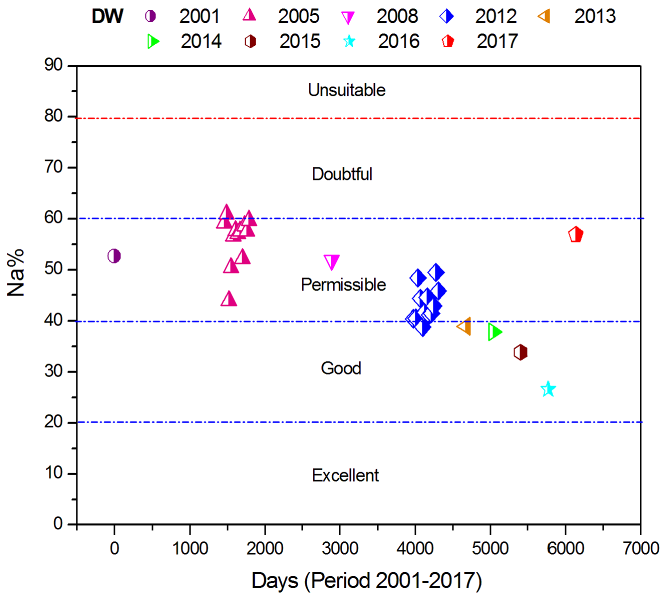

Figure 5.25: Temporal variation of sodium percent (Na%) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

5.6.2.1 Wilcox Diagram

In Wilcox diagram EC is plotted against the sodium percent to evaluate the suitability of water for irrigation. The salts present in the groundwater will affect soil structure, permeability and aeration, which indirectly affect plant growth[23]. During April 2001, water comes in *excellent to good* range. But in the year 2005, due to tsunami encroachment water quality deteriorated to *unsuitable* category in the beginning, but gradually when EC values decreases, water become *doubtful to unsuitable* and later *good to permissible* range. In December 2008, groundwater possesses *good to permissible quality*. Most of the months in 2012 showed *excellent to good* quality for irrigation purposes, except October and December 2012, where the water quality falls down into *good to* *permissible* category. Groundwater remained in *good to permissible* limit in December 2013, but maintain an excellent to good quality in December 2014, 2015 & 2016. In December 2017, water remained in *good to permissible* category.

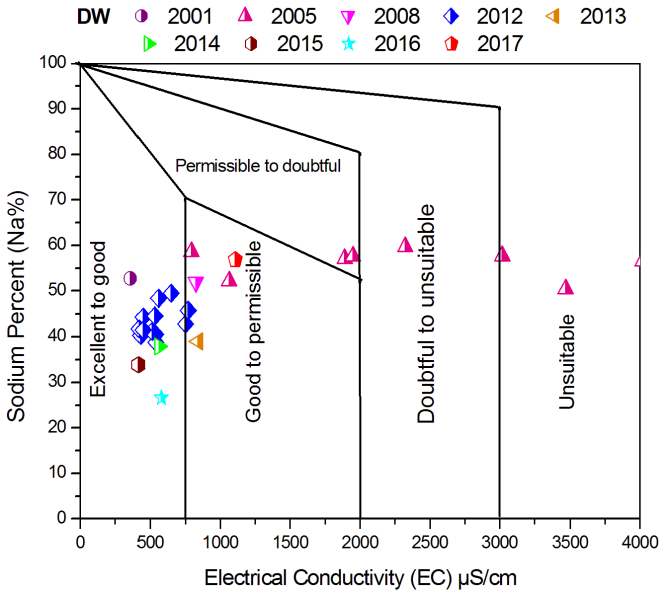

Figure 5.26: Wilcox diagram groundwater samples of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

5.6.3 Permeability Index (PI)

The permeability Index is an irrigation water quality parameter, used to classify water into three categories of class I class II and class III[24]. Table 5.3 shows the permeability index and their respective classes for all the months analyses done from 2001 to 2017. From the Figure 5.27 it is clear that PI in April 2001 falls in Class II, with 63.8% permeability. In the year 2005, till the month of May, water remained in Class II, being permeability index between 25% to 75%. From June 2005 to December 2005, permeability of water is improved with maximum permeability >75% (Class I). But in December 2008 PI is decreased to Class II with 64%. After that, throughout the study period till December 2017, water remained in Class I. From the observations it is inferred that water from dug wells are suitable for irrigation in terms of permeability index throughout the study period from 2001 to 2017 reported and presented.

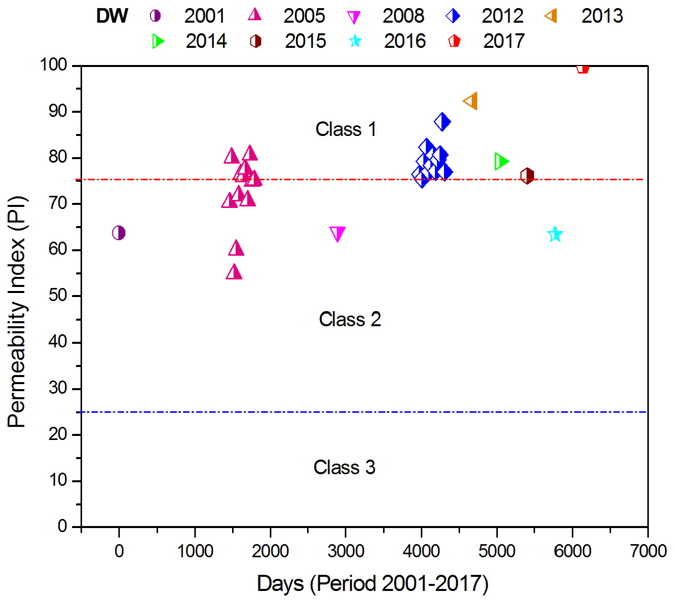

Figure 5.27: Temporal variation of permeability index (PI) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

5.6.4 Kelley's Index (KI)

Kelley's index is a measure of sodium concentration against Ca and Mg ions in groundwater, used to find the irrigation suitability. The ratio less than 1, indicate water is suitable for irrigation. From the Figure 5.28 it is clear that shallow groundwater sources are unsuitable for irrigation purposes in April 2001, being KI>1. The same behaviour of shallow dug wells are observed during the entire 12 months of the year 2005 and December 2008. It is clear that, groundwater having high sodium content than Ca and Mg ions makes it unfit for irrigation. KI become less than 1 in most of the month in the year 2012, reporting its suitability for irrigation during this period. However, an increaced KI is observed in March, October, November and December 2012 making it unsuitable for irrigation. Kelley's index from December 2012 to December 2016 are less than 1 (suitable for irrigation), where as in December 2017 water become unsuitable for irrigation with respect to KI>1.

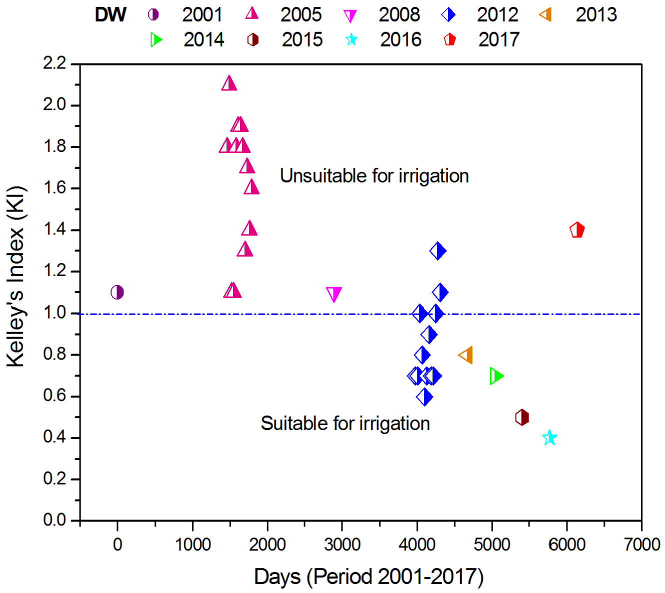

Figure 5.28: Temporal variation of Kelley's index (KI) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Table 5.3: Temporal variation of permeability index (PI) and Kelley's index (KI) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Year/Month	PI	Inference	KI	Inference
Apr 2001	63.8	Class II	1.1	US
Jan 2005	70.4	Class II	1.8	US
Feb 2005	80.1	Class I	2.1	US
Mar 2005	54.9	Class II	1.1	US
Apr 2005	60.1	Class II	1.1	US
May 2005	71.9	Class II	1.8	US
Jun 2005	76.5	Class I	1.9	US
Jul 2005	76.0	Class I	1.9	US
Aug 2005	77.7	Class I	1.8	US
Sep 2005	70.8	Class I	1.3	US
Oct 2005	80.7	Class I	1.7	US
Nov 2005	75.0	Class I	1.4	US
Dec 2005	75.2	Class I	1.6	US
Dec 2008	64.0	Class II	1.1	US
Jan 2012	76.5	Class I	0.7	S
Feb 2012	75.5	Class I	0.7	S
Mar 2012	79.3	Class I	1.0	US
Apr 2012	82.4	Class I	0.8	S
May 2012	77.1	Class I	0.6	S
Jun 2012	78.4	Class I	0.7	S
Jul 2012	80.6	Class I	0.9	S
Aug 2012	77.2	Class I	0.7	S
Sep 2012	79.6	Class I	0.7	S
Oct 2012	80.7	Class I	1.0	US
Nov 2012	87.9	Class I	1.3	US
Dec 2012	77.0	Class I	1.1	US
Dec 2013	92.4	Class I	0.8	S
Dec 2014	79.3	Class I	0.7	S
Dec 2015	76.2	Class I	0.5	S
Dec 2016	63.4	Class I	0.4	S
Dec 2017	96	Class I	1.4	US

US= Unsuitable S = Suitable

5.6.5 Magnesium Adsorption Ratio (MAR)

Magnesium is an essential element for the plant growth. But its increased concentration leads to the reduction in crop yield. The Mg hazard determines the hazard caused by Mg ion in groundwater. If MAR is less than 50%, water is considered suitable for agricultural uses. During April

2001, water reported magnesium adsorption ratio of 32.4%, *suitable* for agricultural purposes. The year 2005, also shows suitability for irrigation evidenced by the MAR<50%, except in April 2005 with increase in MAR to 71.4% and August 2005 with MAR51.8% which makes water unsuitable for irrigation. It is noticeable that even the gaint tsunami waves hit this land badly, magnesium concentration remained low during the immediate post tsunami period in the year 2005. It reaches at 46.9% during the period December 2008. Magnesium adsorption ratio noticed below 50% in year 2012, exceptionally during October 2012, when the MAR value reached 64.2%. In December 2013 and December 2014 water is unsuitable for irrigation as MAR increased to 54.4% and 64% respectively. From December 2015 to December 2017 water is suitable for irrigation with respect to magnesium hazard.

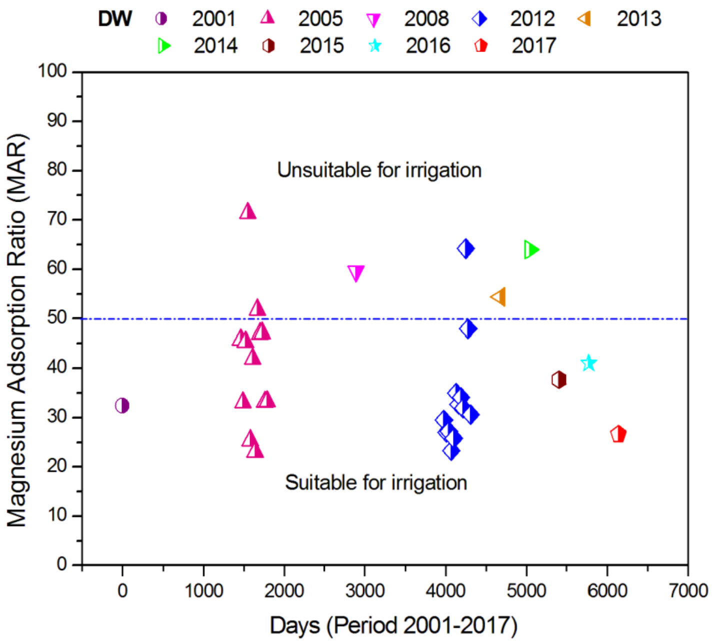

Figure 5.29: Temporal variation of magnesium hazard (MAR) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

5.6.6 Resiual Sodium Carbonate (RSC)

From the graph it is clear that, the shallow dug wells in the year 2001 is *suitable for irrigation* with RSC<1.2. In the year 2005, September and October, have RSC between 1.2 – 2.5, hence water is *moderately suitable* for irrigation. Dug wells in December 2008 have RSC<1.2 and the water is *suitable for irrigation*. All the months in the year 2012 have RSC values *suitable for irrigation*. In the subsequent years 2013 have RSC <1.2, whereas December 2014 show RSC of 2.3 and water is *not suitable* for irrigation. During December 2015, 2016 and 2017 water RSC is in suitable range for irrigation purposes.

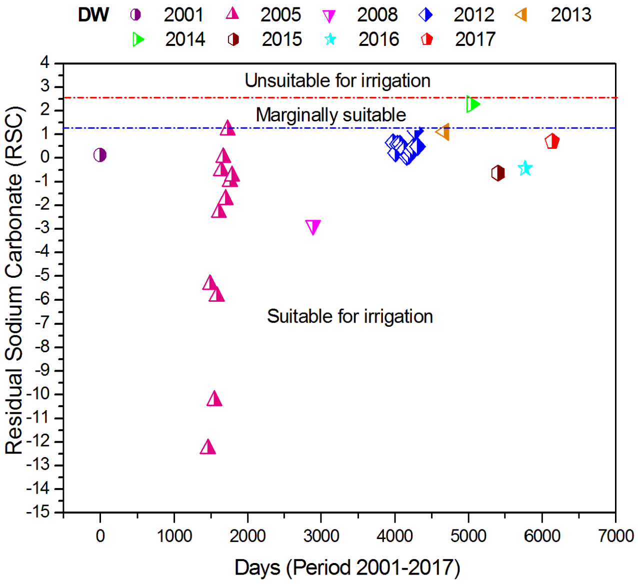

Figure 5.30: Temporal variation of residual sodium carbonate (RSC) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Table 5.4: Temporal variation of magnesium hazard (MH) and residual sodium carbonate (RSC) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Year/Month	MH	Inference	RSC	Inference
Apr 2001	32.4	S	0.1	S
Jan 2005	45.7	S	-12.3	S
Feb 2005	33.1	S	-5.3	S
Mar 2005	45.3	S	-22.1	S
Apr 2005	71.4	US	-10.2	S
May 2005	25.4	S	-5.8	S
Jun 2005	41.9	S	-2.3	S
Jul 2005	23.1	S	-0.5	S
Aug 2005	51.8	US	0.0	S
Sep 2005	47.0	S	-1.8	MS
Oct 2005	47.1	S	1.2	MS
Nov 2005	33.2	S	-1.0	S
Dec 2005	33.3	S	-0.8	S
Dec 2008	59.6	S	-2.8	S
Jan 2012	29.5	S	0.7	S
Feb 2012	27.0	S	0.2	S
Mar 2012	27.2	S	0.6	S
Apr 2012	23.3	S	0.6	S
May 2012	25.8	S	0.4	S
Jun 2012	35.0	S	0.3	S
Jul 2012	32.7	S	0.1	S
Aug 2012	34.1	S	0.1	S
Sep 2012	31.9	S	0.3	S
Oct 2012	64.2	US	0.4	S
Nov 2012	48.0	S	1.2	S
Dec 2012	30.6	S	0.5	S
Dec 2013	54.4	US	1.1	S
Dec 2014	64.0	US	2.3	MS
Dec 2015	37.7	S	-0.6	S
Dec 2016	41.0	S	-0.4	S
Dec 2017	26.6	S	0.7	S

S – Suitable MS - Marginally Suitable US - Unsuitable

5.7 Corrosion Indices

Different types of corrosion indices such as Langelier Saturation Index (LSI), Ryznar Index (RSI), aggressiveness index (AI) and Larson-Skold index (L-S) are calculated to find the corrosion behaviour of groundwater over a period of 2005 to 2017. Here the monthly mean of shallow dug wells of study area are used to interpret the behaviour of the water in terms of corrosion for each sampling months in 2005, 2008, 2012, 2013, 2014, 2015, 2016 and 2017.

5.7.1 Langelier Saturation Index (LSI)

The LSI of water for months January to May, 2005 shows *scale forming and non-corrosive* (SFNC) behaviour in terms of pH, TDS, calcium hardness and alkalinity. During this period, of first five months after 2004 Indian Ocean Tsunami the water has positive LSI value ($LSI>0$), as the water is super saturated with respect to calcium carbonate and scale formation is promoted to prevent corrosion. In June 2005, even though LSI is positive (0.1) it is not sufficient for preventing corrosion and leads to *slightly scale forming but corrosive* (SSFC) type water. Afterwards in July 2005 the LSI shifts to negative value (-0.2) making water *slightly corrosive but non scale forming* (SCNSF) type. However, water quality improves to supersaturated with $CaCO_3$ leading to $LSI>0$ till December 2005. In December 2008, water become undersaturated with calcium carbonate and tend to remove the existing protective scale formations leading to *serious corrosion* (SC) behaviour.

From January 2012 to May 2012 the shallow dug wells are *slightly scale forming but corrosive* (SSFC) in nature, where as during June-July months water become *slightly corrosive but non scale forming* (SCNSF). The same behaviour is observed in November-December 2012 also, where the LSI turn out to be negative. In September 2012 water remain in an equilibrium state ($LSI=0$), where neither scale is formed nor removed. In this situation, water is said to be *balanced but pitting* (BP). During most of the months of the year 2012, experiences *slightly scale forming but corrosive* (SSFC) behaviour of groundwater.

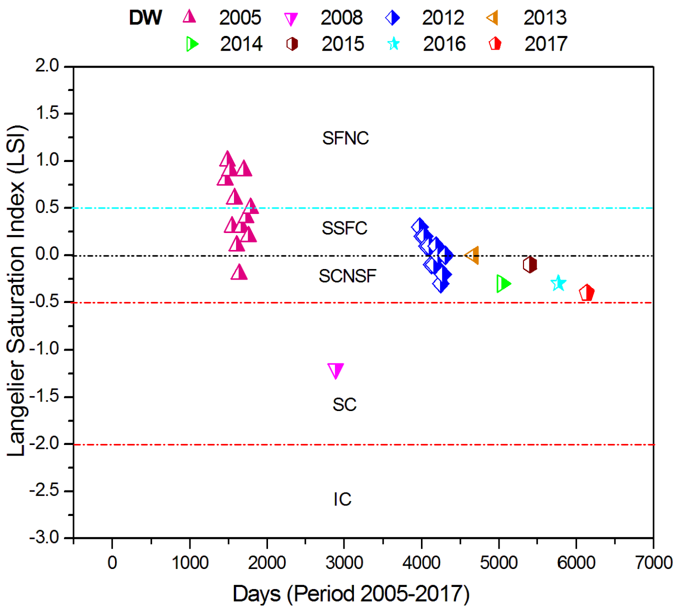

Figure 5.31: Temporal and spacial variation of Langelier saturation index (LSI) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

In December 2013, shallow groundwater sources has *balanced but pitting* (BP) behaviour, being LSI=0, but exhibits *slightly corrosive but non scale forming* (SCNSF) type in December 2014, December 2015, December 2016 and December 2017. From the Figure 5.31, it is evident that, overall LSI of the study area falls between -2.0 to +2.0, confirming corrosive to scale forming nature of shallow dug wells in the study area.

5.7.2 Ryznar Stability Index (RSI)

According to RSI, calculated in this study based on a valuable reported data, shallow groundwater in January to March 2005 is *little scale forming and corrosive* (LSC) that becomes *corrosion significant* (CS) in April 2005. *Little scale forming and corrosive* (LSC) nature of water is observed during May, September and December 2005. Rest of the months in the year 2005 displays *corrosion significant* (CS) water. In December 2008, RSI value reach 9.9 that leads to very intense scale dissolving and *very high corrosion* (HC) behaviour of groundwater.

Table 5.5: Temporal and spacial variation of Langelier saturation index (LSI) and Ryznar stability index (RSI) of shallow dug wells (DW) of Alappad region, Kollam, Kerala, India for the period 2001-2017

Year/Month	LSI	Inference	RSI	Inference
Jan 2005	0.8	SFNC	6.3	LSC
Feb 2005	1.0	SFNC	6.2	LSC
Mar 2005	0.9	SFNC	6.0	LSC
Apr 2005	0.3	SSFC	7.0	CS
May 2005	0.6	SFNC	6.4	LSC
Jun 2005	0.1	SSFC	7.1	CS
Jul 2005	-0.2	SCNSF	7.4	CS
Aug 2005	0.3	SSFC	7.1	CS
Sep 2005	0.9	SFNC	6.5	LSC
Oct 2005	0.4	SSFC	7.0	CS
Nov 2005	0.2	SSFC	7.0	CS
Dec 2005	0.5	SFNC	6.6	LSC
Dec 2008	-1.2	SC	9.9	HC
Jan 2012	0.3	SSFC	7.2	CS
Feb 2012	0.2	SSFC	7.3	CS
Mar 2012	0.2	SSFC	7.5	CS
Apr 2012	0.1	SSFC	7.5	CS
May 2012	0.1	SSFC	7.4	CS
Jun 2012	-0.1	SCNSF	7.9	HC
Jul 2012	-0.1	SCNSF	7.8	HC
Aug 2012	0.1	SSFC	7.6	HC
Sep 2012	0.0	BP	7.6	HC
Oct 2012	-0.3	SCNSF	8.3	HC
Nov 2012	-0.2	SCNSF	8.1	HC
Dec 2012	0.2	SSFC	7.6	HC
Dec 2013	0.0	BP	7.8	HC
Dec 2014	-0.3	SCNSF	7.9	HC
Dec 2015	-0.1	SCNSF	8.2	HC
Dec 2016	-0.3	SCNSF	8.0	HC
Dec 2017	-0.4	SCNSF	8.4	HC

LSI: SFNC - scale forming and non-corrosive SSFC - slightly scale forming but corrosive
SCNSF - slightly corrosive but non scale forming SC - serious corrosion BP - balanced but pitting
RSI: LSC- little scale forming and corrosive CS - corrosion significant HC - Heavy corrosion

From the Figure 5.33, RSI values of all the 12 months in the year 2012 and December 2013 to December 2017, falls between 7.0 and 9.0. This indicates water exhibits significantly high corrosion tendency and able to dissolve existing, calcium carbonate scales. During January to May 2012, water is corrosion significant type, but from June 2012 onwards RSC is greater than 7.5 leading to intense scale removal and *high corrosion* (HC) water.

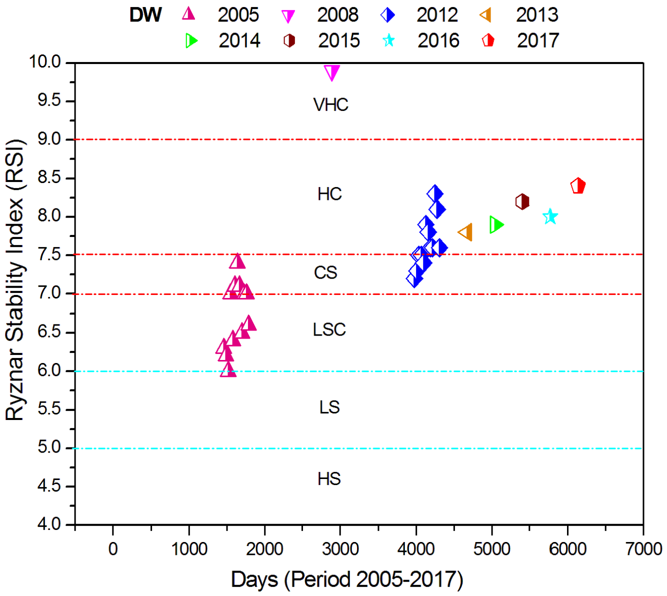

Figure 5.32: Temporal variation of Ryznar stability index (RSI) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

5.7.3 Aggressiveness index (AI)

Aggressiveness index of the year 2005 shows water is in *non-aggressive* (NA) nature except in July 2005, where the water becomes *moderately aggressive* (MA) with AI 11.7. In 2008 water have AI value 10.7, indicating the *moderate aggressive* behaviour of shallow dug wells.

Table 5.6: Temporal and spacial variation of aggressiveness index (AI) and Larson-Skold index (L-S) of shallow dug wells (DW) of Alappad region, Kollam, Kerala, India for the period 2001-2017

Year/Month	AI	Inference	L-S	Inference
Jan 2005	12.7	NA	10.2	HC
Feb 2005	13.0	NA	10.2	HC
Mar 2005	12.8	NA	10.5	HC
Apr 2005	12.3	NA	7.1	HC
May 2005	12.5	NA	5.5	HC
Jun 2005	12.1	NA	6.0	HC
Jul 2005	11.7	MA	4.1	HC
Aug 2005	12.2	NA	3.9	HC
Sep 2005	12.8	NA	4.3	HC
Oct 2005	12.3	NA	2.3	HC
Nov 2005	12.1	NA	2.4	HC
Dec 2005	12.5	NA	2.2	HC
Dec 2008	10.7	MA	5.5	HC
Jan 2012	12.2	NA	0.4	NC
Feb 2012	12.1	NA	0.4	NC
Mar 2012	12.1	NA	0.6	NC
Apr 2012	12.0	MA	0.4	NC
May 2012	12.0	MA	0.4	NC
Jun 2012	11.7	MA	0.5	NC
Jul 2012	11.8	MA	0.8	SC
Aug 2012	12.0	MA	0.8	SC
Sep 2012	11.9	MA	0.5	NC
Oct 2012	11.6	MA	0.4	NC
Nov 2012	11.7	MA	0.5	NC
Dec 2012	12.1	NA	0.5	NC
Dec 2013	11.9	MA	0.4	NC
Dec 2014	11.6	MA	0.3	NC
Dec 2015	11.8	MA	0.4	NC
Dec 2016	11.5	MA	0.4	NC
Dec 2017	11.5	MA	0.7	NC

AI: NA- non-aggressive MA - moderately aggressive

LS: HC- highly corrosive NC- non-corrosive

From the (Figure 5.33) it is clear that, the first three months in the year 2012, AI is in non-aggressive nature, but from April to November 2012, water become moderately aggressive. During December 2012 a slight increase in AI value to 12.1 make the water non-aggressive. In the successive month of December 2013, 2014, 2015, 2016 and 2017 water remained in a moderate aggressive state.

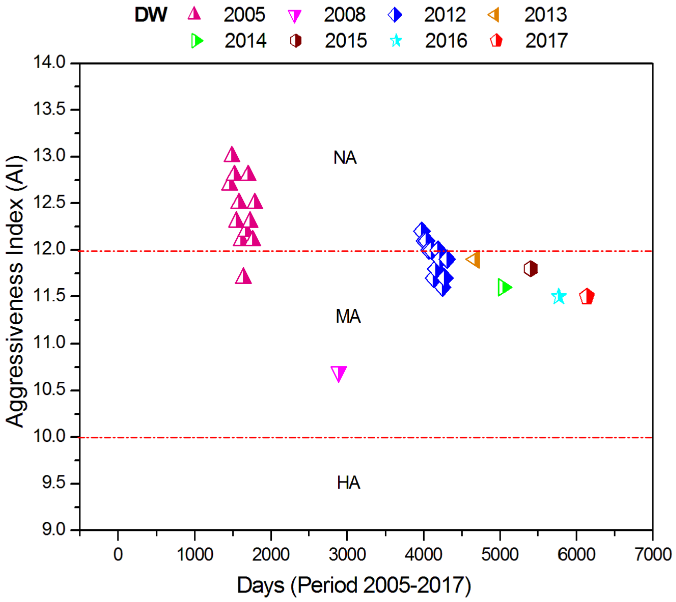

Figure 5.33: Temporal variation of aggressiveness index (AI) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

5.7.4 Larson-Skold index

Larson-Skold index for groundwater during the year 2005 and December 2008 indicate that water remained *highly corrosive* (HC) throughout that period (Figure 5.34). The saline water mixing with fresh water aquifer contribute significant amount of chloride and sulphate which may interfere with the natural scale formation and promote corrosion tendency of the groundwater. Later in the year 2012 corrosion due to anion are reduced to non-corrosive range (NC) and continued to be the same in the subsequent study periods of December 2013, 2014, 2015, 2016 and 2017. This infere that from the year 2012 onwards, chloride and sulphate donot promote the corrosive nature of water.

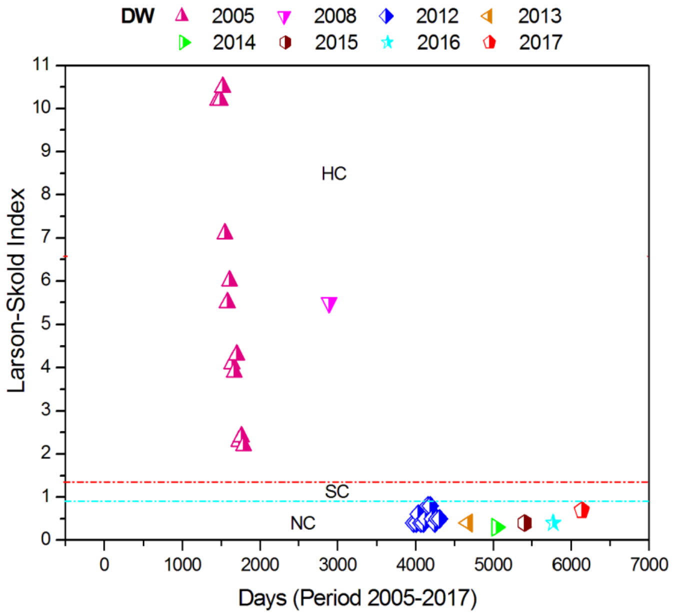

Figure 5.34: Temporal variation of Larson-Skold index (L-S) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

5.8 Statistical Analysis

5.8.1 Analysis of Variance

Hypothesis VII:

> *Whether there is any significant difference in the mean values of the parameters of groundwater sampled from dug well (DW) strata over the years.*

Table 5.7: ANNOVA table for the comparison of mean values of paramaters of groundwater from dug wells during the period from the year 2012 to 2017

Source	**SS**	**df**	**ms**	**F**	**p- value**
Total	1503853.1154	94			
Between years	17639.6607	4	4409.9152	1.75	$p>0.05$
Between Parameters	1305321.4314	18	72517.8573	28.864	$p<0.001$
Residual	180892.0233	72	2512.3892		

Inferences

1) There is no significant difference between years ($p>0.05$).
2) Between parameters depicted a significant difference ($p<0.001$) TDS is significantly higher than all the rest, followed by HCO_3, TA and TH ($p<0.001$). Eh is significantly lower than all the rest followed by PO_4^{3-}, Fe^{2+}, NO_3^-, DO, BOD and EC ($p<0.001$).

Table 5.8: Over all groundwater quality of dug wells of the Alappad coast, Kollam, Kerala, India during the period of 2001, 2005, 2008, 2012, 2013, 201, 2015, 2016 and 2017.

Wate quality parameters	April 2001	Annual Mean 2005	December 2008	Annual Mean 2012	December 2013	December 2014	December 2015	December 2016	December 2017	BIS (IS 10500:2012) Acceptable Limit	BIS (IS 10500:2012) Permissible Limit	WHO (2011)
pH	7.6±0.6	7.7±0.4	7.5±0.4	7.8±0.4	7.8±0.3	7.4±0.3	8±0.2	7.3±0.3	7.6±0.3	6.5-8.5	No relaxation	6.5-8.5
Eh (mV)		-32.1±20.5	-39.4±8.8	-47.6±20.3	-46.3±33	-22.7±15	-69±15.6	-22±19.3	-38.1±20.8			
EC (mS/cm)	0.4±0.1	3.5±5.2	0.8±1	0.5±0.5	0.8±0.5	0.6±0.3	0.4±0.2	0.6±0.4	1.1±1.8			1.5
TDS (mg/L)	236.4±49.8	2948.5±3643.7	697.3±494	396.8±350.4	545.7±341.3	335±166.7	284.9±125.8	376.2±253.7	670.5±1083.9	500	2000	
TA (mg/L)		301.9±177.8	31.3±11.3	189.7±88.4	247.3±103.5	338±145	104.5±38.6	196.3±92.2	139.5±36.2	200	600	
TH (mg/L)	79.5±49.2	557.9±596.9	174.1±102.9	167.3±87	191.7±137.9	224±131	155.5±106.6	218.4±167.4	98.6±70.6	200	600	100
Ca^{2+} (mg/L)	23±19.3	131.4±204.9	22.9±7.3	43.5±22	31.2±23.4	33.2±17.6	41±29	50.8±36.7	28.8±14.9	75	200	75
Mg^{2+} (mg/L)	5.4±2.2	55.1±46.2	28±25.5	14.2±12.7	27.6±24.2	34±21.6	12.8±10	22±21.4	7.9±9.8	30	100	30
Na^+ (mg/L)	30.3±14.5	519.5±927.6	105.3±120.3	64.3±59.3	44.2±22.8	56.6±30	27.9±14.8	28.5±16.8	68.9±63.7			
K^+ (mg/L)	11.9±10.3	19.5±30	7±5.2	8.4±4.9	0.9±1.1	0.9±0.5	4.7±3.2	4.7±3.2	7.5±6.1			
HCO_3^- (mg/L)	42.7±58	368.3±217	38±13.7	231.5±107.9	301.7±126.2	412.5±176.9	151.5±71.9	239.5±112.5	170.2±44.2			
Cl^- (mg/L)	53.3±15	993.8±1618.4	135.7±269.3	65.5±83.6	46±47.6	41.4±31.3	27.9±30.2	41.4±33.4	63.2±78.5	250	1000	
SO_4^{2-} (mg/L)	25.4±19.8	47.9±41.2	21.7±24	2.5±3.1	25±49.7	24.3±32.5	1.4±1.6	2.8±3.2	2.2±2.5	200	400	
PO_4^{3-} (mg/L)		0.1±0.16	102±77.3	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.1	0.1±0.2	0.1±0.1			
NO_3^- (mg/L)		1.1±0.79	1424.4±977.9	0.6±0.9	0.7±0.9	0.6±0.8	0.5±0.8	0.4±0.8	0.5±0.9	45	No relaxation	
Iron (mg/L)		0.2±0.19	165±73.4	0.1±0.6	0±0.1	0±0.1	0.2±0.2	0.1±0.2	0.1±0.2	0.3	No relaxation	0.1
DO (mg/L)		4.5±2.3	6.6±3.2	4.1±1.5	2.2±0.9	4±1.5	2.4±0.8	3.8±1.6	2.1±1.1			
BOD (mg/L)		8.8±5.3	9.2±5.4	3.4±3.2	2.7±1.9	3±2.1	2.4±1.7	2.7±2	5.6±3			

5.9 Conclusion

The physico-chemical parameters investigated shows there is wide variation in water quality parameters from 2005 to 2017 and the shallow dug wells in the Alappad region is severely affected by 26th December 2004 Indian Ocean Tsunami. But during the course of time water regained its fresh water chemical composition. Statistical analysis have proven that there is no significant difference in parameters between years ($p>0.05$), but depicted significant difference between parameters ($p<0.001$). TDS is significantly higher than all the rest, followed by HCO_3^-, TA and TH ($p<0.001$). Eh is significantly lower than all the rest followed by PO_4^{3-}, Fe^{2+}, NO_3^-, DO, BOD and EC ($P<0.001$). The hydrochemical facies of groundwater from dug well sources during April 2001, Year 2005 (annual mean) and December 2008 are Na^+-K^+-Cl^- -SO_4^{2-}. The water type during these periods is *saline water type* with Na^++K^+ dominate cation and Cl^- dominate anion water. This clearly indicates the occurrence of seawater intrusion in shallow fresh water aquifers. From the year 2012 to December 2016 water maintained *temporary hardness water* having non-dominant cation and bicarbonate dominant water. The hydrochemical facies groundwater during this period is Ca^{2+}-Mg^{2+}-HCO_3^-. In December 2017, water exhibited a mixed behaviour. Even though, no prominent hydrochemical facies can be identified here, the dominant cation and anion in groundwater are Na^++ K^+ and Cl^-. Gibb's diagram also support the finding from Hill Piper trilinear plots reporting the *evaporation dominance* on the hydrogeochemistry of groundwater during April 2001, year 2005 and December 2008. From the year 2012 onwards, the major mechanism that control the chemical composition of groundwater is found to be the rock forming minerals, as the water falls in rock dominant field of the Gibb's plot.

Water quality index (WQI) of groundwater in the study area in pre-tsunamic situation is *good* for drinking purposes. But in the post tsunamic period during the entire year of 2005 and in December 2008, water has WQI > 100, which is considered as *unfit for human consumption*. In the year 2012, WQI is comes under *good category* except in December 2012, where water quality degraded to *poor water quality*. In the following years December 2013 groundwater also is unfit for consumption with *poor quality* without any treatment. From December 2001 to December 2016 water have WQI value in the range of good quality, but again in December 2017 water become poor quality. Irrigation water quality studies inferred that sodium content during the year 2005 make it not suitable for irrigation. According to USSL diagram and Wilcox diagram the groundwater exhibits bad water quality during the year 2005, but from December 2008 onwards water is under suitable range for irrigation purposes. Permeability index (PI) and residual sodium carbonate (RSC) are within the safe limit for most of the study period, but Kelley's index and magnesium adsorption ratio (MAR) for the groundwater in the year 2005 cross the safe limit and is considered as not suitable for irrigation due to high concentration of sodium and magnesium driven by seawater intrusion in shallow dug well sources.

Corrosion studies and scale forming properties of the groundwater from dug wells suggested water is potentially corrosive in nature. Langelier Saturation Index (LSI) for the most of the months in the year

2005 is positive; being water has scale forming properties. But this scaling nature in some months is not sufficient to inhibit corrosion and the water becomes slightly scale forming but corrosive nature. In December 2008, water shows slightly corrosive behaviour. From the year 2012 to December 2017, water remained *slightly scale forming but corrosive* to *slightly corrosive but non scale forming* (SCNSF) category. Ryznar Stability Index (RSI) also reveals water have corrosive nature with *little scale forming and corrosive* and *corrosion significant* water in the year 2005 and *very high corrosion* behaviour in December 2008. Most of the months in the year 2012, December 2013, December 2014, December 2015, December 2016 and December 2017 shows significantly high corrosion tendency and able to dissolve existing, calcium carbonate scales in water. Aggressiveness index (AI) shows water is non-aggressive in the year 2005 and moderately aggressive in December 2008. During the period from the year 2012 to December 2017 water is considered as moderately aggressive. According to Larson-Skold index, groundwater in the year 2005 and December 2008 is highly corrosive (HC) which is contradiction to the findings based on aggressiveness index. The reason for this is during this period the corrosion tendency of water is due to the influence of chloride and sulphate. The dominant anion in the year 2005 and December 2008 is chloride, which promote the corrosive behaviour of water by inhibiting natural scale formation.

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Chapter 6

TEMPORAL VARIATIONS IN OVERALL QUALITY OF GROUNDWATER OF BORE WELLS IN ALAPPAD COAST, INTERMITTENTLY DURING THE PERIOD 2001 TO 2017

6.1 Introduction

This chapter discusses the temporal variations of groundwater quality of deep bore wells of Alappad coast for a period of 2001 to 2017. This study have special significance as this region is hit by 26th December 2004 Indian Ocean Tsunami and the reports says maximum inundations ranged between 50 and 320 m from swash zone leading to sever salt water intrusion in this coastal belt[1]. The analysis of groundwater for this long period from 2001 to 2017 give understanding of the long term impact on groundwater hydrogeochemistry of groundwater of the region and the extent of these changes to the deep aquifers of the region[2-7]. The variation of water quality parameters throughout the 12 months of year 2012 is discussed in Chapter 3, Chapter 4 that delivers insight into the hydrogeochemistry and quality of the deep bore well sources of the region. A follow-up of the study is continued for next 5 years intermittently during December months of 2013, 2014, 2015, 2016 & 2017. This data is compared with the reported data of 2001 as a reference of pre-tsunami water quality available[8] and post-tsunami water quality data available during the entire 12 months in the year 2005 and December 2008[9]. The major findings of the study includes temporal variations of physico-chemical parameters analysed. Variations in water quality index, irrigation water quality and suitability of the groundwater for industrial purposes in deep aquifers. The major objective of this chapter is to evaluate the overall water quality of deep groundwater resources of Alappad region.

6.2 Physico-chemical Parameters

6.2.1 pH

pH of deep groundwater in 2001 is 7.5 and just after the tsunami event, pH become strictly alkaline in nature (8.2±0.4) in January 2005. There is a gradual decrease in pH value till July 2005, when the pH is reduced to acidic nature (6.5±0). The water overcome this situation by increase in pH to 7.3±0.2 in August 2005 and continued this pH range till December 2005 (7.2±0.0). In December 2008, the water reached in a neutral pH of 7.0. During the year 2012 7.4±0.4, with confidence interval of 7.1-7.4, refers to water is existing near stable conditions. The pH of the subsequent years are 7.4±0.2 (2013), 7.2 (2014), 7.0±0.8 (2015), 6.8±0.8 (2016) and 7.2 (2017).

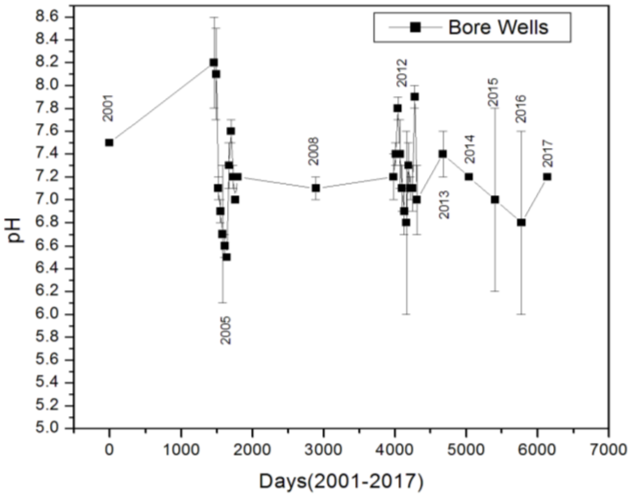

Figure 6.1: Temporal variation of pH of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

6.2.2 Redox Potential (Eh)

Redox potential, Eh during January and February 2005 is 6.5± 27.6 mV reported in an earlier study[9]. This high standard deviation displays the variation in Eh between different sampling locations. During this period including April, the water is in oxidising state. Whereas, the subsequent four months (March - June 2005), the water exsists in a reduced environment. During the course of monsoon in July and August 2005, water become oxidising in nature and continued in this state till in September 2005. The annual mean of Eh is reported -16.7±12.3 mV water is within a confidence interval of -24.3 to -9.1 mV, at 95% level of significance. The monthly mean of Eh in December 2008 also indicate water is in reduced state (-36.0±7.1).

In the year 2012, the water remained in reduced state mostly the whole year except during heavy monsoon periods of July and August 2012. The annual mean of Eh in the year 2012 is -17.3 ±16.3, with a confidence interval of -27.3 to -7.2, at 95% significant level and the monthly mean of the following period of analysis are -26.0±8.7 (2013), -0.5±0.3 (2014), -7.0 ±51.5 (2015), -7.0±21.2 (2016) and -13.5±0.7 (2017). Thus, the data generated over the last 16 years reveal that the Eh of bore well strata show the presence of a reducing environment in shallow groundwater sources of the study area.

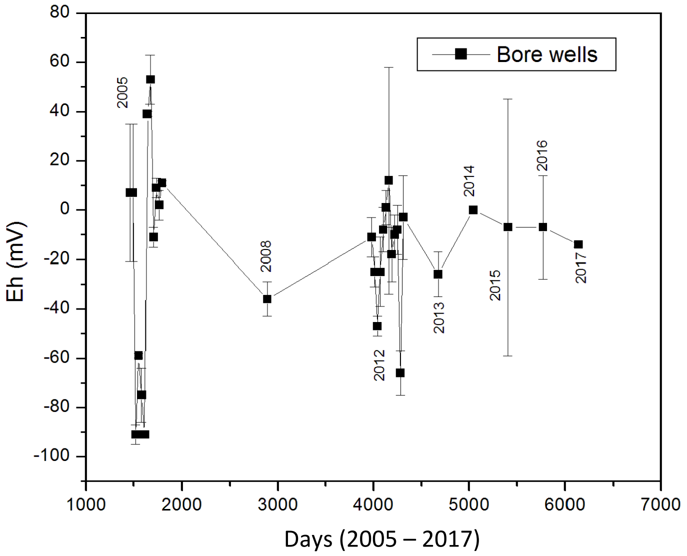

Figure 6.2: Temporal variation of Eh of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

6.2.3 Electrical Conductivity (EC)

Electrical conductivity is very useful water quality parameter especially in coastal aquifers as a function of salinity hazard. EC in 2001 is reported[10] very low about 0.31 mS/cm and in post tsunami situation also, the EC value is < 0.650 mS/cm, indicating that the water possess low salinity even though giant tsunami waves swipe the entire barrier island and its impact is clearly reflected on the EC of the shallow groundwater sources. A slight increase from low salinity to medium salinity is observed in some months particularly in September 2005, where the monthly mean reaches 1.03±0.1 mS/cm, but the annual mean of EC in the year 2005 is 0.6±0.1 mS/cm, with a confidence interval of 0.538 to 0.662 mS/cm, at 95% level of significance. The EC of December 2008 also exhibit a low salinity range, with monthly mean of 0.3±0.1 mS/cm. The EC of deep groundwater (bore wells) in the year 2012 is also < 0.650 mS/cm establishing low salinity nature of water, except in the month of July where the water falls in very high salinity class, with huge increase in EC, 3.7±5.8 mS/cm and variation among sampling locations is observed with an extraordinary error bar (Figure 6.3). Afterwards, that water maintained low salinity but have a slight increase in December 2012 (0.7±0.6 mS/cm). An increase in EC is notable in the rest of the intermittent study period with medium salinity of 0.7±0.2 mS/cm (2013), 2.2±3.0 (2014) and 2.2±3.0 (2015). In December 2016, EC changed to low saline nature with a monthly mean of 0.3±0 mS/cm, but increase to medium saline water in December 2017 (0.7±0.1).

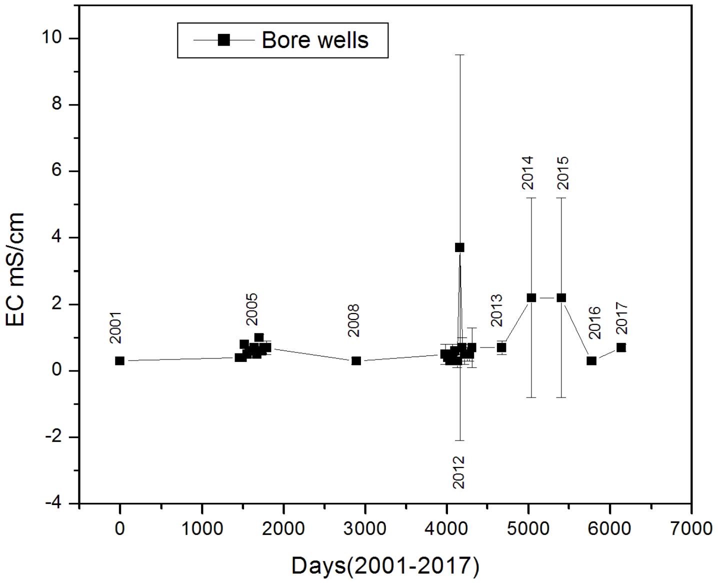

Figure 6.3: Temporal variation of electrical conductivity (EC) of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

The electrical conductivity data over the period of 2001 to 2017 reveals that the deep groundwater (bore wells) are not affected by 2004 December Indian Ocean tsunami, But sporadic increase in EC is not an unusual event in this coastal segment may be due to the intrusion of sea water due to over pumping.

6.2.4 Total Dissolved Solids (TDS)

TDS concentration of bore well waters in January 2005 is 2318.5±813.2 mg/L and February 2005 is 2324.7±818.9 mg/L. Afterwards, a steady decrease in TDS is observed for March -April 2005, but again a hike in May 2005 with a monthly mean of 2736.5±2515.6 mg/l and 2331.1±2313.7 mg/L in June 2005 is noticed. From July 2005 onwards, water showed a fall in TDS < 1000mg/L till December 2005. The annual mean of 1413±1070.4 mg/l TDS is recorded in the year 2005, with a confidence interval of 754.5 - 2071.5 mg/L, at 95% level of significance. In 2008 TDS falls within the acceptable limit of 411.8±81.0 mg/L, prescribed by WHO and BIS standards.

Bore well waters in year 2012 continued to have TDS < 500 mg/L for the first six months, after that a tremendous increase in concentration is recorded with a monthly mean of 3018.7 ± 4861.4 mg/L in July 2012. The wide range of variability in TDS concentration is noted with the abnormal standard error from the graph (Figure 6.4). A sudden fall in TDS is noticeable from the next month onwards, when the TDS become 427.0±189.8 mg/L in August 2012 and this normal TDS range < 500 mg/L is pertained in the rest of the months. The annual mean of TDS in the year 2012 is 591.9 ± 1414.3 mg/l.

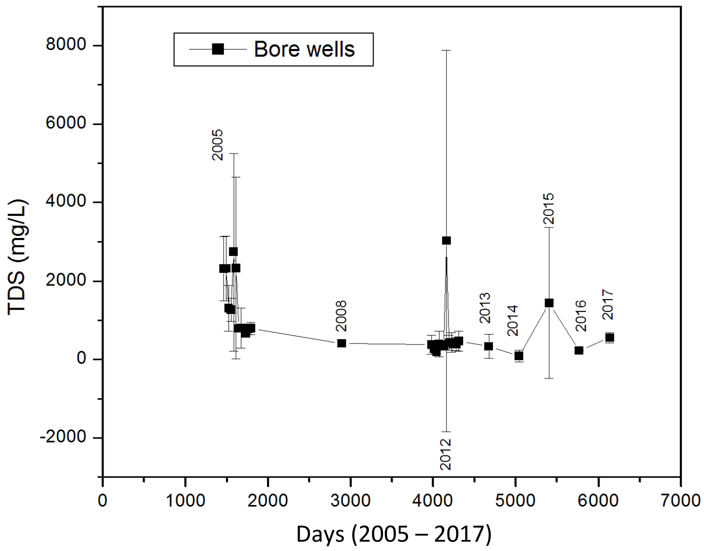

Figure 6.4: Temporal variation of total dissolved solids (TDS) of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

In 2013, TDS become 338.0±304.7 mg/L and decreased to very small concentration of 88.8±153.9 mg/L in December 2014. But in December 2016, a huge increase in monthly TDS mean with a high standard deviation is observed (1440.0±1919.8 mg/L). In 2016, water retained its quality with TDS value 232.0±2.8 mg/L but increased to 556.5±129.4 mg/L in December 2017.

6.2.5 Alkalinity

Alkalinity is the ability to neutralize the pH of water. The major sources of alkalinity in water are carbon dioxide in atmosphere and bicarbonate formed as a result of carbonate mineral dissolution. Thus increase in CO_2 may lead to high alkalinity[11]. The concentration of alkalinity in groundwater samples collected from bore well in April 2001 is only 4.3 mg/L. In the year 2005 alkalinity shows high range in many occasions beyond the accepted limit of 200 mg/L recommended by BIS[12] with an annual mean of 228±51.4 mg/L and confidence interval of 196.4 - 259.6 mg/L, at 95% significant level. In December 2008, alkalinity is reduced to 25.0±7.1 mg/L. During the year 2012, the first six months have alkalinity greater than the prescribed acceptable limit (200 mg/L) suggested by BIS. In July 2012, the alkalinity comes down to 183.5±71.0 mg/L, but later on increases to more than 200 mg/L that is considered as undesirable concentrations. The annual mean of alkalinity in the year 2012 for deep bore wells is 227.2±60.3 mg/L with a confidence interval, CI of 135.3 - 244.1 mg/L. That clearly shows the concentration of alkalinity in the bore well samples are beyond permissible limits suggested by BIS[12] drinking water standards.

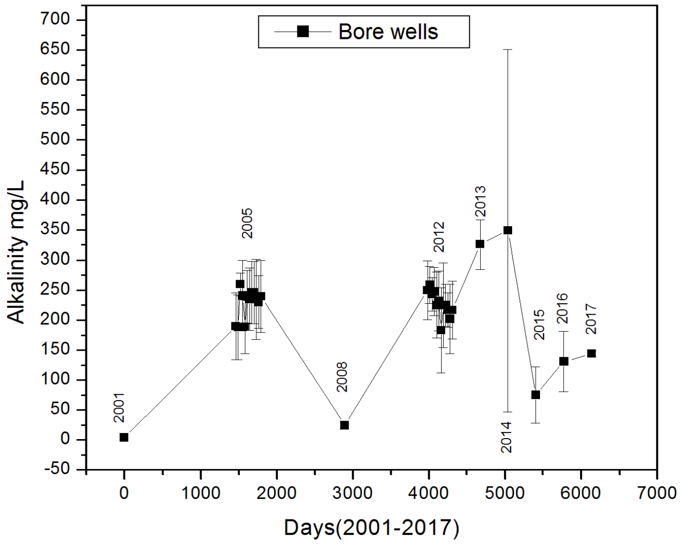

Figure 6.5: Temporal variation of alkalinity of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

A further increase in concentration is observed in December 2013 and December 2014 with very high monthly mean of 325.9±40.6 and 348.8±302.3 mg/L respectively. But in December 2015, an unusual trend of decrease is observed with 74.7±46.6 mg/L. Alkalinity in December 2016 is 130.6±50.4 mg/L and in December 2017, it increased to 143.5±4.9 mg/L.

6.2.6 Total Hardness

Total hardness is an important water quality parameter especially for water used for domestic purposes. Due to its high boiling point, hard water consumes more fuel while cooking and hard water prevents soap from lather formation which is unfavourable for bathing and washing[14].

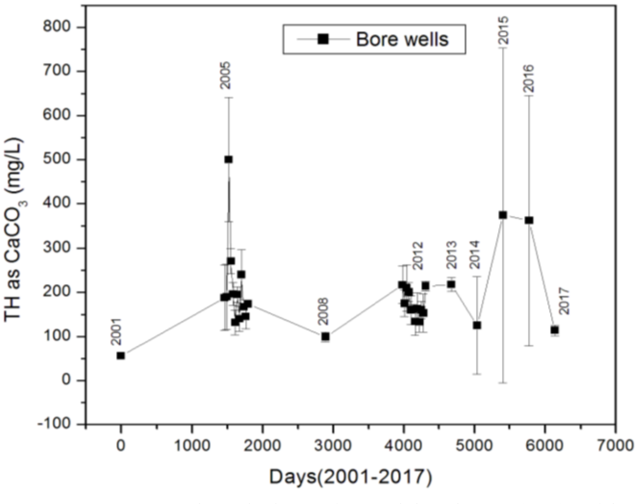

Figure 6.6: Temporal variation of total hardness (TH) of bore well waters (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017.

In 2001, the water is having total hardness of 22 mg/L. After 26th December 2004 Indian Ocean Tsunami, the groundwater samples collected from bore wells shown a total hardness of 187.5±74.2 mg/L in January 2005 and

189.5±74.2 mg/L in February 2005. But during March 2005, the concentration hikes to 500±141.4 mg/L and gradually decreases to reach a lower concentration of 132±28.3 mg/L in June 2005. In September 2005, the total hardness reaches to 240±56.6 mg/L and to the end of the year, it is reduced to 173.5±2.1 mg/L in December 2005.

In December 2008, the total hardness for groundwater samples from bore wells is 99±11.3 mg/L. In the year 2012, the annual mean of total hardness is noted as 173.4±31.9 mg/L. In the subsequent years analysis reported the total hardness concentration as 218.3±15.7 mg/L (December 2013), 125.3±110.5 mg/L (December 2014), 373.7±379.3 mg/L (December 2015), 361.8±282.6 mg/L (December 2016) and 114.4±12.4 mg/L (December 2017).

6.2.7 Calcium (Ca^{2+})

In 2001 calcium ion concentration in bore well is found to be very low to 4.8 mg/L. The concentration of calcium ion in January 2005 is 60±28.3 mg/L. It gradually decreased to 24±0.0 mg/L in April 2005. During May 2005 and July 2005 the calcium concentration are 61.4±7.6 mg/L and 67.6±7.4 mg/L respectively. Towards the end of the year in December 2005, the concentration of calcium in water collected from bore wells is 43.7±20.0 mg/L. The annual mean of calcium in the year 2005 is 49.6±16.3mg/L which is under permissible limit as per BIS[12] and WHO[13] standards for drinking water. In December 2008, calcium is reported to be 15.2±2.3 mg/L. The overall calcium concentration in the year 2012 is found to be 47.8±10.1 mg/L which is same as in the year 2005. This inferred that the calcium ion profile of the study area remained unchanged without much variation just after the catastrophic incident in 26th December 2004 Indian Ocean Tsunami and after six years in the year 2012.

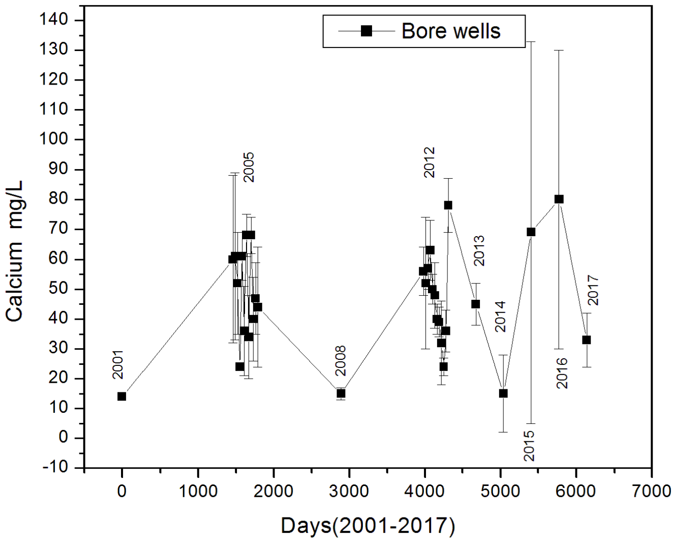

Figure 6.7: Temporal variation of calcium of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017.

In the subsequent year's assessment, the calcium concentration December 2013 is 45±7 mg/L, which is reduced to a concentration of 15±13.2 mg/L in December 2014. In the subsequent years the concentration are 69±64 mg/L (December 2015), 80±50 mg/L (December 2016) and 33.4±9.5 mg/L (December 2017).

6.2.8 Magnesium (Mg^{2+})

Magnesium concentration in groundwater samples collected in April 2001 is reported as 2.4 mg/L. After tsunami event in 26th December 2004, the water samples from bore wells reported less concentration of magnesium in the first two months in the year 2005. But afterwards in March 2005, an abrupt hike in Magnesium is very well noticeable with a monthly mean of 88.8±23.8 mg/l. This is a clear indication of the leaching of sea water to deep aquifers. It gradually decreased in the following months and reached 15.4±11.5 mg/L in December 2005. The annual mean of magnesium concentration during the year 2005 is 21±10 mg/L. In December 2008, the concentration of magnesium is found to be 14.6±4 mg/L. This trend is observable in the year 2012 with an annual mean of 13±7 mg/L. In the following years the magnesium concentration is noted as 25.5 ±3.3 mg/L (December 2013), 21.2±18.8 mg/L (December 2014), 48.7±53.4 mg/L (December 2015), 39.2±38.2 mg/L (December 2016) and 7.4±2.7 mg/L (December 2017).

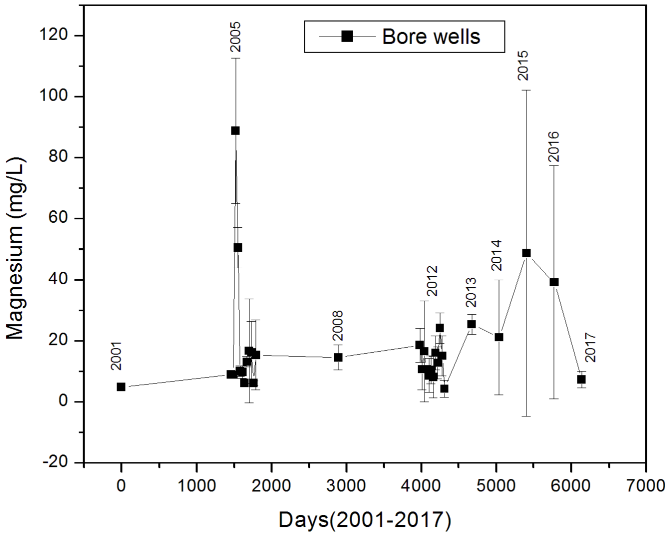

Figure 6.8: Temporal variation of magnesium of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017.

6.2.9 Sodium

In April 2001, the sodium concentration in the Alappad region is found to be 46 mg/L. In the year 2005, a maximum sodium concentration of 40±11 mg/L is reported in July 2005 and in the next month itself a minimum concentration of the year, 19±13 mg/L is reported in August 2005. The annual mean of sodium in bore wells during the year 2005 is 30.4±13.4 mg/L.

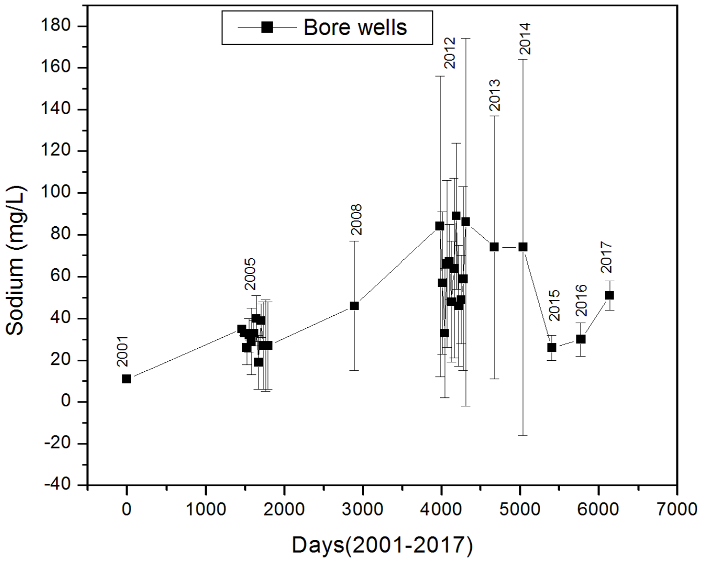

Figure 6.9: Temporal variation of sodium of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017.

In December 2008, the sodium concentration in the deep aquifer is reported as 46±31 mg/L. From the graph, it is clear that the concentration of sodium increased from 2008 onwards. The annual mean of sodium in the year 2012 is 62.5±45 mg/L. In the following year analysis the concentration of sodium is 73.8±63 mg/L (December 2013), 73.7±90 mg/L (December 2014), 26.3±6 mg/L (December 2015), 30±8 mg/L (December 2016) and 51.2±7 mg/L (December 2017).

6.2.10 Potassium

In April 2001, concentration of potassium in bore well groundwater samples is reported to be 2.5 mg/L. After the Indian Ocean Tsunami event, the water shows K^+content 8±4.2 mg/L (January 2005) and increased to 9.5±5 mg/L in February 2005. From March 2005 onwards, the potassium concentration decreased and reaches 4 mg/L in June 2005. But again in July 2005 the concentration rose to 7.9±6 mg/L and attains the maximum concentration, 10±7 mg/L in September 2005.

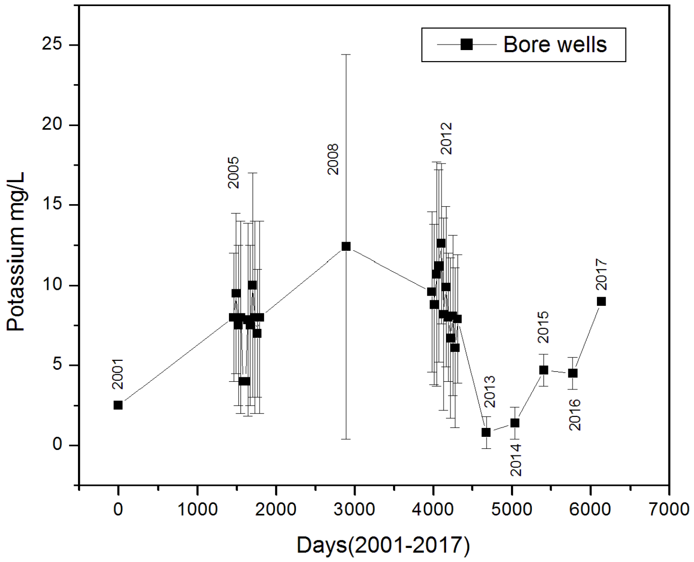

Figure 6.10: Temporal variation of potassium of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2001-2017.

The annual mean of potassium concentration in the year 2005 is 7.4±5 mg/L. In December 2008, the potassium content from deep groundwaters of bore wells is 12.4±12.2 mg/L which is far more than beyond the BIS[12] (2012) and WHO[13] (2011) standards. From this, it can be inferred that in the year 2005, the deep aquifers were least affected by seawater whereas in December 2008, the coastal aquifers are effected by seawater mixing[15].

The annual mean of potassium in the year 2012 is 9±5.2 mg/L and in the subsequent years, the potassium profile in the study area is 0.8±0.7 mg/L (December 2013), 1.4±0.8 mg/L (December 2014), 4.7±0.6 mg/L (December 2015), 4.5±0.7 mg/L (December 2016) and 9 mg/L (December 2017).

6.2.11 Bicarbonate

When water percolates through soils and rock, the carbon dioxide reacts with carbonate minerals to form bicarbonates[16]. In January 2005, the bicarbonate content in groundwater collected from deep groundwaters is 231.2±68 mg/L. There is no much variation in bicarbonate throughout this year with a minimum concentration of 228.8±66 mg/L and maximum concentration of 316.6±23 mg/L. The annual mean of bicarbonate in the year 2005 is 278±63 mg/L. During December 2008, bicarbonate is reported to be 30.5±8.6 mg/L which is very less compared to the entire study period.

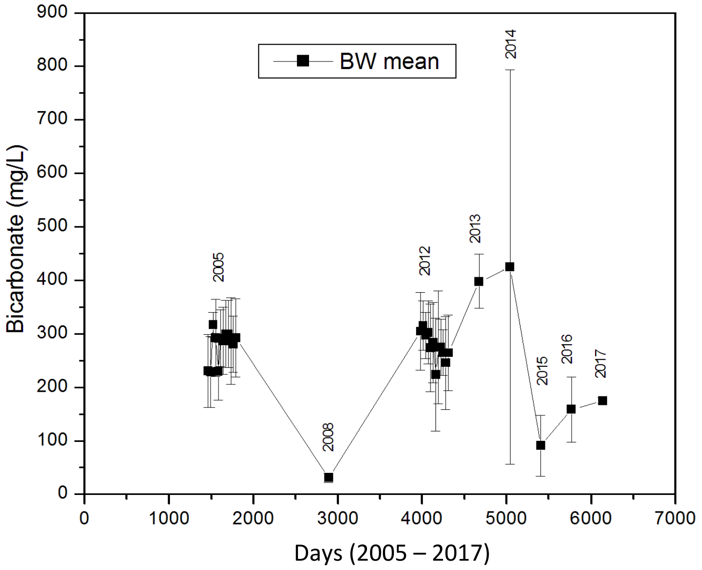

Figure 6.11: Temporal variation of bicarbonate of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

From the graph it is evident that, the concentration of bicarbonate shows a similar pattern during the year 2005 and 2012. The annual mean of bicarbonate in the year 2012 is 277±73.5 mg/L. The following years, concentrations are 398±50 mg/L (December 2013), 425±369 mg/L (December 2014), 91±57 mg/L (December 2015), 159±61 mg/L (December 2016) and 175±6 mg/L (December 2017).

6.2.12 Chloride

Major source of chloride in fresh water in coastal areas is the chloride salt from sodium chloride and excess concentration of chloride in drinking water forms laxative effects[17]. Along with sulphate and nitrate, high content of chloride is also considered as an implication of corrosion (WHO; 2011[13]). In April 2001, the concentration of chloride in Alappad study region is 70 mg/L. In the year 2005, the monthly mean of chloride concentration remained 72 mg/L during January and February. But during March 2005 to May 2005 an abrupt hike in concentration of chloride ion is reported due to mixing of sea water with deep fresh water aquifers. From June 2005 onwards, chloride concentration decreased gradually and reaches 27.6±11 mg/L in September 2005. But in November 2005, it again increased to 156±181.0 mg/L and remained 161.3±168 mg/L in December 2005. The annual mean of chloride concentration in the year 2005 is 104±84.4 mg/L. In December 2008, concentration of chloride is reported to be 12.5±5.0 mg/L.

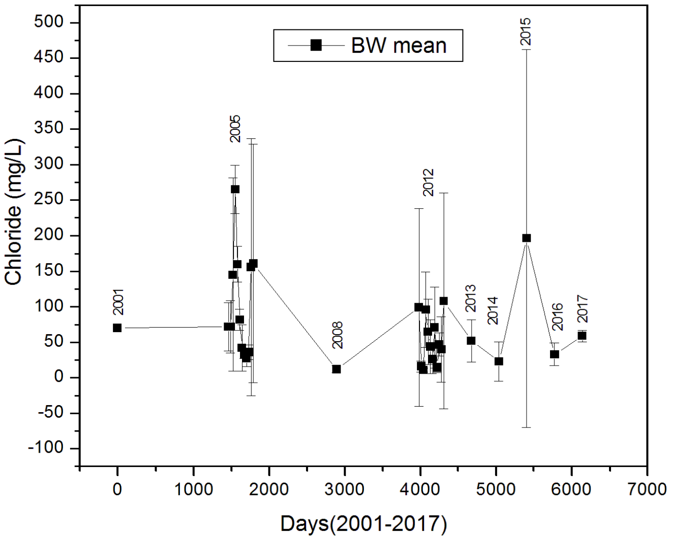

Figure 6.12: Temporal variation of chloride of deep groundwaters (bore wells BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In the year 2012, the annual mean of chloride concentration is 53.0±67.7 mg/L. Continuous monitoring of the groundwater from the bore wells during the subsequent years in the month of December revealed that the chloride concentration is 52±30.4 mg/L in December 2013, 23±28.2 mg/L (December 2014), 195.8±266 mg/L (December 2015), 33.5±16.3 mg/L (December 2016) and 59±8.5 mg/L (December 2017).

6.2.13 Iron

Weathering processes accompanied with corrosion discharge iron to groundwater in bore wells (Smith, 1981). In January 2005, total iron concentration in bore wells are 1.7±1.0 mg/L and it also continued as same in February 2005. During March 2005, the concentration reduced to 0.2±0.3 mg/L, but again from April 2005, the iron concentration increases till June 2005. In July 2005 concentration of iron is decreased to 0.1 mg/L, but suddenly in August 2005 it becomes 0.3±0.4 mg/L. From September 2005 onwards, the concentration remained 0.1 mg/L. The annual mean of total iron in bore wells during the year 2005 is 0.7±1.1 mg/L, which is above the recommended limit by BIS[12] (2012).

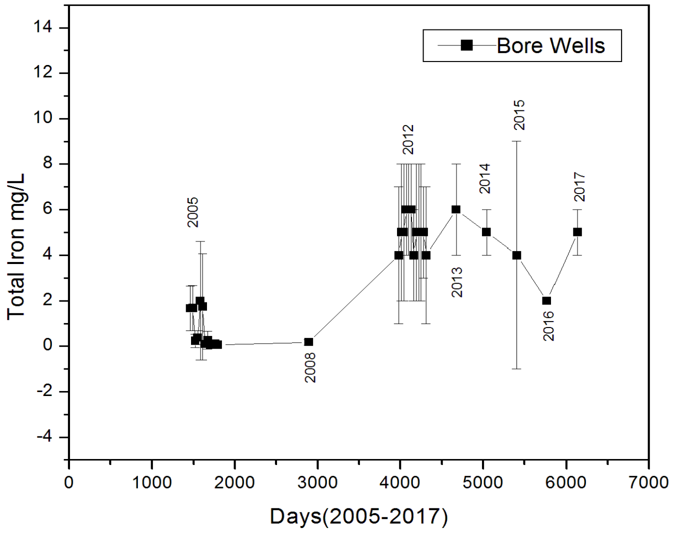

Figure 6.13: Temporal variation of iron of bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

In December 2008, the monthly mean of iron is found to be below the acceptable limit with 0.2±0.1 mg/L. But the year 2012 witnesses a drastic increase in iron concentration in every month with an annual mean of 4.9±2.6 mg/L. The concentration of iron in the following years are 6±2 mg/L (December 2013), 4.7±1.2 mg/L (December 2014), 3.7±4.7 mg/L (December 2015), 1.7±0.5 mg/L (December 2016) and 4.5±0.7 mg/L (December 2017). This very high concentration of iron may be due to corrosion of iron metal casings and pipes in the bore wells leading to coloration of water and sedimentation in the water supply system[18].

6.2.14 Dissolved Oxygen (DO)

Dissolved oxygen (DO) in water occurs mainly when air is directly diffused into the water and decreased DO is an indicator of oxygen demanding pollutants[19]. In the case of bore wells constructed for deep aquifers, the microorganisms accumulated as colonies on the metal surfaces such as iron and steel deplete dissolved oxygen by consuming it. This further leads to corrosion mediated by microorganisms[20].

In Alappad coast, dissolved oxygen in 2005 January just after tsunami event is reported to be 3.0±1.1 mg/L. In April 2005, the DO is again drops to 1.4±0.6 mg/L and increased to 2.3±3.2 mg/L in May 2005. In the second half of the year 2005 from July to October 2005 DO is found to be less than 2.0 mg/L but a slight increase to 2.2±0.1 mg/L and 2.1±0.4 mg/L is reported in November and December 2005 respectively. The annual mean of DO in the year 2005 is 2.1±1.2 mg/L with a confidence interval CI of 1.4 - 2.8 mg/L. In December 2008, the monthly mean of DO become 3.1±0.6 mg/L.

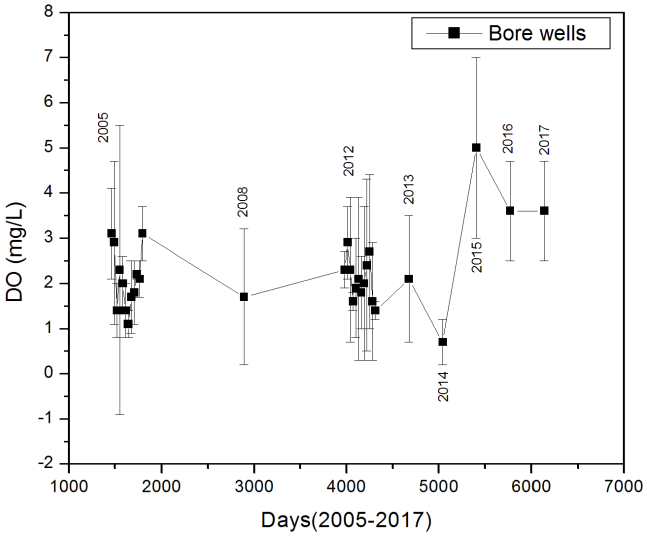

Figure 6.14: Temporal variation of bore wells (BW) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad , Kollam, Kerala, India for the period 2005-2017

In the year 2012, the annual mean of DO is found to be similar to that of the year 2005 with 2.1±1.3 mg/L and confidence interval of 1.3 - 2.9 mg/L at 95% significance level. In the subsequent years, the DO of groundwater from bore well sources are 1.4±0.2 mg/L (December 2013), 2.1±1.4 mg/L (December 2014), 0.7±0.5 mg/L (December 2015), 5.0±2.0 mg/L (December 2016) and 3.6±1.1 mg/L (December 2017).

6.2.15 Biological Oxygen Demand (BOD)

BOD level in deep bore wells during the year 2005 is high when compared to the subsequent years of research period. The annual mean of BOD in the year 2005 is 11.5±9.4 mg/L, with a confidence interval of 5.7-17.3 mg/L, at 95% level of significance. In 2008 December, monthly mean of BOD is 6.4±2.3 mg/L.

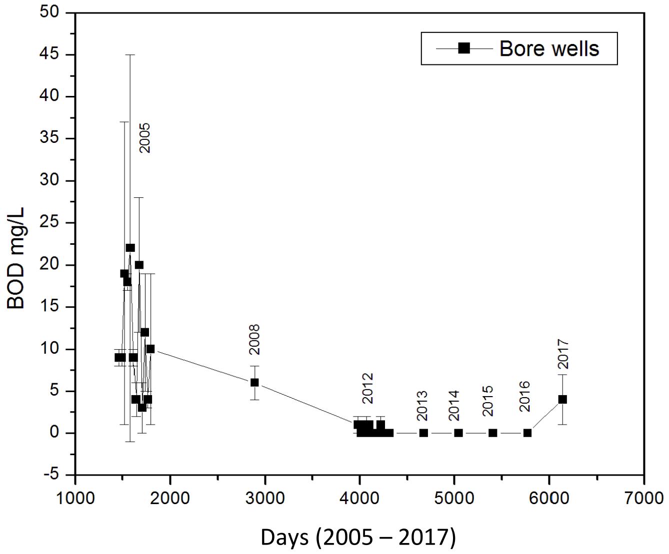

Figure 6.15: Temporal variation of bore wells (BW) of shallow dug wells (DW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017

Year 2012 witnessed very low BOD values for bore wells, with an annual mean of 0.5±0.5 mg/L, with a confidence interval of 0.2 - 0.8 mg/L, at 95 % significant level. In the remaining years BOD is found to be 0.3±0.1 mg/L in both 2013 & 2014, 0.3±0.1 mg/L in December 2015, 0.2 mg/L in December 2016 and 3.6±3.4 mg/L in 2017.

6.3 Hydrochemical Facies

Hill-Piper-Trilinear plots (Figure 6.16) are noteworthy on hydrochemistry and water type based on prominent cation and anion ratio of the groundwater[21,22]. During April 2001 the water is *saline water type* with a hydrochemical facies of Na^{+}-K^{+}-Cl^{-} -SO_4^{2-}. After 24th December 2004 Indian Ocean Tsunami the overall water type of bore well sources in the year 2005 becomes *temporary hardness water type* with hydrochemical facies Ca^{2+}-Mg^{2+}-HCO_3^-. The proportional percentage of cations are approximately 45% (Ca^{2+})>30% (Mg^{2+})>25% (Na^++K^+) and anions are 60% (HCO_3^-)> 40% (Cl^-) and a very negligible concentration of SO_4^{2-}. But in December 2008, the water type plotted in the *mixed water type* region of diamond plot in junction with saline water type and hardness water type (Permanent as well as temporary) being the dominated cation Na^+ is 52% and anion HCO_3^- is 50% with hydrochemical facies mixed Ca^{2+}-Na^+-HCO_3^-. In the year 2012, the overall water type moves towards *temporary hardness water type* being hydrochemical facies Ca^{2+}-Mg^{2+}-HCO_3^- with non-dominant cations and anions. The relative percentages of cations are in the order Na^+ (45%)> Ca^{2+} (38%) > Mg^{2+} (17%) whereas the anions are HCO_3^- (75%) > Cl^- (25%) with a negligible proportion of sulphate.

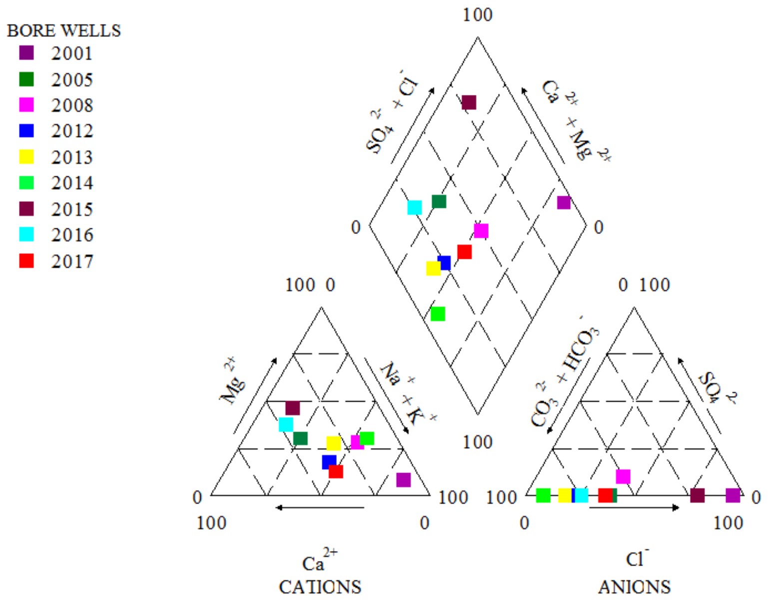

Figure 6.16: Hill-Piper trilinear plot for bore wells along the Alappad coast, Kollam, Kerala, India during the period 2001 to 2017.

In December 2013, also water maintains *temporary hardness water type,* with relative proportional of cations and anions in percentage are $Na^{+}+K^{+}$ (44%) > Ca^{2+} (30%)> Mg^{2+} (26%) and HCO_3^{-}(82%) > Cl^{-}(18%). *Mixed water type* is reported in December 2014 with sodium dominate cation and bicarbonate anion water and hence no definite hydrochemical facies is identified. The water type of groundwater from bore wells in December 2015 is *Permanent hardness water type* with non-dominant cation to chloride dominant anion. But in December 2016, the water type shifts to left corner of the Hill-Piper diamond plot, making it *temporary hardness water type*. The relative percentage of concentration of major cations and anions during this period is Ca^{2+} (8%) > Mg^{2+} (38%) > $Na^{+}+K^{+}$ (14%) and HCO_3^{-} (75%) > Cl^{-} (25%). In December 2017 also the water remained as *temporary hardness water type*. The hydrochemical facies of the mean of bore wells in December 2016 and December 2017 are $Ca^{2+}\text{-}Mg^{2+}\text{-}HCO_3^{-}$ · The sequence of the abundance of major cations and anions during December 2017 are in the order Ca^{2+} (38%) > $Na^{+}+K^{+}$ (50%) Mg^{2+} (12%) > and HCO_3^{-} (65%) > Cl^{-} (35%).

6.4 Gibb's Diagram

Gibb's diagram shows water quality in April 2001 is evolved from rock dominant mechanism, where dissolved salts in groundwater are attributed to the dissolution of rock forming minerals. Most of the months in the year 2005 are controlled by evaporation dominance mechanism. High salinity and increased concentration of sodium are the characteristic feature of evaporation dominant water. Evaporation dominant water is derived from saline intrusion into the fresh water aquifers. December 2008 water from bore well comes under rock dominance, where dissolved salts in the groundwater is derived from interaction of water with minerals from rock.

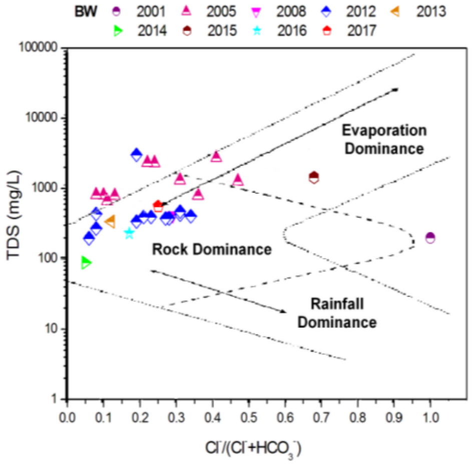

Figure 6.17: Gibb's a for groundwater from bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

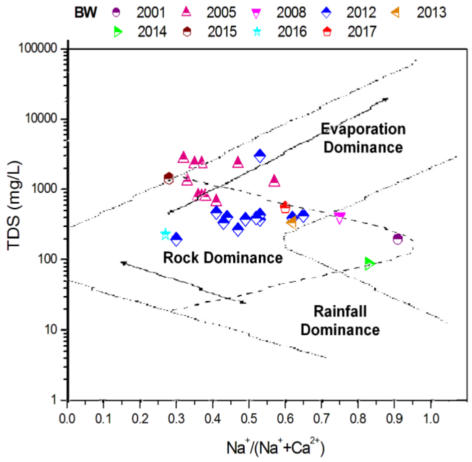

Figure 6.18: Gibb's b for groundwater from bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

In the year 2012, except July 2012, all the months water falls in rock dominance field of the Gibb's diagram indicating the contribution of rock forming minerals in the hydrochemistry of groundwater. The end member due to this mechanism is calcium rich medium saline water. Groundwater in December 2013, 2014, 2016 and 2017 comes in the rock dominance field where as December 2015 has evaporation dominance water.

6.5 Water Quality Index (WQI)

Water Quality Index (WQI) of groundwater from bore well during April 2001 is suitable for drinking purposes with *excellent water quality* **(Grade A)**. In the year 2005, most of the months come under **Grade B** with *good water quality*, except in March and September 2005 where water degraded to **Grade C** with *poor water quality* for drinking purposes. The water quality in December 2008 is *excellent* **(Grade A)**. During the year 2012, groundwater quality in most of the months are considered *good* for human consumption **(Grade B)**, with excellent water quality in June 2012 **(Grade A)** and in the next month water degraded to **Grade E** as it become *unfit for human consumption* due to very high electrical conductivity and total dissolved solid concentration. In December 2013, water continued in *good quality* **(Grade B)**, but December 2014, December 2015 and December 2017 water quality turned to be *unfit for human consumption* **(Grade E)**. The December 2016 water falls in **Grade A** category, which is considered as excellent water quality.

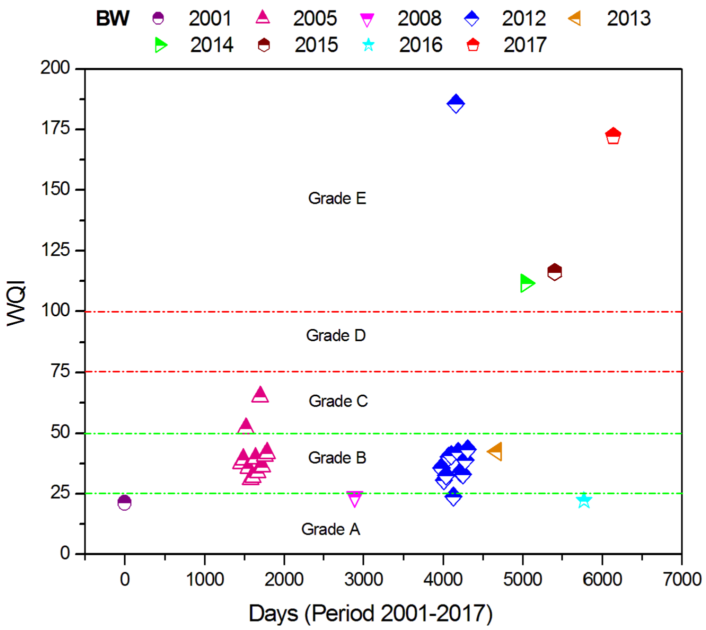

Figure 6.19: Temporal variation in water quality index (WQI) of groundwater from bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Table 6.1: Temporal variation in water quality index (WQI) of groundwater from bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Year/Month	WQI	Water Quality	Grade
Apr 2001	21.3	Excellent	A
Jan 2005	37.7	Good	B
Feb 2005	39.2	Good	B
Mar 2005	52	Poor	C
Apr 2005	35.6	Good	B
May 2005	31	Good	B
Jun 2005	31.9	Good	B
Jul 2005	39.6	Good	B
Aug 2005	33.8	Good	B
Sep 2005	65.1	Poor	B
Oct 2005	36.2	Good	B
Nov 2005	40.6	Good	B
Dec 2005	41.8	Good	B
Dec 2008	23.8	Excellent	A
Jan 2012	35.7	Good	B
Feb 2012	30.6	Good	B
Mar 2012	32.7	Good	B
Apr 2012	40.3	Good	B
May 2012	40.9	Good	B
Jun 2012	24	Excellent	A
Jul 2012	185.8	Unfit	E
Aug 2012	42.2	Good	B
Sep 2012	34	Good	B
Oct 2012	33	Good	B
Nov 2012	39	Good	B
Dec 2012	43.4	Good	B
Dec 2013	42.4	Good	B
Dec 2014	111.7	Unfit	E
Dec 2015	116.2	Unfit	E
Dec 2016	22.2	Excellent	A
Dec 2017	172.3	Unfit	E

**Unfit- Unfit for human consumption*

6.6 Irrigation water quality parameters

Irrigation parameters include sodium adsorption ratio, sodium percent, permeability index, Kelley's index, magnesium hazard and residual sodium carbonate are evaluated to find the overall water quality with respect to suitability for irrigation from 2001 to 2017.

6.6.1 Sodium Adsorption Raito (SAR)

Sodium adsorption ratio (SAR) is a measure of sodium in the water sample against calcium and magnesium ions. In the coastal aquifers, occasional salt water intrusion leads to high sodium concentration, which in turn have the tendency to replace Ca^{2+} or Mg^{2+} present in the soil or aquifer material. In 2001, SAR is 1.2 and comes in *excellent class*. After tsunami from January 2005 to March 2005 and again in May 2005, SAR is between 10 -18, so the water quality during this period falls under *good class*. From June 2005 onwards, water is having SAR < 10 for all the studied months including year 2012, December 2013, 2014, 2015, 2016 and 2017 indicating water is of *excellent quality* in terms of sodium adsorption ratio (Figure 6.20).

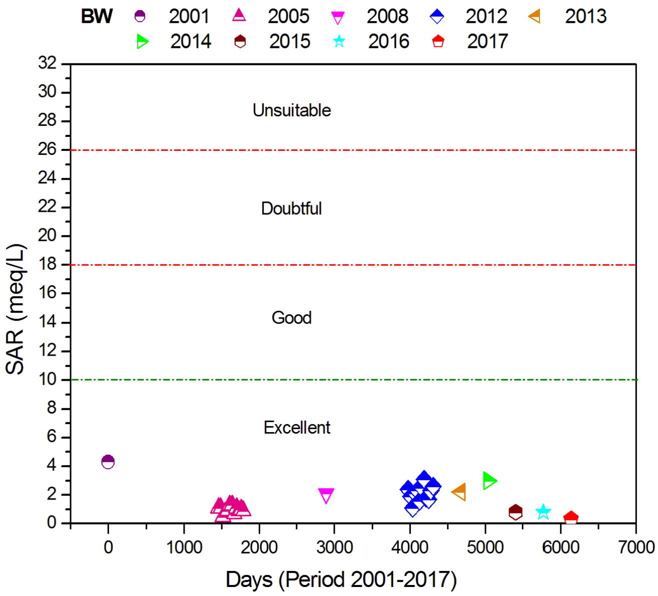

Figure 6.20: Temporal variation of sodium adsorption ratio (SAR) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

6.6.1.1 USSL Diagram

USSL diagram divides groundwater sources with respect to SAR and electrical conductivity (EC) totally into 16 sub classes. In this diagram groundwater comes under C1S1 indicates, water having *low salinity with low sodium hazard* and C2S1 class means, water is *medium salinity and low sodium hazard.* Both the classes are good for irrigation. Water with *low sodium hazard and high salinity hazard* falls in C3S1 and C3S2 class consist of *high salinity with medium sodium* water, equally comes under moderate water quality. The C4S1 type water is having *very high salinity hazard and low sodium hazard* and all other subclasses (C1S3, C1S4, C2S3, C2S4, C3S3, C3S4, C4S3 & C4S4) belongs under bad water quality that is unfit for irrigation.

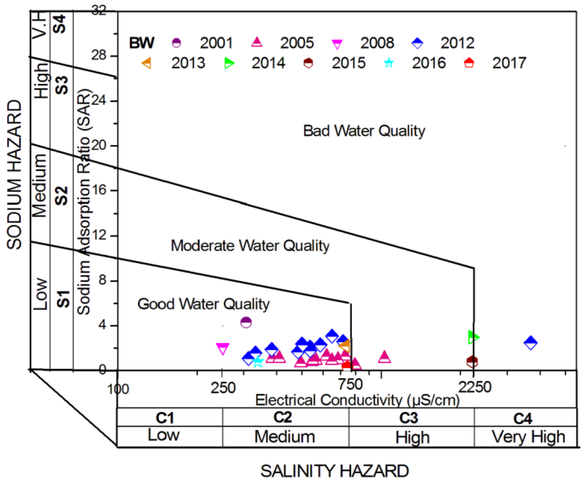

Figure 6.21: USSL diagram of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

From the Figure 6.21, it is clear that the groundwater during 2001 and most of the months of the year 2012, December 2014, December 2015 and December 2016 falls in C2S1 class (good water quality). After 26th December 2004

Indian Ocean Tsunami, most of the dug wells have high EC, hence it is spread in C3S2 (moderate water quality) and C4S2 classes (bad water quality).

6.6.2 Sodium Percent (Na%)

Shallow groundwater sources in April 2001 have 52.7% of sodium percent that comes under *permissible* class for irrigation purposes.

Table 6.2: Temporal variation of sodium adsorption ratio (SAR) and sodium percent (Na%) of shallow dug well (DW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

ear/Month	SAR	Inference	% Na	Inference
Apr 2001	4.3	E	82.5	US
Jan 2005	1.1	E	32.7	G
Feb 2005	1.1	E	31.7	G
Mar 2005	0.5	E	12.5	E
Apr 2005	0.8	E	22.7	G
May 2005	0.9	E	24.7	G
Jun 2005	1.3	E	36.9	G
Jul 2005	1.3	E	33.0	G
Aug 2005	0.7	E	25.2	G
Sep 2005	1.1	E	29.0	G
Oct 2005	0.9	E	27.3	G
Nov 2005	1.0	E	30.3	G
Dec 2005	0.9	E	26.8	G
Dec 2008	2.1	E	50.4	P
Jan 2012	2.4	E	41.8	P
Feb 2012	1.9	E	41.2	P
Mar 2012	1.1	E	27.3	G
Apr 2012	2.1	E	41.3	P
May 2012	2.3	E	49.8	P
Jun 2012	1.6	E	38.8	G
Jul 2012	2.5	E	49.5	P
Aug 2012	3.1	E	54.6	P
Sep 2012	1.8	E	42.4	P
Oct 2012	1.7	E	41.2	P
Nov 2012	2.3	E	43.3	P
Dec 2012	2.6	E	40.4	P
Dec 2013	2.2	E	37.6	G
Dec 2014	3.0	E	62.3	D
Dec 2015	0.8	E	21.9	G
Dec 2016	0.8	E	21.7	G
Dec 2017	0.3	E	51.5	P

Even though tsunami hit this barrier island badly, the Na% during the year 2005 falls in *permissible limit* (40% -60%), except in March 2005, where a slight increase (61%) in sodium percent is observed. In December 2008, the %Na is 50.4%, which comes under *permissible limit.* In the year 2012, all the 11 months of sampling reported Na% between 40% to 60 %, inferring water have Na% below *permissible* limit and in May 2012, Na% dropped to 38.8%, that includes under *good water quality.* From December 2013 to December 2016, water have Na% between 20 - 40%, indicating *good category*, where as in December 2017 Na% increased to 57% and falls in *permissible category*.

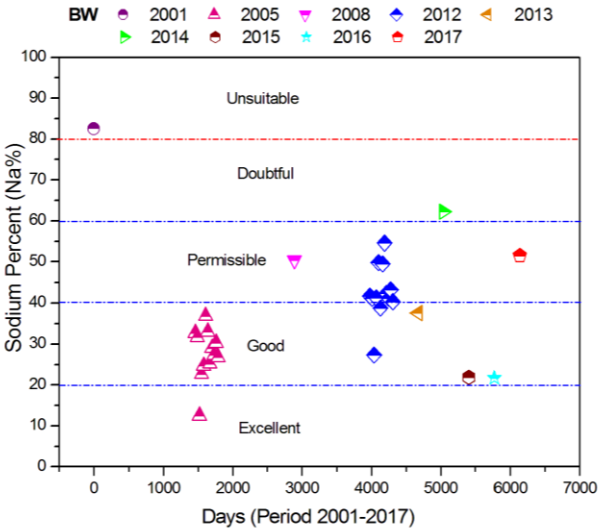

Figure 6.22: Temporal variation of sodium percent (Na%) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

6.6.2.1 Wilcox Diagram

In Wilcox diagram EC is plotted against the sodium percent to evaluate the suitability of water for irrigation. The salts present in the groundwater will affect soil structure, permeability and aeration, which indirectly affect plant growth (Singh et al., 2008). During April 2001, water comes in *excellent to good* range. But in the year 2005, due to tsunami inundation water quality deteriorated to *unsuitable* category in the beginning, but gradually when EC values decreases, water become *doubtful to unsuitable* and later *good to permissible* range. In December 2008, groundwater possesses *good to permissible quality*. Most of the months in 2012, water showed *excellent to good* quality for irrigation purposes, except October and December 2012, where the water quality falls down into *good to permissible* category. Groundwater remained in *good to permissible* limit in December 2013, but maintain an excellent to good quality in December 2014, 2015 and 2016. In December 2017, water remained in *good to permissible* category.

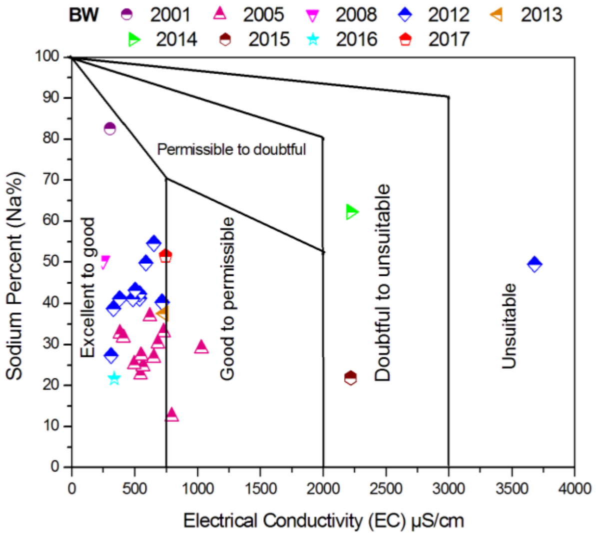

Figure 6.23: Wilcox diagram of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

6.6.3 Permeability Index (PI)

The permeability Index is an irrigation water quality parameter, which classified the water[23] into three categories of class I class II and class III. Table 6.2 shows the permeability index and their respective classes for all the months analysed from 2001 to 2017. From the Figure, it is clear that PI in April 2005 falls in Class II, with 6.8% permeability. In the year 2005, till the month of May, water remained in Class II, being permeability index between 25% to 75%. From June 2005 to December 2005, permeability of water is improved with maximum permeability >75% (Class I). But in December 2008 PI is decreased to Class II with 64%. After that, throughout the study period till December 2017, water remained in Class I. From the observations, it is inferred that water from dug wells are suitable for irrigation in terms of permeability index throughout the study period from 2001 to 2017.

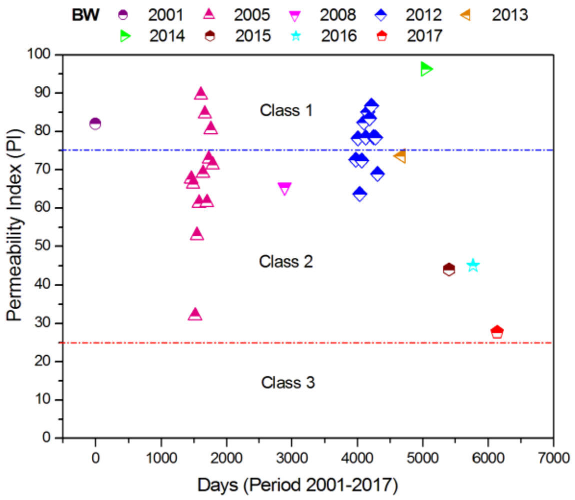

Figure 6.24: Temporal variation of permeability index (PI) of of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

6.6.4 Kelley's Index (KI)

Kelley's index is a measure of sodium concentration against Ca and Mg ions in groundwater, used to find the irrigation suitability. The ratio less than 1, indicate water is suitable for irrigation. From the Figure it is clear that shallow groundwater sources are unsuitable for irrigation purposes in April 2001, being KI>1. The same behaviour of shallow dug wells are observed during the entire 12 months of the year 2005 and December 2008. It is clear that, groundwater having high sodium content than Ca and Mg ions makes it unfit for irrigation. KI become less than 1.0 in most of the months in the year 2012, reporting its suitability for irrigation during this period. However, an increase in KI is observed in March, October, November and December 2012 making it unsuitable for irrigation. Kelley's index from December 2012 to December 2016 are less than 1 (suitable for irrigation), where as in December 2017 water become unsuitable for irrigation with respect to KI>1.

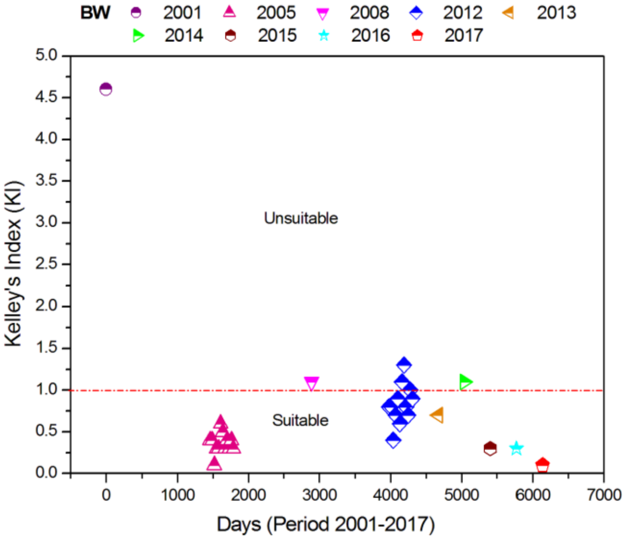

Figure 6.25: Temporal variation of Kelley's index (KI) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Table 6.3: Temporal variation of permeability index (PI) and Kelley's index (KI) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Year/Month	PI	Inference	KI	Inference
Apr 2001	82.0	Class I	4.6	US
Jan 2005	67.6	Class II	0.4	S
Feb 2005	66.3	Class II	0.4	S
Mar 2005	32.0	Class II	0.1	S
Apr 2005	52.9	Class II	0.3	S
May 2005	61.3	Class II	0.3	S
Jun 2005	89.5	Class I	0.6	S
Jul 2005	69.1	Class II	0.5	S
Aug 2005	84.6	Class I	0.3	S
Sep 2005	61.5	Class II	0.4	S
Oct 2005	72.8	Class II	0.3	S
Nov 2005	80.5	Class I	0.4	S
Dec 2005	71.3	Class II	0.3	S
Dec 2008	65.5	Class II	1.1	US
Jan 2012	72.7	Class II	0.8	S
Feb 2012	78.2	Class I	0.8	S
Mar 2012	63.7	Class II	0.4	S
Apr 2012	72.5	Class II	0.7	S
May 2012	82.4	Class I	0.9	S
Jun 2012	78.4	Class I	0.6	S
Jul 2012	85.1	Class I	1.1	US
Aug 2012	83.5	Class I	1.3	US
Sep 2012	86.7	Class I	0.8	S
Oct 2012	78.5	Class I	0.7	S
Nov 2012	78.4	Class I	1.0	US
Dec 2012	69.0	Class II	0.9	S
Dec 2013	73.6	Class II	0.7	S
Dec 2014	96.3	Class I	1.1	US
Dec 2015	44.1	Class II	0.3	S
Dec 2016	45.1	Class II	0.3	S
Dec 2017	27.7	Class II	0.1	S

6.6.5 Magnesium Adsorption Ratio (MAR)

Magnesium is an essential element for the plant growth. But its increased concentration leads to the reduction in crop yield. The Mg hazard determines the hazard caused by Mg ion in groundwater. If the ratio less than 50, indicates the suitability of water for agricultural uses. During

April 2001, water reported magnesium adsorption ratio of 32.4%, *suitable* for agricultural purposes. The year 2005, also showed suitability for irrigation evidenced by the MAR<50%, except in April 2005 with increase in MAR to 71.4% and August 2005 with MAR 51.8% which makes water unsuitable for irrigation. It is noticeable that, even the giant tsunami waves hit this land badly, magnesium concentration remained low during the immediate post tsunami period in the year 2005. It reaches at 46.9 during the period December 2008. Magnesium adsorption ratio noticed below 50% in year 2012, exceptionally during October 2012, when the MAR value reached 64.2%. In December 2013 and December 2014 water is unsuitable for irrigation as MAR increased to 54.4% and 64% respectively. From December 2015 to December 2017 water is suitable for irrigation with respect to magnesium adsorption ratio.

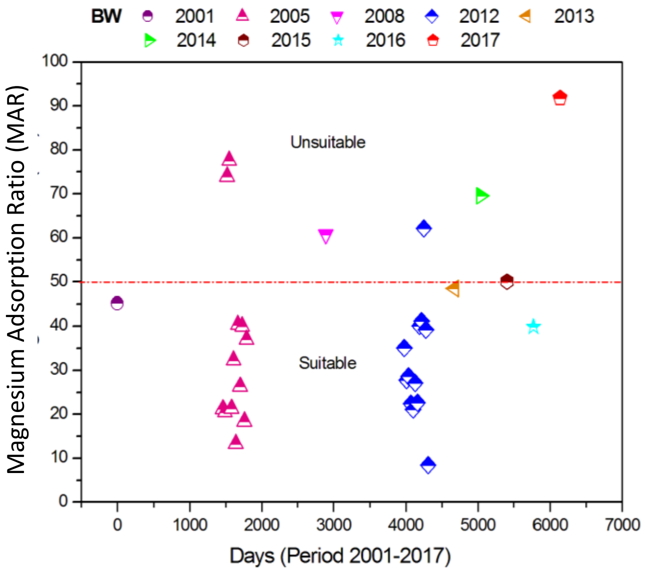

Figure 6.26: Temporal variation of magnesium adsorption ratio (MAR) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

6.6.6 Resiual Sodium Carbonate (RSC)

From the graph, it is clear that water of the shallow dug wells in the year 2001 is *suitable for irrigation* with RSC<1.2. In the year 2005, September and October months water have RSC between 1.2 – 2.5, hence water is *moderately suitable* for irrigation. Dug wells in December 2008 have RSC<1.2 and the water is *suitable for irrigation*. All the months in the year 2012 have RSC values *suitable for irrigation*. In the subsequent years; 2013 have RSC <1.2, whereas December 2014 show RSC of 2.3 and water is *not suitable* for irrigation. During December 2015, 2016 and 2017 water RSC is in suitable range for irrigation purposes.

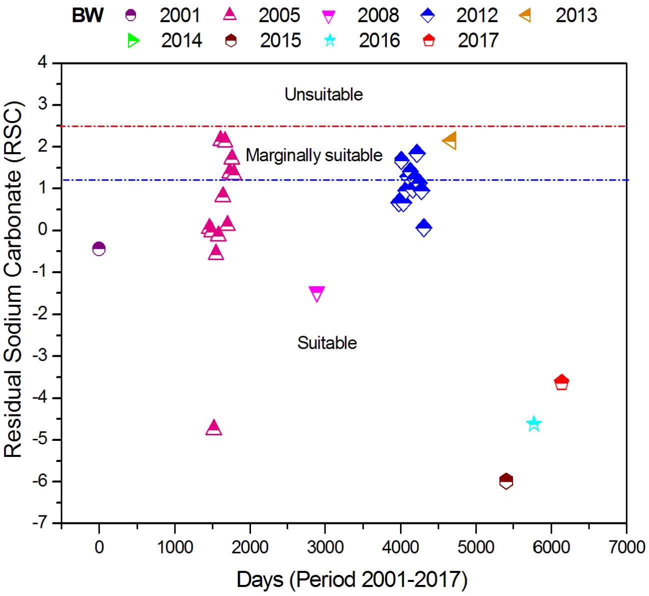

Figure 6.27: Temporal variation of residual sodium carbonate (RSC) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017.

Table 6.4: Temporal variation of magnesium hazard (MH) and residual sodium carbonate (RSC) of deep bore well (BW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2001-2017

Year/Month	MH	Inference	RSC	Inference
Apr 2001	45.2	S	-0.4	S
Jan 2005	21.2	S	0.0	S
Feb 2005	20.5	S	0.0	S
Mar 2005	74.0	US	-4.7	S
Apr 2005	77.6	US	-0.6	S
May 2005	21.3	S	-0.1	S
Jun 2005	32.3	S	2.1	MS
Jul 2005	13.3	S	0.8	S
Aug 2005	40.4	S	2.1	MS
Sep 2005	26.3	S	0.1	S
Oct 2005	40.0	S	1.4	MS
Nov 2005	18.4	S	1.7	MS
Dec 2005	37.0	S	1.3	MS
Dec 2008	60.8	US	-1.5	S
Jan 2012	35.1	S	0.7	S
Feb 2012	27.8	S	1.7	MS
Mar 2012	28.7	S	0.7	S
Apr 2012	22.4	S	0.9	S
May 2012	21.1	S	1.3	MS
Jun 2012	27.1	S	1.4	MS
Jul 2012	22.6	S	1.0	MS
Aug 2012	40.1	S	1.2	MS
Sep 2012	41.2	S	1.8	MS
Oct 2012	62.2	US	1.1	MS
Nov 2012	39.2	S	1.0	MS
Dec 2012	8.5	S	0.1	S
Dec 2013	48.5	S	2.2	MS
Dec 2014	69.6	US	6.7	US
Dec 2015	50.1	US	-6.0	S
Dec 2016	39.9	S	-4.6	S
Dec 2017	91.8	US	-3.6	S

6.7 Corrosion Indices

Corrosion indices such as Langelier Saturation Index (LSI), Ryznar Index (RSI), aggressiveness index (AI) and Larson-Skold index (L-S) are calculated to find the corrosion behaviour of water over a period of 2005 to 2017 for bore wells; are evaluated and monthly mean of the representing months are tabulated with inference.

6.7.1 Langelier Saturation Index (LSI)

During January and February 2005 LSI is positive so that water is scale forming and non- corrosive. In March 2005, water is slightly corrosive with non-scale forming (SCNSF) and thereafter, serious corrosion occurred till July 2005. This effect is decreased to slightly corrosive non-scale forming during July 2005, but the negative LSI is continued for the rest of the year.

Table 6.5: Temporal variation of Langelier saturation index (LSI) and Ryznar stability index (RSI) of deep dug wells (BW) of Alappad region, Kollam, Kerala, India for the period 2005-2017

Year/Month	LSI	Inference	RSI	Inference
Jan 2005	0.6	SFNC	6.9	LSC
Feb 2005	0.5	SFNC	7.0	CS
Mar 2005	-0.3	SCNSF	7.7	HC
Apr 2005	-0.9	SC	8.7	HC
May 2005	-0.8	SC	8.3	HC
Jun 2005	-1.1	SC	8.7	HC
Jul 2005	-0.8	SC	8.1	HC
Aug 2005	-0.4	SCNSF	8.0	HC
Sep 2005	0.3	SSFC	7.0	CS
Oct 2005	-0.4	SCNSF	8.0	HC
Nov 2005	-0.5	SC	8.0	HC
Dec 2005	-0.3	SCNSF	7.8	HC
Dec 2008	-1.8	SC	10.7	VHC
Jan 2012	-0.2	SCNSF	7.5	CS
Feb 2012	0.0	BP	7.4	CS
Mar 2012	0.5	SFNC	6.7	LSC
Apr 2012	0.1	SSFC	7.1	CS
May 2012	-0.3	SCNSF	7.7	HC
Jun 2012	-0.5	SC	7.9	HC
Jul 2012	-0.1	SCNSF	7.5	CS
Aug 2012	-0.3	SCNSF	7.8	HC
Sep 2012	-0.5	SC	8.2	HC
Oct 2012	-0.6	SC	8.4	HC
Nov 2012	0.3	SSFC	7.3	CS
Dec 2012	-0.2	SCNSF	7.4	CS
Dec 2013	0.1	SSFC	7.2	CS
Dec 2014	-0.1	SCNSF	7.5	CS
Dec 2015	-0.9	SC	8.9	HC
Dec 2016	-0.7	SC	8.2	HC
Dec 2017	-0.6	SC	8.4	HC

From the figure, it is clear that in December 2008 also water is seriously corrosive, but later from the data obtained in the year 2012 it is witnessed that the scaling properties of water is enhanced not in the required level so as to inhibit corrosion rate. In December 2013 water becomes slightly scale forming and corrosive, but turned to negative LSI in December 2014 and the rest of the period from December 2015 to December 2017 water is in seriously corrosive state.

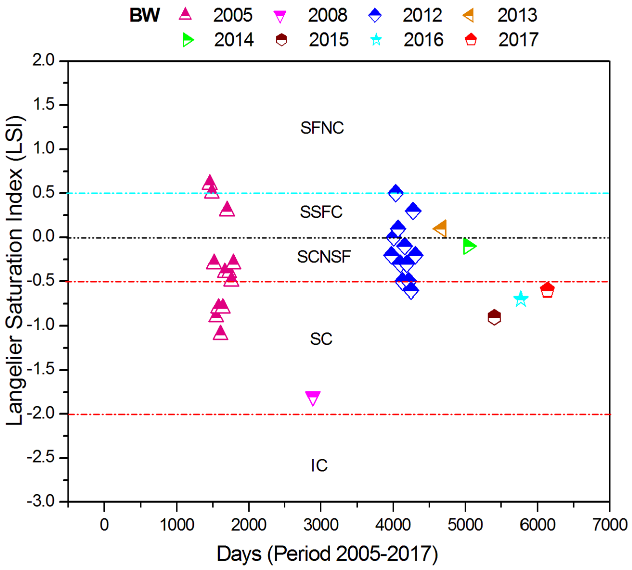

Figure 6.28: Temporal variation of Langelier saturation index (L-S) of deep bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

6.7.2 Ryznar Stability Index (RSI)

In January 2005, water is *little scale forming and corrosive* (LSC) and shifts to *corrosion significant* (CS) in February. From March 2005 onwards, the water becomes *highly corrosive* (HC) except in September 2005, when the RSI comes to 7.0 with *corrosion significant* (CS) water. In

December 2008 the water is reported to have *very high corrosion* (VHC) behaviour leading to very intensive scale dissolving properties.

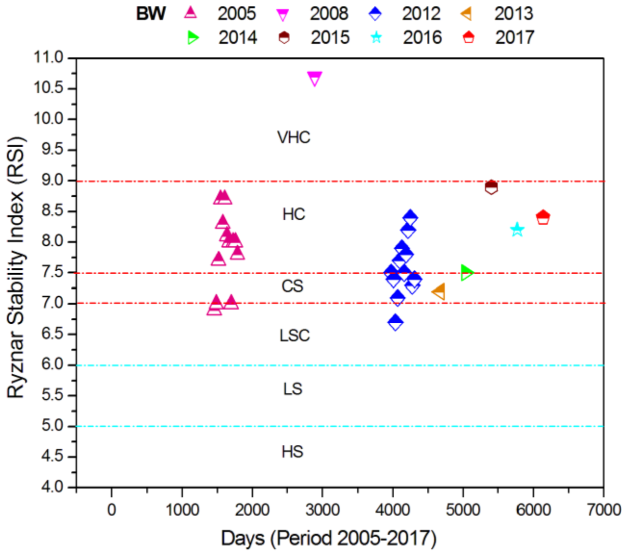

Figure 6.29: Temporal variation of Ryznar stability index (RSI) of deep bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

In the Year 2012, water is generally corrosive with little scale forming tendency during March 2012. In rest of the months, water is completely corrosive in nature. During December 2013 and December 2014, water tend to be *corrosion significant* (CS) with RSI 7.2 and 7.5 respectively. But in the months December 2015, 2016 & 2017, water remained *very high corrosion* (VHC) nature.

6.7.3 Aggressiveness Index (AI)

According to pH, alkalinity and calcium hardness of water collected from bore wells in the study area during January and February 2005, water is *non-aggressive* (NA) as the calculated aggressiveness index is greater than 12. But from March 2005 onwards water has AI < 12, but greater than 10.0, which is considered as *moderately aggressive* in nature. In December 2008 also, water is reported to be *moderately aggressive.*

Table 6.6: Temporal variation of aggressiveness index (AI) and Larson-Skold index (L-S) of deep dug wells (BW) of Alappad region, Kollam, Kerala, India for the period 2005-2017.

Year/Month	AI	Inference	L-S	Inference
Jan 2005	12.6	NA	0.6	NC
Feb 2005	12.5	NA	0.6	NC
Mar 2005	11.6	MA	0.8	SC
Apr 2005	11.0	MA	1.6	HC
May 2005	11.1	MA	1.2	HC
Jun 2005	10.9	MA	0.5	NC
Jul 2005	11.1	MA	0.3	NC
Aug 2005	11.5	MA	0.2	NC
Sep 2005	12.2	NA	0.2	NC
Oct 2005	11.5	MA	0.2	NC
Nov 2005	11.4	MA	0.9	SC
Dec 2005	11.6	MA	1.1	SC
Dec 2008	10.1	MA	0.9	SC
Jan 2012	11.7	MA	0.7	NC
Feb 2012	11.9	MA	0.1	NC
Mar 2012	12.3	NA	0.1	NC
Apr 2012	11.9	MA	0.5	NC
May 2012	11.5	MA	0.4	NC
Jun 2012	11.4	MA	0.3	NC
Jul 2012	11.0	MA	0.3	NC
Aug 2012	11.6	MA	0.6	NC
Sep 2012	11.3	MA	0.1	NC
Oct 2012	11.2	MA	0.3	NC
Nov 2012	12.2	NA	0.4	NC
Dec 2012	11.6	MA	0.9	SC
Dec 2013	12.0	MA	0.2	NC
Dec 2014	10.2	MA	0.1	NC
Dec 2015	10.9	MA	11.6	HC
Dec 2016	11.1	MA	0.4	NC
Dec 2017	11.3	MA	0.6	NC

In the year 2012, most of the months have AI < 12.0 (*moderately aggressive*), except in March 2012 and November 2012 where AI > 12.0, which is considered as *non-aggressive* (NA). In December 2013, 2014, 2015, 2016 & 2017, water remained in *moderately aggressive* (MA) range (10.0 < AI < 12.0).

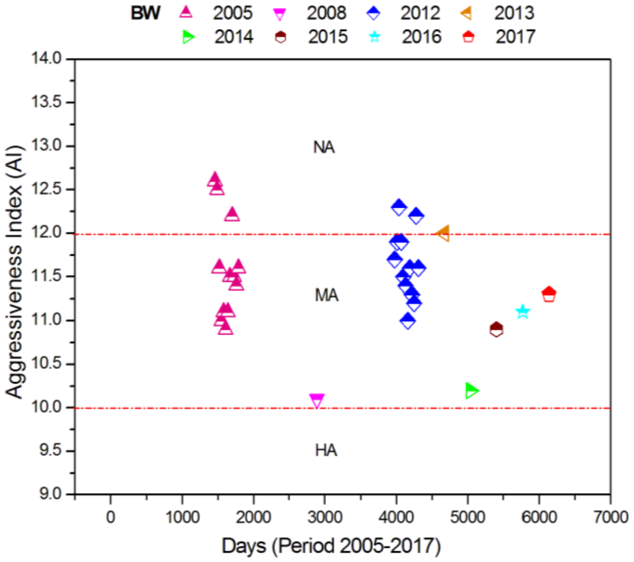

Figure 6.30: Temporal variation of Aggressiveness index (AI) of deep bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

6.7.4 Larson-Skold Index (L-S Index)

Larson-Skold index describe the corrosion behaviour of water in terms of chloride, sulphate and bicarbonates. It helps to find whether chloride and sulphate are present sufficient to promote corrosion with respect to the concentration of bicarbonate to inhibit corrosion tendency[24-26].

In the year 2005, the first two months after the 26th December 2004 Indian Ocean Tsunami, the chloride and sulphate concentration in the water is not enough to promote corrosion. The water remained *non-corrosive* (NC) in January and February 2005. But in March 2005, water have slight corrosion tendency which rose to *highly corrosive* (HC) in April and May 2005. From June 2005 to October 2005, water tend to be *non-corrosive* (NC), but become *slightly corrosive* (SC) during November and December 2012. In December 2008, water from the bore wells in the study area again confirms the *slightly corrosive* (SC) nature of water.

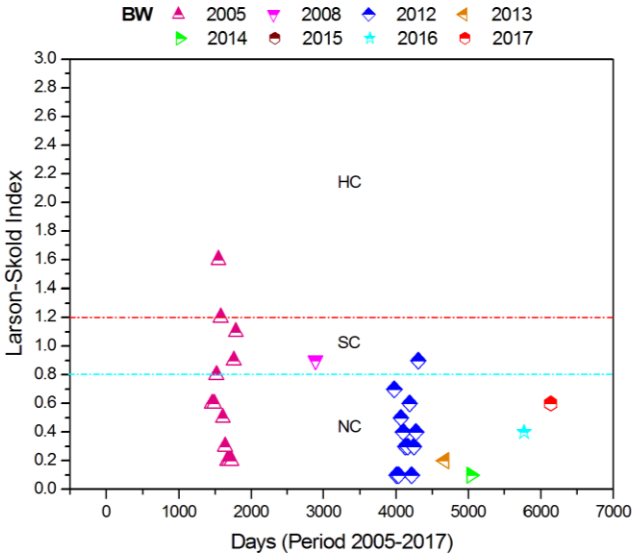

Figure 6.31: Temporal variation of Larson-Skold index (L-S) of deep bore wells (BW) along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Alappad, Kollam, Kerala, India for the period 2005-2017.

In the year 2012, the concentration of chloride and sulphate is not sufficient enough to enhance corrosion and the water shows *non-corrosive* (NC) behaviour throughout the study period except in December 2012, where the concentration of chloride higher compared to other months of the year which definitely interfere with the corrosion tendency of water and becomes *slightly corrosive* (SC) in nature. In the following years of analysis from December 2013 to December 2017, water is non-corrosive (NC) with respect to chloride and sulphate concentration.

Analysis of Variance

ANOVA test is conducted to check the following hypothesis

Hypothesis VIII:

> *Whether there is any significant difference in the mean values of the parameters of groundwater sampled from bore well (BW) strata over the years.*

Table 6.7: ANOVA table for the comparison of water quality parameters of groundwater from bore wells over the years

Source	SS	df	Ms	F	p- value
Total	78963318.8228	647			
Between BW's	383306.9904	2	191653.4952	1.867	$p>0.05$
Between Parameters	14254664.1734	17	838509.6573	8.168	$p<0.001$
Residual	63343775.3111	617	102664.1415		

Inferences

1) There is no significant difference between water quality in different bore wells ($p>0.05$).

2) Water quality variations between months is also not significant ($p>0.05$).

3) There is significant difference between parameters ($p<0.001$). TDS is significantly higher than all the rest, followed by Alkalinity, TH, Na and HCO_3. Eh is significantly lower, followed by pH, K, SO_4^{2-}, PO_4^{3-}, NO_3^- and BOD.

Table 6.8: Over all groundwater quality of dug wells of the Alappad coast, Kollam, Kerala, India during the period of 2001, 2005, 2008, 2012, 2013, 201, 2015, 2016 and 2017.

Water Quality parameters	April 2001	Annual Mean 2005	December 2008	Annual Mean 2012	December 2013	December 2014	December 2015	December 2016	December 2017	BIS (IS 10500:2012) Acceptable Limit	BIS (IS 10500:2012) Permissible Limit	WHO (2011)
pH	7.5	7.2±0.2	7.1±0.14	7.2±0.3	7.4±0.16	7.2±0	7.0±0.8	6.8±0.8	7.2±0.01	6.5-8.5	No relaxation	6.5-8.5
Eh (mV)		-16.7±12.3	-36±7.1	-17.3±16.3	-26.0±8.7	-0.5±0.2	-7.0±51.5	-7.0±21.2	-13.5±0.7			
EC (mS/cm)	0.3	0.6±0.1	0.25±0.1	768.0±1698.0	0.7±0.15	2.2±3.01	2.2±3.0	0.3±0.03	0.7±0.1			1.5
TDS (mg/L)		1413±1070.4	411.75±80.9	591.9±1414.3	338.0±304.6	88.8±153.8	1440.0±1919.8	232.0±2.8	556.5±129.4	500	2000	
TA (mg/L)		228±51.4	25±7.07	227.2±60.3	325.9±40.6	348.8±302.3	74.7±46.6	130.6±50.4	143.5±4.9	200	600	
TH (mg/L)	22	211.3±56.6	99±11.3	173.4±31.9	218.3±15.7	125.3±110.5	373.7±379.3	361.8±282.6	114.4±12.4	200	600	100
Ca^{2+} (mg/L)	4.8	49.6±16.3	15.2±2.3	47.8±10.1	45.1±7.04	15.1±13.2	69.0±63.9	79.9±49.9	33.4±9.4	75	200	75
Mg^{2+} (mg/L)	2.4	20.9±9.8	14.64±4.07	13.0±7.0	25.5±3.3	21.2±18.8	48.7±3.4	39.2±38.2	7.4±2.7	30	100	30
Na^{+} (mg/L)	46	30.4±13.4	46±31.1	62.5±44.9	73.8±63.1	73.7±90.4	26.3±5.9	30.0±8.5	51.2±7.1			
K^{+} (mg/L)	2.5	7.4±4.9	12.4±12.2	9.0±5.2	0.8±0.7	1.4±0.8	4.7±0.6	4.5±0.7	9.0±0			
HCO_3^{-} (mg/L)		278.1±62.7	30.5±8.6	277.2±73.5	397.6±49.6	425.5±368.6	91.1±56.9	159.4±61.5	175.1±6.0			
Cl^{-} (mg/L)	70	104±84.4	12.45±5.02	53.0±67.7	52.1±30.4	23.1±28.2	195.8±266.0	33.5±16.3	59.0±8.5	250	1000	
SO_4^{2-} (mg/L)	0.5	ND	2.9±0.99	0.4±0.5	0.0±0	0.0±0	0.0±0	0.0±0	0.4±0	200	400	
PO_4^{3-} (mg/L)		0.02±0.02	16.5±0.7	ND	0.0±0	0.0±0	0.0±0	0.0±0	0.0±0			
NO_3^{-} (mg/L)		0.6±0.40	2076±820.2	ND	0.0±0	0.0±0	0.0±0	0.0±0	0.0±0	45	No relaxation	
Iron (mg/L)		0.7±1.10	176±121.6	4.9±2.6	6.0±2.0	4.7±1.2	3.7±4.7	1.7±0.5	4.5±0.7	0.3	No relaxation	0.1
DO (mg/L)		2.1±1.2	3.1±0.6	2.1±1.3	1.4±0.2	2.1±1.4	0.7±0.47	5.0±1.99	3.6±1.1			
BOD (mg/L)		11.5±9.4	6.4±2.3	0.5±0.5	0.3±0.1	0.3±0.1	0.3±0.12	0.2±0	3.6±3.4			

6.8 Conclusion

Temporal variations in water quality parameters for bore wells over an intermittent period from 2001 to 2017 are assessed and presented in this chapter. Unlike dug wells, there is no significant variation can be seen in the water quality parameters of groundwater from bore well strata. After the tsunami event in 26th December 2004, from January 2005 onwards, total dissolved solids in the water are very high. In 2008, TDS falls within the acceptable limit prescribed by WHO and BIS standards. In the year 2012, an abrupt increase in TDS and electrical conductivity in observed in June 2012, may be due to seawater ingress into deep aquifers as a result of over pumping. An increase in chloride concentration is noticeable in the year 2005 as a result of seawater intrusion but a subsequent increase in sodium ion concentration is not found, reveals the instances of the ion-exchange process prevailed in the study area. Hill piper trilinear diagram demarcate, the water type during April 2001 as *saline water type*, with hydrochemical facies of Na^+-K^+-Cl^- -SO_4^2. After 26th December 2004 Indian Ocean Tsunami, water becomes *temporary hardness water type* with hydrochemical facies Ca^{2+}-Mg^{2+}-HCO_3^-. There is no variation observed in the water type of groundwater from deep aquifers and continued to be *temporary hardness water type* from the year 2012 to December 2017. The major irrigation water quality parameters analysed confirmed that the water from bore wells are suitable for irrigation and they are not much affected by tsunami waves except in some months magnesium hazard is observed. USSL diagram clearly shows the groundwater during 2001 and most of the months in the year 2012, December months of 2014, 2015 and 2016 falls in C2S1 class having *medium saline low sodium water* (good water quality). After 26th December 2004 Indian Ocean Tsunami, most of the dug wells have high EC, hence it is spread in *high salinity and medium sodium water*, C3S2 (moderate water quality) and very high salinity and medium sodium water, class C4S2 (bad water quality). Corrosion indices like Langelier Saturation Index (LSI), Ryznar Index (RSI) and aggressiveness index (AI) indicates water is potentially corrosive in nature. Larson-Skold index confirms that during the year 2005, chloride concentration in the deep groundwater aquifers promote corrosion tendency of water. ANOVA test confirms that over these years there is no significant difference in water quality in bore wells. But there is significant difference between water quality parameters like TDS is significantly higher than rest of all other physico-chemical parameters, followed by Alkalinity, TH, Na^+ and HCO_3^-.

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Chapter 7

SUMMARY AND CONCLUSION

The study presented in the preceding chapters discussed the hydrogeochemistry and groundwater quality of coastal aquifers of Alappad region of Kollam district in Kerala. The study areas groundwater chemistry of this region is mainly controlled by many natural as well as anthropogenic factors. The region is one of the tsunami inundated coasts of Kerala, subjected to economic developments such as tourism. This coastal segment elaborately studied the groundwater quality for a period of 2001-2017.

This bound thesis discusses about the hydrogeochemistry of the groundwater of Alappad regions physico-chemical parameters, water type with hydrochemical facies, major ionic ratios, water quality index, irrigation water quality and corrosion indices. Diagrams such as Gibb’s plots, Hill-Piper plots, ionic ratios, USSL diagram and Wilcox diagram are used to interpret the primary data. Statistical analysis are done for inferences in the respective sections exhaustively, critically and their interpretations are presented for control well (CW), dug wells (DW) and bore wells (BW) in Alappad coast during each month of the year 2012 and also in the subsequent years 2013, 2014, 2015, 2016 & 2017. The overall water quality are determined for a period 2001-2017.

The main objective of this research study of groundwater chemistry is to evaluate compositions and quality of groundwater on a regional scale as well as create a primary data bank on different chemical constituents of groundwater. The prime objectives of the present study are;

(1) To determine the physico-chemical parameters and to evaluate the groundwater chemistry of groundwater sources during every month of the year 2012. (2) To identify the drinking water quality of groundwater sources with respect to BIS (Bureau of Indian Standards, IS 10500:2012) and WHO (World Health Organization) standards during the year 2012. (3) To characterize the hydrochemical facies of groundwater to identify and differentiate the water type using Hill-Piper Trilinear plots. (4) To study the hydrogeochemistry of groundwater of the study area by using Gibb's plot and ionic ratios during the year 2012. (5)To check the incidence of seawater intrusion using Revelle's co-efficient for each month in the year 2012. (6) To compute the monthly water quality index (WQI) of the groundwater by giving adequate weightage to significant water quality parameters. (7)To assess the irrigation water quality of the groundwater to find the suitability for irrigation purposes. (8)To evaluate various corrosion indices for studying the industrial utility of shallow and deep groundwater. (9) To analyze the trace element content of shallow and deep groundwater sources. (10) To classify the groundwater using designated best use (DBU) suggested by CPCB (Central Pollution Control Board, Government of India). (11)To evaluate the temporal variations of groundwater quality of the dug well sources in Alappad coast intermittently for a period from the year 2001 to 2017. (12) To evaluate the temporal variations of groundwater

quality of the bore well sources in Alappad coast intermittently for a period from the year 2001 to 2017.

Hypothesis tested accordingly are,

a) Whether there is any significant difference between mean values of various parameters of groundwater sampled from the control well (CW) stratum in different months of the year 2012.

b) Whether there is any significant difference between mean values of various parameters of groundwater sampled from dug well (DW) strata in different months of the year 2012.

c) Whether there is any significant difference between mean values of various parameters of groundwater sampled from bore well (BW) strata in different months of the year 2012.

d) Whether there is any significant difference between mean values of various parameters of groundwater sampled from control well (CW), dug well (DW) and bore well (BW) strata in different months of the year 2012.

e) Whether there is any significant difference between water quality index of groundwater sampled from dug well (DW) and bore well (BW) strata in the year 2012.

f) Whether there is any significant difference between water quality index of groundwater sampled from the control well (CW), dug wells (DW) and bore wells (BW) in different months of the year 2012.

g) Whether there is any significant difference in the mean values of the parameters of groundwater sampled from dug well (DW) strata over the years.

h) Whether there is any significant difference in the mean values of the parameters of groundwater sampled from bore well (BW) strata over the years.

Primary data obtained from laboratory studies are subjected to statistical analysis using two-factor and three factor ANOVA. Whereever, treatment effects are found to be significant, least significant difference (LSD) at 5% level are calculated to identify the significant treatment effects: The results concerning each stratum are discussed in the respective chapters.

The study is focused on the groundwater chemistry of shallow and deep groundwater sources along the ecologically sensitive coastal segment, Alappad coast, Kollam district, Kerala, India. The coastal erosion in this stretch is one of the recurring natural hazards owing to the proximity to sea and narrow width of the study area. As an area of high population density, renowned tourist destination, the stress on available fresh water is increasing. This region is an environmentally sensitive area and research studies and reports are available with respect to impact of Tsunami for the year 2005. Study of seawater intrusion and groundwater quality has great significance to coastal ecological conservation. Sampling at these stations started in January 2012 for annual mean and continued in each month till December 2012. In the subsequent years, 2013, 2014, 2015, 2016 & 2017 sampling and analysis were done for the month of December. Post-tsunami study data of year 2005 and those available for year 2001, help in generating a database intermittently for a period 2001-2017. The present work is an evaluation of groundwater chemistry and quality with respect pre and post tsunami situation.

Chemical analysis of water generates the fundamental data essential for the determination of groundwater quality. Major constituents are measured in milligrams per litre and trace constituents in microgram per litre. Water quality standards for domestic, agricultural and industrial use published by various agencies are used for evaluating the water quality of the present study area. Presentation of results in graphical forms helps studying temporal and spatial variation of constituents. Results of chemical analysis are statistically evaluated by correlation study which help to identify relationship among parameters. Water Quality Index (WQI) calculated using WHO standards help for easily identifying the quality of water. The ratios of sodium and chloride concentrations are particularly important because they give suggestions regarding the groundwater processes like ion exchange and reverse ion exchange. Hill-Piper Trilinear diagrams are particularly useful to infer hydrogeochemical facies. Gibb's plot is another diagrammatical method to evaluate the prominent hydrogeochemical processes occurring in the study area. Different parameters used for the evaluation of irrigational quality are sodium adsorption ratio (SAR), sodium percentage (Na %), magnesium adsorption ratio (MAR), residual sodium carbonate (RSC), permeability index (PI) and Kelly's index (KR). USSL and WILCOX diagrams are graphical plots to classify water samples based on irrigation suitability. Saturation indices calculation help in evaluating the industrial use of water. Major findings and inferences developed out of this study are given in the respective chapters in a highly descriptive approach.

Major findings and conclusions are summarized as

- The physico-chemical water quality parameters of groundwater from control well are pH (7.7±0.2), Eh (-42.0±10.3) mV, EC (403±139) µS/cm, Alkalinity (160.3±22.3) mg/L, TH (139.5±24) mg/L, Ca^{2+} (40.2±8.4) mg/L, Mg^{2+} (9.5±5.2) mg/L, TDS (298±72) mg/L, Na^+(53.4±12) mg/L, K^+ (12.3±3.5) mg/L, Cl^- (45.6±20) mg/L, SO_4^{2-} (1.3±0.6) mg/L, NO_3^- (0.9±0.3) mg/L, DO (4.5±0.9) mg/L and BOD (0.3±2.0) mg/L. All the water quality parameters are well below the acceptable limit prescribed by BIS (IS 10500:2012) and WHO (2011). The ANOVA test proves, there is significant difference between months, ($P<0.05$). November and December 2012 experienced significantly lower values ($P<0.0$). Parameters also differ significantly between them ($P<0.001$). TDS is significantly higher than all the rest followed by HCO_3^-. Eh is significantly lower compared to all others, followed by Mg^{2+}, SO_4^{2-}, PO_4^{3-}, Iron, DO and BOD.
- The groundwater quality of dug well sources are pH (7.8±0.4), Eh –(47.6±20) mV, EC (550±521) µS/cm, Alkalinity (189.7±88.4) mg/L, TH (167.3±86.9) mg/L, Ca^{2+} (43.5±22) mg/L, Mg^{2+} (14.2±12.7) mg/L, TDS (396.8±350.4) mg/L, Na^+ (64.3±59.3) mg/L, K^+ (8.4±4.9) mg/L, HCO_3^- (231.5±108) mg/L, Cl^- (65.5±83.6) mg/L, SO_4^{2-} (2.5±3) mg/L, NO_3^- (0.6±0.9) mg/L, PO_4^{3-} (0.1±0.1) mg/L, Total Iron (0.1±0.6) mg/L DO (4.1±1.5) mg/L and BOD (3.4±3) mg/L. According to ANOVA test, there is no significant difference between months with respect to the water quality parameters ($P<0.05$) of groundwater from dug well sources. But parameters differ significantly between them ($P<0.001$). TDS is significantly higher than all others, followed by SO_4^{2-} and

TH, Eh, temperature, pH, EC, DO, BOD, PO_4^{3-}, total iron and NO_3^- are significantly lower than all others (P<0.001).

- In the water samples collected from bore wells the pH (7.2±0.3), Eh (-17.3±16.3) mV, EC(768±1698) µS/cm, Alkalinity (227.2±60.3) mg/L, TH (173.4±32) mg/L, Ca^{2+} (47.8±10) mg/L, Mg^{2+} (13±7) mg/L, TDS (592±1414.3) mg/L, Na^+ (62.5±45) mg/L, K^+ (9.0±5.2) mg/L, Cl^- (53±67.7) mg/L, HCO_3^- (277.2±73.5) mg/L, SO_4^{2-} (0.4±0.5) mg/L, Total Iron (4.9±2.6) mg/L, DO (2.1±1.3) mg/L and BOD (0.5±0.5) mg/L. The annual mean of all the water quality parameters are well below the acceptable limit prescribed by BIS (IS 10500:2012) and WHO (2011), except for iron in bore wells. The bore wells in the year 2012 is reported to have a very high iron content may be due to the corrosion and leaching of iron metal used in pumping and water supply system. Results of ANOVA test shows that there is significant difference in parameters between months (P<0.001). January and December 2012 showed significantly higher values for the parameters whereas March and April 2012 reported significantly lower values (P<0.001).
- ANOVA test proves that there is significant difference between groundwater from different sources (P<0.05). Bore wells (BW) showed significantly higher values followed by DW and CW (P<0.05). Parameters also exhibited a significant difference between them (P<0.001). TDS is significantly higher among all the parameters, followed by TA, TH and calcium hardness (P<0.001). Significantly lower values was registered for water quality parameters such as Eh, followed by PO_4^{3-}, NO_3^-, EC, BOD and SO_4^{2-}.

- Total hardness in water from control well and dug wells are classified as *hard to very hard water* (HVH) and deep groundwater sources comes in *very hard to excessively hard* (VHEH) water. Since alkalinity of the groundwater is greater than total hardness in all the dug well and bore well strata, the hardness of the groundwater is contributed by carbonate or temporary hardness.
- Hydrochemical facies of groundwater in the year 2012 is **Ca^{2+}- Mg^{2+}- HCO_3^-**. The water type overall groundwater hydrochemistry is distinguished as ***temporary hardness water type*** with non-dominant cation and bicarbonate anion water. The relative abundance of cations and anions in the groundwater are in the order $Na^+ > Ca^{2+} > Mg^{2+}$ and $HCO_3^- > Cl^- > SO_4^{2-}$. The overall hydrochemical facies of both dug well and bore well strata suggests that under the natural environment pertain in the hydrogeological settings, the groundwater in the study region is actually originated from fresh water sources which is altered subsequently due to marine activities supplemented by persistent anthropogenic interventions leading to alter coastal hydrogeological system.
- According to Gibb's diagram, hydrogeochemistry of the study area is controlled by dissolution of rock forming minerals. Evaporation dominance is reported in July 2012 for groundwater from bore well strata, may be due to up-coming of sea water as a consequence of over pumping. Revelle's co-efficient, $R < 1$ for most of the time that proves, even though the entire study area is located in the proximity of brine, the natural hydrodynamics of groundwater and seawater is balanced to some extend so that invasion of sea water is restricted.

- The average ratio of Na^+ and Cl^- of groundwater from shallow and deep sources throughout the study period prove *ion exchange* process is dominant but with intermittent reverse ion exchange in different locations irrespective of seasons. This suggests that, rainfall does not have direct influence on hydrogeochemistry of this coastal area except as a carrier of sea spray aerosols. Molar ratio of sodium to chloride suggests multiple sources for sodium ion than chloride. This can be attributed to silicate weathering of silicate mineral containing rocks. Ca^{2+}/Mg^{2+} molar ratio, plots (i) total cations versus $(Ca^{2+}+Mg^{2+})$ and (ii) $(Na^{+}+K^{+})$ versus total cations also supports the dissolution of silicate minerals. Whereas, the ratio of $Ca^{2+}+Mg^{2+}$ to $HCO_3^{-}+SO_4^{2-}$ give insight to the dominance of ion-exchange process along with the involvement of silicate weathering in the hydrogeochemistry of the study area.
- Water quality index (WQI) for control well and dug well strata falls in **Grade B** inferring water is *Good* for human consumption with respect to the physico-chemical parameters taken under consideration for calculating WQI. In the case of bore wells, overall water quality is *Good* with **Grade B**, except in July 2012. In July 2012, water moved to a WQI > 100, which is considered *Unfit for drinking purposes* (**Grade E**), due to high TDS in the water during that period. Concentration of trace metals present in groundwater are well below the standard permissible limits recommended by BIS (2012) and WHO (2011). ANOVA test confirmed that WQI does not differ significantly between wells and between months ($P>0.05$) in the year 2012.

- All the irrigation water quality parameters analysed shows the groundwater in the study region is suitable for irrigation purposes in most of the period. Groundwater sources in the Alappad study area comes under *excellent* groundwater quality with respect to sodium adsorption ratio (SAR). In the US salinity Laboratory diagram (USSL) control well fall in **C2S1** category confirming good quality water with *medium saline and low sodium* water. Shallow dug wells in most of the months shown *medium saline with low sodium hazard* (**C2S1**). But during October and December 2012 a slight increase in salinity hazard leads to shift the water sources to *high salinity and low sodium* (**C3S1**) category with moderate water quality. The groundwater from bore wells have good water quality with *medium saline and low sodium water* (**C2S1**), except in the month of July 2012 with *very high salinity hazard and low sodium water* (**C4S1**). The salinity hazard may be associated with very high dissolved constituents during monsoon dilution. The overall irrigation water quality of groundwater in the study region with respect to SAR recommends that water is suitable for irrigation with moderate leaching requirements, without any distinct salinity control. Chloro-alkalinity indices refer to chloro-alkalinity disequilibrium that signifies the exchange of calcium and magnesium in groundwater with sodium and potassium from aquifer material for both shallow and deep groundwater sources.
- According to Langelier Saturation Index (LSI) water is *slightly scale forming but corrosive* (SSFC) for control well and dug wells. Here, even though the calcium carbonate scale is forming, it is not

sufficient to inhibit corrosion. In bore wells, water is *slightly corrosive but non scale forming* (SCNSF). Ryznar Stability Index (RSI) confirms the water in both dug well and bore well strata are *heavy corrosion* promoting and have intense scale dissolving capacity. The groundwater from the study area is corrosive in nature but *moderately aggressive* with respect to aggressiveness index (AI). Larson-Skold index eliminate the possibilities of the chloride and sulphate ions to take part in the corrosive property of water, as there concentrations are too low to induce corrosion.

- The overall groundwater quality of dug wells for the period from 2001 to 2017 is revealed that the study area is mainly dominated by ***temporary hardness water type.*** The major hydrochemical facies of the study area comprises of $\mathbf{Ca^{2+}\text{-}\ Mg^{2+}\text{-}\ HCO_3^-}$, with interventions of *saline water type* with hydrochemical facies $\mathbf{Na^+\text{-}K^+\text{-}Cl^-\ \text{-}SO_4^{2-}}$ during the year 2001, 2005 & 2008 in dug wells and year 2005 in bore wells. The hydrogeochemistry of the study area is controlled by ion-exchange process and weathering of silicate minerals of rocks. The WQI indicates groundwater is suitable for drinking purposes only after conventional treatments and disinfection. Water is suitable for irrigation purposes as per the irrigation water quality parameters analyzed. The corrosion indices evinced that water is moderately aggressive and the calcium carbonate scale formation is not sufficient enough to inhibit corrosion. It is also confirmed that in the year 2005, the chloride and sulphate took part in corrosion activities, where as in all other periods, these ions have no effect in promotion of corrosive nature of groundwater.

- Groundwater in the bore wells during December 2013 exhibit *temporary hardness water type,* which shifts to *mixed water type* in December 2014. The water type becomes *permanent hardness type* in December 2015. Over pumping of groundwater cause upconing of seawater to freshwater aquifers. As a result, sodium chloride concentration in groundwater increases. The high amount of sodium also enhances the occurrence of reverse ion exchange process. Finally, the resulting water having high calcium content than sodium ion. The presence of chloride of calcium in groundwater is the cause of permanent hardness in water. In December 2016 and 2017, water maintained *temporary hardness water type*.

- Statistical analysis (ANOVA) of groundwater from dug wells for the entire period from 2001 to 2017 relieved that there is no significant difference between years for dug wells ($P>0.05$) but there depicted a significant difference between parameters ($P<0.001$). TDS is significantly higher than all the others, followed by HCO_3^-, TA and TH ($P<0.001$). Eh is significantly lower than all the rest followed by PO_4^{3-}, total iron, NO_3^-, DO, BOD and EC ($P<0.001$). In the case of groundwater from bore wells there is no significant difference between wells ($P>0.05$) and between months variation is also not significant ($P>0.05$). There is significant difference between parameters ($P<0.001$). TDS is significantly higher than all the rest, followed by Alkalinity, TH, Na and HCO_3. Eh is significantly lower, followed by pH, K, SO_4^{2-}, PO_4^{3-}, NO_3^- and BOD.

Groundwater (from dug well sources) of Alappad during April 2001, year 2005 (annual mean) and December 2008 have hydrochemical facies Na^+-K^+-Cl^- - SO_4^{2-}. The water type during these periods is found to be *saline water type* with Na^++ K^+ as dominate cations and Cl^- dominate anion water due to the impact of tsunami inundation. This clearly indicates the occurrence of contamination in shallow fresh water aquifers. From the year 2012 to December 2016 water maintained *temporary hardness water* having non–dominant cation and bicarbonate dominant water. The hydrochemical facies of groundwater during this period is Ca^{2+}-Mg^{2+}-HCO_3^{2-}. In December 2017 water exhibited a mixed behavior. Eventhough no prominent hydrochemical facies can be identified here the dominant cation and anion in groundwater are Na^+-K^+ and Cl^-. However over the years (for shallow and deep groundwater) there is no significant difference in the quality of groundwater but the variability is visible among the prominent physicochemical parameters

Future Scope of the Study

The study of Alappad coast, Kollam, Kerala, India is planned to continue for the years to come with respect to the evaluation of total environmental quality of air, soil & water. The presence of radioactive minerals such as monazite & illmonite in the black sand deposits of the Alappad coast, made the region ecologically and economically important. The study of trace elements in the groundwaters of Alappad coast is of much significance to be taken up as a new research program.

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List of Publications

[1] Achari, V. S.; George, R. T.; Deepa, P.; Ambili, M.S.; Jayasree, S.; Rajalakshmi, A. S.; Lopez, R. M. Hydrochemistry of Groundwater Along a Tsunami Devastated Coastal Segment of Kerala: Arattupuzha Village, Alappuzha, India. *Indian Journal of Geo Marine Sciences.* **2017**, *46(09),* 1765-1779.

[2] Achari, V. S.; Ambili, M. S.; Jaison, C. A.; Deepa, P.; George, R. T. Groundwater hydrochemical facies of tsunami affected Alappad coast of Kollam, Kerala, India. *Journal of the Academy of Chemistry Teachers*, **2017**, *3(1),* 40-44.

[3] Achari, V. S.; Deepa, P.; Ambili, M. S.; George, R. T. Corrosion Indices, Drinking and Irrigation Water Quality of Andhakaranazhy and Cherai Coastal Regions of Kerala. *Journal of the Academy of Chemistry Teachers*. **2017***, 3(1)*, 10-14.

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[5] Achari, V. S.; Ambili, M. S.; Deepa, P. Irrigation Water Quality and Corrosion Indices of Groundwater Sources of Tsunami Affected Alappad Coast, Kollam, Kerala, India. *Indian Journal of Scientific Research*. **2018**, *18(2),* 102-108.

[6] Achari, V. S.; Deepa, P.; Ambili, M. S. Groundwater Quality of Andhakaranazhy Coast, Alappuzha, Kerala, India. *Indian Journal of Scientific Research*. **2018,** *18(2),* 119-125.