HYDROCHEMISTRY AND GROUNDWATER QUALITY OF COASTAL PHREATIC AQUIFERS OF ALAPPUZHA AND ERNAKULAM REGIONS OF KERALA, INDIA

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Certificate

Certified that the work presented in the thesis entitled **“Hydrochemistry and Groundwater Quality of Coastal Phreatic Aquifers of Alappuzha and Ernakulam Regions of Kerala, India”** is an authentic record of research work carried out by **Ms. Deepa P** 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 **"Hydrochemistry and Groundwater Quality of Coastal Phreatic Aquifers of Alappuzha and Ernakulam Regions of Kerala, India"** is based on the original work done by me under the supervision of **Dr. V. Sivanandan Achari**, 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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Preface

Groundwater is an important resource, especially in the regions, where blue water sources are limited. Study, planning and management of groundwater play a significant role with respect to effective utilization for domestic, irrigation, industrial, and other purposes. Groundwater studies give us insight into the nature of minerals and processes occurring in a specific study area. Groundwater chemistry deals with the chemistry and quality indices of groundwater. It is a broad subject area with many interrelations with fundamentals of science. Fresh water availability is very low in many coastal regions of Kerala due to the salt water intrusion and peculiar features of backwaters, lagoons and barrier islet and their inter connections make the region prone to hazard. Only few dependable (fresh water) groundwater sources are available and demand for freshwater is a concern of many coastal villages. Study of groundwater and evaluation of hazards is an active area of research there after Indian Ocean tsunami 26th Dec 2004. Andhakaranazhy and Cherai coasts are considered as a water stress region of Kerala, India with thickly populated fisherman community, facing many natural and anthropogenic hazards. This stretch of coast is recently facing many aspect of economic development in the form of tourism, fishing and navigation. Sand mining is another way of resource exploitation in one of the study area, may lead to subsidence. Groundwater quality evaluation of the region in post tsunamic situation over the period of time (2001- 2017) after an extensive inundation by tsunami waves forms the basis of this study. Eighteen (18) groundwater sources have been selected along this coastal section to identify the variability of groundwater chemistry over the years. The groundwater sampling and analysis (APHA; 2005, 2012) have been done for a period starting from January-December 2012, also in December 2013, 2014, 2015, 2016 & 2017. The samples were subjected to drinking water quality analysis as per Indian Standard (BIS 10500: 2012) and water quality indices were computed. Hill-Piper-Trilinear plots were made to evaluate the water type of the study area using GW chart software. Irrigation suitability is measured by sodium percent (Na %), sodium adsorption ratio (SAR), Kelley's ratio (KR), permeability index (PI), magnesium adsorption ratio (MAR), USSL and Wilcox diagrams. Gibb's plots were made to evaluate the chemical composition of groundwater. Corrosive behavior of the groundwater is determined by Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI). The data obtained from the study was compared with available pre-tsunami and post-tsunami data. The study will help to understand the groundwater chemistry, occurrence of processes and water quality problems facing in the region. The prominent inferences of the study are: Water quality parameters of Andhakaranazhy coast showed a very high significant differences ($p < 0.001$), TDS is significantly the highest followed by Alkalinity and TH. Total iron, PO_4^{3-}, DO, EC, pH and BOD showed significantly low values. Between years there is no significant difference ($p > 0.05$) during the period 2008-2017. In Cherai coast, parameters differ significantly over the years ($p < 0.001$). TDS showed significantly higher value followed by Cl^-, and TH. Significantly lower values for the parameters are observed for PO_4^{3-}, NO_3^-, SO_4^{2-}, EC, pH, DO and BOD during the period 2008-2017. Years also showed a significant difference between them ($p < 0.001$). Results of study done in year 2016 and 2017 showed significantly higher values for the parameters ($p < 0.001$). Significantly lower values for the parameters occur during 2008, 2013, 2014 and 2015.

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List of Abbreviations

CW - Control well
SGW - Shallow groundwater
MSL - Mean Sea Level
bgl - Below Ground Level
BW - Bore well
OP - Open pond
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 - Tocal Carbon
TIC - Total Inorganic Carbon
TOC - Total Organic Carbon
KR - Kelly’s Ratio
MAR - Magnesium Adsorption Ratio
PI - Permeability Index
SAR - Sodium Adsorption Ratio
USSL - United States Salinity Laboratory
AI - Aggressiveness Index
LSI - Langelier Saturation Index
RSI - Ryznar Stability index
p value - Significance level
ms - Mean square
ANOVA - Analysis of variance

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Chapter 1

INTRODUCTION

1.1 Groundwater Resources

Water is the most important, valuable and limited natural resource in the world since and without it life cannot exist. Human civilizations had originated, developed and flourished in places where there is an easy access to fresh water sources. The presence of safe and reliable water sources are necessary for the establishment of a stable community [1]. Dirty water and poor sanitation creates health problems, destabilization of social structure. In many parts of the world, water quality has been steadily degraded by the growing pressures on their water resources. Globally increasing demand for fresh water is decided by rising human population sprawling irrigated agriculture and fast economic development. Global irrigational water demand is estimated as 205 km^3a^{-1} of which 1478 km^3a^{-1} is met from blue water sources - water from local sources of rivers, lakes and reservoirs. The remaining part is met by exploitation/abstraction of groundwater. Over the years groundwater abstraction leads to depletion both in quality and quantity. India is characterized by great geographical diversities in the physical features. These diversities have their own impact on the occurrence of groundwater in different places where a balance between abstraction and recharge of groundwater is necessary. As regards to Kerala, coastal plain in the surroundings of Palghat Gap and in the south of Kerala is very relatively extensive. Offshore bars with enclosed lagoons running parallel to the southern Kerala coast. These lagoons are termed as Kayal formation. In western coast, unconsolidated formations of alluvial deposits are restricted to a small region of Western Ghats or backwaters, which have been cut-off by sand bars along the coast. Kerala is having both abundance and scarcity when considering water resources. The average annual rainfall of the state is 3000mm, the bulk of which (70%) is received from the South-West monsoon which starts in June and extends up to September. We also get rains from the North-East monsoon during October to December. These contribute better natural stream flow, recharge, maintain wetlands and ecosystems.

Groundwater is found below the earth surface, that fills in the cracks and other openings of rocks and sand, have the capacity to retain water. It is a dynamic and replenishable resource, which has to be estimated primarily depending on the factors such as groundwater recharge. The flow of groundwater from higher elevation to lower one occurs due to difference in the flow head between the points. The annual groundwater potential consists of existing groundwater withdrawal. The quantity of water available from an aquifer is mainly dependent on three factors-groundwater recharge, discharge and the available groundwater storage. When the discharge exceeds the recharge, will leads to the decline in the water quantity in aquifer. The groundwater became steadily more reducing condition when move to downward, as evidenced by the presence of sulphide species, detectable in many of the pumping boreholes. This will lead to an increase in solubility of iron and denitrification of nitrate to N_2 [2]. Indian coastal aquifers are the second largest groundwater reservoirs in the world after the Indo-Gangetic alluvial plain [3]. The physico-chemical characteristics of groundwater determine its best indented and designated use decided by geochemical transform it is being subjected to the soil formations.

1.2 Geochemical Processes occurring in Groundwater

Carbonate rocks are a type of sedimentary rock which include limestone, marble and dolomite, among these limestone found very extensively. Most of the dolomite is formed from the geochemical alteration process takes place in the calcite. This transformation of dolomite from calcite increases the porosity and permeability of the crystalline structure. Water flowing over the ground will react with the rocks and minerals, which give the water its characteristic chemistry. The weathering of these minerals constitutes the groundwater chemistry of a region.

The main mechanism for the dissolution of calcite is as follows:

$$\mathbf{CaCO_3 + CO_2(g) + H_2O = Ca^{2+} + 2HCO_3^-}$$

This reaction occurs through the following steps:

$$\mathbf{CO_2(g) + H_2O = H^+ + HCO_3^-}$$

$$\mathbf{CaCO_3 + H^+ = Ca^{2+} + HCO_3^-}$$

Dissolution process mainly depends on the pH and CO_2 availability. When the sources of CO_2 are exhausted, water becomes saturated with calcite and there is no further dissolution of calcium carbonate. Groundwater that is primarily controlled by carbonate weathering will have relatively high calcium and bicarbonate contents.

Oxygen is required for the many of the reactions but its absence leads to the reducing condition in the groundwater system. Chemical reactions which take part in the transfer of electrons from one ion to another are called oxidation-reduction reactions. The reduction of ferric iron to ferrous iron

$$\mathbf{Fe^{3+} + e = Fe^{2+}}$$

When groundwater contains organic matter, which consumes the oxygen for microbial decomposition and finally the water contains bicarbonate ion and hydrogen sulphide gas. This process is known as sulphate reduction mechanism.

Generally, the ions in water have a tendency to be attracted onto solid surfaces of minerals due to their electrical charge. In ion exchange process, Ca^{2+} in the groundwater replaces the Na^{+} present in aquifer and finally the resulting water produces relatively high Na^{+} content than Ca^{2+} depending on the cation exchange capacity of the material. The process is also known as softening of water. But some occasions, sodium concentration was very high in groundwater, it has a tendency to replace the adsorbed Ca^{2+} ions from clay layer of aquifer having low Na^{+} content than Ca^{2+} and reverse ion exchange takes place.

1.3 Factors affecting the groundwater quality

Many of the coastal low lands are underlain by huge sedimentary basins that undergo slow tectonic subsidence, which consists of basement subsidence enhanced by subsidence due to isostatic loading of the sediments in the basin. In coastal areas, subsidence can cause the tidal encroachment resulting in the saline water intrusion into the aquifer. Moreover, due to the increased subsidence, some regions have become subject to inundation even under normal tides. Generally, these tectonic subsidence has happened not more than a few centimeter/ century. Excessive withdrawal of groundwater in the regions where underlain by Cenozoic sediments are also subjected to land subsidence. The excess pumping or over exploitation of groundwater results in the decline of water table, which decreases the water pressure. This will leads to the compaction of fine water particles and causes the sinking of land above the aquifer. This phenomenon can damage properties and land [4].

Coastal ecosystems are very dynamic in nature that undergoes considerable changes in the geomorphology by the human intervention. The geomorphology of coasts are composed of a wide range of land forms, only some of which are in equilibrium, or quasi-equilibrium with prevailing processes' [5]. Coastal sand is derived from both land and sea. Every coast has a sand budget how much they deposit and take in sand. Sand mining in the coastal regions and its surroundings is a serious and common issue found in the study area of Andhakaranazhy and Cherai beaches of Kerala. It leads to lowering of the water table and create several environmental problems. Environmental problems occur when the rate of extraction of sand exceeds the rate at which natural processes generate the material [6]. An economically important natural phenomenon in the coast the 'Mud banks' (locally called chakara) is becoming scarce due to the sand mining activities [7]. Coastal tourism plays a significant role in the economy of Kerala, but it may degrade our natural resources and cause environmental pollution [8].

Coastal areas represent zones where land and sea meet and comprises variety of complex environments including deltas, estuaries, bays, marshes, dunes and beaches. Coastal aquifers have boundaries in contact with seawater and are always under dynamic equilibrium with it. The fresh water floats on a layer of saline water in aquifer system, because of its lower specific gravity. Inland salinity is differ from the normal salt water intrusion, occurs in the areas where low rain fall, infiltration, surface run off with very high rate of evaporation. The soluble salts derived from the weathering of minerals tend to accumulate in the soil and it enhances the salt concentration. Because of slow rate of groundwater discharge and movement increase the salinity of groundwater. Withdrawal of fresh groundwater from the coastal aquifers, which results an imbalance in the system and causes the intrusion of saline water. The migration saltwater into the freshwater system happens mainly because of reversal or reduction of the piezometric head gradient, which allows the movement of saline water into freshwater aquifer. However, natural hazards, such as tidal waves deteriorates the groundwater quality to a great extent and leads to the percolation of seawater into shallow and unconfined aquifers [9-13]. Brackish groundwater contains total dissolved solids between 1,000 to 10,000 mg/L and unpleasantly salty, but less saline than seawater. Several studies reported that water quality of the shallow aquifers situated in the coastal zone of Kerala is having variability in their physic-chemical characterization over the years specifically after the incidence of 26th December 2004 Indian Ocean Tsunami [14-16].

Land filling is a commonly used method for the disposal of waste generated. Solid waste disposal is a great issue in current scenario, which can contaminate the groundwater sorces due to leachate infiltration. A study conducted on the groundwater quality in the vicinity of Vamanjoor dump yard in Mangalore draws special attention. Twenty eight groundwater samples were collected and analyzed for physical and chemical parameters as per standard methods of APHA. The results were compared with BIS guideline for drinking water to quantify the extent of contamination and its impact on health. The study reveals that groundwater is contaminated with landfill leachate, contains excessive concentrations of iron, nitrate, cadmium, total dissolved solids and fluorides. The presence of these contaminants has made the groundwater unpalatable. GIS mapping was also used to understand the variation in groundwater quality parameters in this study. [17].

Agricultural land-use and cultivation practices have been shown to exert detrimental effects on groundwater quality. Many of the pesticide chemical compounds, which are widely used for the agricultural practices significantly react to groundwater and contaminate our water sources. The hydrogeological environments with shallow water tables and coarse textured soils low in organic matter are more vulnerable to the leaching of pesticides [18].

Rapid urbanization and improper waste disposal considerably affects the groundwater quality because of the impervious surfaces and pollution. One of the groundwater study reported to assess the geochemical reactions occurs in the groundwater system, found that, enhanced concentrations of anions and cations are resulting from the extensive evaporation, silicate weathering and anthropogenic activities [19].

Wide spread faecal contamination of groundwater sources were reported many authors, which require immediate attention. Laluraj and their group (2005) studied the groundwater chemistry of shallow coastal aquifers of Cochin, indicated that the quality was found to be deteriorated. In reference to Hill-Piper trilinear diagram, some of the dug wells were characterised by high amount of sodium and chloride (>200 mg/l) indicating the influence of sea water intrusion. It is also reported that the presence of E. coli in all groundwater sources [11].

The trace metals are considered as the most harmful pollutants because of their non-biodegradability and their potential to cause adverse effects on humans and the environment, produced by natural and anthropogenic activities. Aquifer contamination by trace metals has become a prominent problem in the present situation. A systematic hydrochemical study carried out in coastal aquifers, Tuticorin, Tamil Nadu, to assess groundwater quality, the results showed that total dissolved solids (TDS), sodium (Na^+), magnesium (Mg^{2+}), chloride (Cl^-), and sulfate (SO_4^{2-}) significantly high in the groundwater sources. Toxic elements such as lead & arsenic were also higher than the maximum permissible limits of drinking water quality standards [20].

The higher concentration of fluoride in groundwater is linked with igneous and metamorphic rocks. However, some anthropogenic activities such as use of phosphatic fertilizers, pesticides and sewage and sludges, depletion of groundwater table will enhance the chances of concentration by fluoride in groundwater. [21]. Fluoride contamination of hard rock aquifer of Palghat district was reveals the intensive and long-term irrigation, comparatively low rainfall, an alkaline environment, longer residence time of water in the aquifer zone and a low rate of dilution are favourable factors for the dissolution of fluorine-bearing minerals in groundwater [22].

In rural areas, most of the people dependent on traditional groundwater systems for water to meet their daily needs. The occurrence and availability of groundwater vary considerably from place to place within the state depending on the existing climatic, geomorphological and hydrogeological conditions. As the demand of water increasing day by day, while the availability of water resources is decreasing gradually by the erratic monsoon. Sustainable utilization of groundwater depends on the constant supply with sustained yield and fresh water quality. In India, the development and use of these groundwater sources has enormous potential with respect to the time of economic development. But the exponential growth of population and injudicious use water, facing tremendous pressure on this natural resource. In areas, where withdrawal of groundwater is more than their recharge, diminishes the resource through decline in the yield and productivity of wells, invasion of salt water and quality degradation.

1.4 Review of Literature

A study conducted on groundwater salinity of the shallow aquifers in the central Kerala, suggested that salt-water encroachment into shallow aquifers can be minimized by construction of tidal barriers [23]. A groundwater quality survey has been carried out along the coast of Visakhapatnam to assess the phenomena in the groundwater aquifer. The results suggest that the brackish nature of the groundwater sources was not only by the seawater influence, but also the hydrogeochemical process. The combined effect of seawater and urban wastewaters deteriorates the quality of groundwater in certain locations, where they lies near to the coast [24].

Major ion chemistry of groundwater sources around sub-urban city of Chennai was studied by Kumaresan and Riyazuddin (2006), found that most of the groundwater sources in the city were unsuitable for irrigation purposes evidenced by USSL diagram or Wilcox diagram. Hill-Piper trilinear plots were showed NaCl type water during pre-monsoon, but it changed to Ca-HCO_3 type because of the increased solubility of calcium and magnesium minerals during monsoon season [25]. Seasonal variation of groundwater quality of agriculture flourished region of Guntur district was carried out to find the suitability for drinking and irrigation use. Most of the groundwater sources are not suitable for irrigation purposes, supported by irrigation parameters. This may be attributed by the leaching of salts and ions from land surfaces [26].

Preliminary post-tsunami water quality survey was conducted in Phang-Nga Province, reveals that both surface water and groundwater were deteriorates its quality very much and need improvement [27]. Physico-chemical evaluation of groundwater sorces of Bantwal Taluk, south-western Karnataka was carried out to find the determination of suitability for irrigation [28]. The hydrochemical evolution in the Cretaceous-Eocene limestone aquifer are controlled by carbonate equilibria, silicate weathering reactions, limited mixing with saline water, and ion exchange [29].

A GIS based groundwater quality study was carried out in Sunamganj of Bangladesh to check the irrigation and drinking uses. The results revealed that the total hardness was found to be very high at Bishamvarpur. According to GIS, it classified the groundwater into classI, classII and class III based on the suitability of irrigation [30]. A study comprised the suitability of groundwater for drinking, irrigation, and industrial use indicate that, most of the groundwater is not fit for drinking purposes, due to the presence of high amount of chemical constituents. This may be attributed by the lithology of the study area [31].

Physico chemical analysis of groundwater of selected area of Gazipur city is found that, the water is nearly suitable for drinking purpose when compared with ICMR standards but it is recommended that groundwater analysis should be carried out from time to time to monitor the rate and kind of contamination along with analysis of DBPs to corroborate the study [32]. Physico-chemical characteristics of groundwater quality in Bhopal was found that the extent of pollution occurred due to over exploitation of groundwater, urbanization and anthropogenic activities [33].

The groundwater study of shallow and deep aquifers of Dhampur tehsil area reveals that the groundwater quality varies with depth and time span in shallow and deep aquifers and the level of the pollution is maximum in shallow aquifers, unfit for human consumption [34]. Groundwater quality in an industrial area of Bangalore using water quality index (WQI) was studied by Charmaine Jerome and co-worker found that, the study zone had a higher WQI value indicates the deterioration in the quality of water [35].

A groundwater quality assessment was various villages of Kadi, Tehsil districts of Gujarat found that a positive correlation between pH and fluoride, which indicate that high alkaline nature of the water promotes leaching of fluoride and thus affects the concentration of fluoride in groundwater [36]. Two distinct geochemical environments of inner and outer coastal plains were studied to represent a range of conditions found that outer coastal plain waters are more reducing than inner coastal plain waters. Low dissolved oxygen, nitrate concentrations and high iron (Fe) concentrations indicate that ferric iron (Fe^{3+}) is an important electron acceptor in the outer coastal plain, while in the inner coastal plain, dissolved O_2 act as the terminal electron acceptor. The presence of aerobic conditions in the inner coastal plain setting makes this region is more subjected to contamination by constituents which are more stable in these conditions. Herbicides and their transformation products were frequently detected in this zone at low concentrations. Shallow water table depths are also posing increased risk of detection of pesticides that degrade rapidly in the unsaturated zone [37].

The nitrate pollution in the coastal aquifers of Korinthos Prefecture was assessed by Voudouris and collegues (2004), indicate that the nitrate was exceeds the maximum permissible limit [38]. The quality deterioration was contributed by crop over fertilization and use of abandoned shallow wells as septic tanks, inducing increased nitrogen compound concentrations. Quality of groundwater of Peddavanka watershed, a semi-arid region of south India is evaluated for its suitability for drinking and irrigation purposes for post and pre-monsoon seasons. The study identifies that, all constituents of groundwater was high during the post-monsoon period [39].

Sarath and their co-workers studied the groundwater suitability of coastal stretch of Alappuzha for drinking and irrigation purpose. The study revealed that the groundwater is not fit for drinking purpose with respect to pH, EC, Ca^{2+}, Mg^{2+}, Na^{+} and Cl^{-}. However, the water is suitable for irrigation except a few locations and the groundwater is characterized by Ca–Mg–HCO3 type. Another research work on the hydrogeochemical characteristics of groundwater in phreatic aquifers of Alleppey district was carried out [40]. In this study, the researcher reported that, the water is saline type and the hydrogeochemistry of groundwater in the phreatic aquifer system is controlled by mineralogy and marine aerosols.

Groundwater quality of coastal aquifers in the Chennam-Pallippuram Panchayath of Alappuzha district, Kerala have been extensively monitored to assess the domestic and irrigation suitability of groundwater. Study reveals that chemical composition is controlled by precipitation rather than weathering of rocks. The water is suitable for agricultural usage according to irrigation parameters [41]. A study on shallow groundwater sources of a hard rock terrane of Tinneveli found that, the chemistry was controlled by mixing of connate water with fresh water, dissolution of silicate minerals and readily leachable salts to a certain extent [42].

The groundwater in the study area is chemically potable, except in few locations having the presence of iron. However, it can be used for both domestic and agricultural purposes. The nutrient contributions from on-site waste disposal systems (OSDS) to the groundwater was conducted in Buttermilk Bay of Massachusetts, showed that of nitrogen to the bay was attributed to onsite disposal systems [43].

Studies on the removal of surface and groundwater was carried out by many researchers. Ion exchange and biological denitrification are more efficient than reverse osmosis. However the ion exchange is more viable for groundwater and biological denitrification is most suitable for surface water [44]. Hydrochemical evaluation of groundwater sources of northeastern Yucatan, Mexico was studied to assess the drinking water quality. It reveals that several parameters exceed the Mexican Drinking Water Standards (MDWS). But they do not not pose any significant effect on health, can be used as drinking water [45].

The occurrence of pesticides in shallow aquifers of United States was point out that urban and agricultural area affected by pesticides. Although the concentration is below the MCL. Hoever , only one pesticide atrazine exceeds its limits [46]. Source identification of sodium and chloride contamination in natural waters carried out is known [47]. The results explains that the input of Na^+ and Cl^- is coming from rock salt in the northern U.S. Seawater intrusion is the main source along the coastal areas; animal and human waste in rural areas; leaking landfills and natural saline seeps in other areas. Hydrogeochemical assessment of groundwater quality of south-eastern part of the Ranga Reddy district was indicates that the major ions are exceeding the permissible limits and comprising Ca^{2+}, Mg^{2+}, Na^+, K^+, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^-, Cl^- and F^-. Ion such as NO_3^-, Cl^- and F^- are mainly controlled by the extensive use of fertilizers and discharge of municipal wastes into the open drainage system of the area [48].

According to Suhendrayatna (2009) Water quality in the selected area has shown that the surface water was contaminated due to the tsunami.

TDS, TSS, acidity and salinity were high in the affected areas indicating saline water intrusion into surface water tables. Dugwells also showed very high concentration of heavy metals ions like Mn, Pb, Cu, Cd, Fe, and Zn compared to the reference points. No mercury content was reported in all samples of the study area [49]. Major ion chemistry of Tumkur amanikere lake watershed groundwater was studied by found that the type of the water predominant in the study area is Ca-Mg-Cl type. The region is comprises of igneous rocks with crystalline nature [50]. Influence of anthropogenic activities such as intense agricultural practices like application of fertilizers, irrigation practices, urban and industrial waste discharge influence the quality of the groundwater [51].

Q-mode cluster analysis of the Mio-plio-Quarternary aquifer in the Ain Azel area of Algeria resulted in three distinct water types. R-mode cluster analysis found that water rock interaction is the major source of contamination of groundwater in the area. Geo chemical modelling results showed that carbonates, gypsum, halite, carbon dioxide (gas) and chlorite were dissolving whereas Ca-montmorillonite, gibbsite, like, K-mica, kaiolinite and quartz mostly precipitating along different flow paths in the groundwater system of the area [52].

The physico chemical parameters of groundwater sources of some villages of Dag Block in Rajasthan reveals that the quality of under groundwater varies from hand pump to hand pump. Higher values in some parameters at certain hand pumps indicate the poor quality of water for drinking purpose [53]. A groundwater quality study conducted by Subba Rao *et al* (2005) in Adhra Pradesh found that brackish nature of most of the groundwaters was not due to the sea water influence, but also caused by the hydrogeochemical process. The quality of groundwater was deteriorated due to the combined effect of sea water and urban wastes waters at topographic lows close to the coast [54].

The hydro chemical characteristics of coastal aquifers in Tuticorin, Tamilnadu, indicates that groundwater are significantly degraded and suffer from extensive salinization due to anthropogenic pollution as well as sea water inputs [55]. A reported study paper demonstrates the variation in hydrochemical quality of groundwater and its evolution processes in two different seasons in the coastal alluvial aquifer of East Godavari District, Andrapradesh [56].

Izabela A Talalaj (2014) was used modified water quality index to evaluate the variability of water quality of near the land fill site [57]. A groundwater study from Krishnagiri district of Tamilnadu shows that dominantion of Mg^{2+} water type has higher F^- than Na^+ type. This is due to the reason of fluoride from the magnesium bearing minerals like biotite, homblende etc or weathering of apatite hydroxy apatites found in charnickites [58].

Groundwater hydrochemistry in Thoothukudi district of Tamilnadu showed that groundwater of the region are chiefly affected by sea water intrusion and in most of the places water is unsafe for irrigation and domestic purposes due to anthropogenic contamination due to salt pans and fertilizers [59].

A study conducted in Cudallore district of Tamilnadu, India to determine the geochemical processes occurring in the coastal aquifers. The results found that the groundwater chemistry in the study area is principally influenced by saline sources, reverse ion exchange, anthropogenic pollutants and minerals dissolution or precipitation reactions [60]. An assessment of the hydrochemical aspects of the groundwater as well as their suitability for domestic use was studied by Tijani [61]. Studies have shown that drinking water is contaminated by human or animal waste and also by the breakage of pipe lines [62]. The groundwater is getting contaminated due to leachate percolation from the dump yard site because of unscientific disposal methods, leads to various health problems [63]. Rapid industrialisation polluting the groundwater quality in Peenya industrial area of Bangalore [64].

Groundwater chemistry in Nagapattinam coastal town of Tamilnadu shown that majority of the groundwater sources have undergone the evolution towards more mineralisation along with the process of contamination [65]. Concentration of fluoride is more in deep groundwater sources, because of the water- rock interaction with fluoride bearing minerals [66]. The presence of certain degree of anions in groundwater of basaltic catchments of upper Bhatsai regions of Maharashtra indicate that the region is facing stress which could damage the water quality in near future [67]. Study of groundwater chemistry is an active area of research with respect to coastal region of Kerala for evaluation of physico-chemical characterisation in the recent years [68-77].

It is inferred that groundwater accounts for about two-thirds of the freshwater resources of the world. It is an essential and vital component of our life support system, contains wide varieties of dissolved inorganic chemical constituents as a result of chemical and biochemical interactions between water and the geological materials. The occurrence and availability of groundwater vary considerably from place to place within the state depending on the existing climatic, geomorphological and hydrogeological conditions. Coastal groundwater aquifers of Kerala are exposed to sea water intrusion intensified over the years due to over exploitation and natural coastal disasters. Large scale inundation occurred during 26th December 2004 Indian Ocean Tsunami has an example. Present study discusses the hydrochemical characteristics of shallow groundwater sources of Alappuzha and Ernakulam regions of Kerala coast, India during the period 2001-2017.

This research study discusses the hydrochemistry of two prominent coastal segments of Andhakaranazhy in Alappuzha district and Cherai in Ernakulam district. Andhakaranazhy is a coastal village, situated in Pattanakkad Panchayath under Cherthala Taluk of Alappuzha District, Kerala. It lies between 09° 44’ 50’’ N latitude and 76° 17’ 07’’ E longitude. The eastern side is covered with Vembanad Lake, one of the Ramsar sites in Kerala. Cherai coast is the northern part of Vypin island and comes under Paravoor Taluk of Ernakulam District, Kerala. It lies between 10° 14’ 22” N latitude and 76° 17’ 82” E longitude. These two coastal regions are known for freshwater shortage, affected by occasional salt water intrusion, lies below the mean sea level (MSL). Generally the water table is very shallow. Hence, the aquifer system is phreatic and composed of coastal alluvium, which constitutes with sand and clay. The coastal regions are also affected by Indian Ocean Tsunami on 26th December 2004, caused wide spread devastation and ecological damages. Tourism is the main activity takes place in the study area. Eighteen groundwater sources have been selected for the present study consists of nine shallow dug wells & two bore well in Andhakaranazhy coast and shallow dug wells & one bore well in Cherai, to identify the variability of groundwater chemistry over the years. The sampling and analysis [79-80] have been done for a period starting from January-December 2012, also in December months of 2013, 2014, 2015, 2016 & 2017.

1.5 Objectives

- To study the groundwater chemistry and monthly variation of major groundwater quality parameters of shallow groundwater sources of the study area Andhakaranazhy (Alappuzha) and Cherai (Ernakulam) during year 2012.
- To evaluate the drinking water suitability of various sources by comparing with IS &WHO standards and also to classify them using designated best use (DBU) suggested by CPCB, Government of India.
- To compute the monthly water quality index of groundwater sources by giving adequate weightage to significant water quality parameters.
- To study in detail the irrigational quality of various groundwater sources
- To establish the temporal groundwater quality variation profile of a coastal segment of Kerala in Alappuzha and Ernakulam regions over a decade (2001-2017).

- To analyse the trace element content of shallow groundwater sources.
- To evaluate the statistical relationship between the water quality parameters using Pearson correlation matrix.
- To evaluate saturation indices for studying industrial utility of various groundwater sources.
- To plot Hill-Piper Trilinear diagrams to understand the hydrochemical facies of the study area.
- To evaluate ionic ratios (sodium-chloride) and to study the major processes occurring in the study area.
- To plot ionic ratios in Gibb’s plot to study the major processes controlling the groundwater quality of the study area.

1.6 Scope of the study

Coastal regions of Kerala, particularly Andhakaranazhy and Cherai coastal segments are facing many hydrogeochemical issues when considering the existing state of groundwater sources. Only few dependable of fresh water sources are available in these areas, affected by scarcity of fresh water. Tourism and other economic developments are well flourished in the study area causing pollution load to the present water sources. A detailed study on groundwater quality analysis of the region will help us to identify the current problems facing the groundwater sources, and leads to generation of new knowledge in the field of hydro analytical chemistry and water sciences.

1.7 Hypothesis

In the bound thesis, the following hypothesis are proposed, tested and presented

Hypothesis tested in the study are: (1) *Whether there is any significant difference between mean values of various parameters in control well (CW) at different months of 2012 of Andhakaranazhy coast.* (2) *Whether there is any significant difference between mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the each month of year 2012* (3) *Whether there is any significant difference between mean values of WQI in shallow groundwater sources and control well (CW) strata in each month of year 2012* (4) *Whether there is any significant difference between mean values of various parameters in control well (CW) at different months of 2012 Cherai coast.* (5) *Whether there is any significant difference between mean values of various parameters in shallow groundwater sources of Cherai coast during the each month of year 2012* (6) *Whether there is any significant difference between mean values of WQI in shallow groundwater sources and control well (CW) strata in each month of year 2012* (7) *Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the months of December for years 2008, 2013, 2014, 2015, 2016 and December 2017.* (8) *Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Cherai coast during the months of December for years 2008, 2013, 2014, 2015, 2016 and December 2017.*

1.8 Materials & Methods

Standard analytical procedures are followed for sampling, preservation and analysis of the groundwater samples. The prominent parameters analysed are, pH value (Method: 4500 - H+): pH measurements are made with a digital pH meter (Systronics 1011 model). Electrical conductivity (Method: 2510 B): The electrical conductivity of the water samples were measured using Digital conductivity meter (Century CC 601-P N- model). Hardness (Method: 2340 C EDTA Titrimetric Method). Alkalinity (Method: 2320 B; Titration Method). Dissolved oxygen (Method: 4500 - O C; Azide Modification Method). Total Iron (Method: 3500 Fe - B; Phenanthroline Method). Chloride (Method: 4500 Cl^- - B; Argentometric method). Biochemical Oxygen Demand (Method: 5210 B; 5- Day BOD Test). BOD determination was made for the each water samples by incubating under thermostatically controlled condition for five days. Nitrate: (Method 4500 NO_3^- E; Cadmium Reduction Method). Sulphate (Method: 4500- SO_4^{2-} E; Turbidimetric Method). Phosphate (Method: 4500 – P E; Ascorbic Acid Method). Sodium (Method: 3500 – Na B) and potassium (Method: 3500 – K B) are determined by flame photometry (Elico CL 378 Flamephotometer). Total Carbon analysis (Elementar Vario TOC Cube, made in Germany, Model No.38092033). Enzyme Substrate Coliform Test (Method: 9223 B; Enzyme Substrate Test). Delayed – Incubation Total Coliform Procedure was followed to determine Total Coliform content of the water samples. Most Probable Number (MPN) method is used to estimate the concentration of viable microorganisms in a sample of water by means of replicate liquid broth growth in ten-fold dilutions. Trace Metals are analysed by Inductively Coupled Plasma/Mass

Spectrometry (ICP/MS) method. Hill-Piper-Trilinear plots were made to evaluate the water type of the study area using GW chart software. Irrigation suitability is measured by sodium percent (Na %), sodium adsorption ratio (SAR) and Kelly's ratio (KR), permeability index (PI), magnesium adsorption ratio (MAR), USSL and Wilcox diagrams. Gibb's plots were made to the chemical composition of groundwater. Corrosive behavior of the groundwater is determined by Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI). These indices values will give us an insight into the actual groundwater chemistry of the region. Sodium –chloride ratio was determines the ion exchange character of the groundwater sources. The overall water quality of the study area can understood by water quality index calculation (weighted arithmetic index method). Statistical analysis was done using Pearson's Correlation, t-test and ANOVA. These results were compared with the previous year's data April 2001, 2005 and December 2008 (Jaison, C.A., 2012).

1.9 Structure of the Thesis

The bound thesis is organised in seven chapters.

Chapter 1: Introduction

Chapter 2: Materials and Methods

Chapter 3: Evaluation of groundwater chemistry and quality along the Andhakaranazhy coast, Alappuzha, Kerala during the year 2012

Chapter 4: Evaluation of groundwater chemistry and quality along the Cherai coast, Ernakulam, Kerala during the year 2012

Chapter 5: Temporal and spatial variation of groundwater quality along the Andhakaranazhy coast, Alappuzha during the period 2001-2017

Chapter 6: Temporal and spatial variation of groundwater quality along the Cherai coast, Ernakulam during the period 2001-2017

Chapter 7: Summary and Conclusion

These chapters are followed by a brief description of future scope of the study. The chapters and their contents are presented accordingly in the following sections for precise reference.

Chapter 1 presented as a concise introduction of the thesis. It briefly introduces the topic groundwater science. This chapter also gives an overview of importance of knowledge on water resources and current water pollution problems which refers salt water intrusion and other anthropogenic pollution. It also describes the review of the literature, aim and scope of the study, hypothesis and chapter is followed by a description of the structure of the thesis.

Chapter 2 describes the methodology followed in this research study. It includes materials and methods, instrumentation, the locations of the sampling stations and their significance, sampling protocols, standard operating procedures. Analytical chemistry and hydro analytical methods followed for the determination of each parameter is briefly described. This is followed by trace elemental analysis study, TOC analysis and designated best use (DBU). Irrigation parameters such as sodium percent (Na %), sodium adsorption ratio (SAR) and Kelly's ratio (KR), permeability index (PI), magnesium adsorption ratio (MAR), USSL & Wlicox diagrams; corrosion and scaling indices such as Langelier saturation index, Ryznar stability index & aggressiveness index; ionic ratios including sodium-chloride ratio and water quality index are also briefly explained. Other specific graphical diagrams used for the study includes Gibb's diagrams, Hill-Piper- Trilinear plots and statistical tools of Pearson's correlation matrix.

Chapter 3 explains the hydrochemistry of shallow groundwater sources of Andhakaranazhy coast during the year 2012. It comprises of the results and discussions on the monthly variation of physico-chemical parameters and other interpretation methods of the shallow groundwater sources. The groundwater chemistry of the region was determined using the irrigation water quality parameters, scaling and corrosion indices, Hill – Piper – Trilinear Plots, ionic ratios, Gibb's diagrams and water quality index (WQI). It is followed by trace element study, TOC analysis, statistical study using Pearson correlation matrix and the classification of groundwater based on designated best use (DBU). The results are very prominent and can be used to know the present groundwater chemistry of the Andhakaranazhy coast, one of the water scarce region of Alappuzha district. The chapter ends with a conclusion followed by references.

Chapter 4 explains the hydrochemistry of shallow groundwater sources of Cherai coast during the year 2012. It comprises of the results and discussions on the monthly variation of physico-chemical parameters and other interpretation methods of the shallow groundwater sources. The groundwater chemistry of the region was determined using the irrigation water quality parameters, scaling and corrosion indices, Hill – Piper – Trilinear Plot, ionic ratios, Gibb's diagrams and water quality index (WQI). It is followed by trace element study, TOC analysis, statistical study using Pearson correlation matrix and the classification of groundwater based on designated best use (DBU). The results were very much useful to know the chemical composition of the groundwater along the Cherai coast, Ernakulam district.This chapter ends with conclusion followed by references.

Chapter 5 discusses the temporal variation of major groundwater quality parameters of shallow groundwater sources of the Andhakaranazhy coast intermittently for the last 12 years (2005-2017) along with the reported data of 2001. Graphical representations of 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 of water quality index (WQI), ionic ratio, Hill-Piper Trilinear plot, Gibb's diagrams, irrigation parameters and corrosion measures are presented for shallow groundwater sources of the study area in view of pre and post tsunami situations. The chapter ends up with conclusion followed by references.

Chapter 6 discusses the temporal variation of major groundwater quality parameters of shallow groundwater sources of the Andhakaranazhy coast intermittently for the last 17 years (2005-2017) together with the reported data of 2001. Interpretation of water quality index, ionic ratio, irrigation quality parameters, corrosion measures, Hill-Piper Trilinear plot for hydrochemical facies and Gibb's diagrams are critically presented for shallow groundwater sources of the Cherai coast with respect to the pre and post tsunami situations. The chapter ends up with conclusion followed by references.

Chapter 7 summarizes the major outcome of this research based on critical analysis of the findings as well as on the basis of statistical analysis of water quality parameters analysed. Present situation of groundwater along a coastal region can be useful for the identification and mitigate of water quality problems. The thesis ends with concluding remarks and a discussion on the future scope of the study, followed by list of publications.

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Chapter 2

MATERIALS AND METHODS

2.1 Introduction

This research study is focused on two prominent coastal segments of Kerala namely-Andhakaranazhy in Alappuzha District and Cherai in Ernakulam District. They were seriously affected by Indian Ocean of Tsunami on 26 December 2004 causing extensive sea water inundation and damages. At present they are subjected to fast emerging developments of tourism and fisheries. Fresh water is a scarce resource in these areas. For this study, there are 18 groundwater sources from selected locations of the two places were considered, this includes dug wells and bore wells. Eleven (11) shallow groundwater sources were chosen in Andhakaranazhy coast (8 dug wells, 2 bore wells and 1 open pond). In Cherai coast, seven (7) shallow groundwaters were taken for study (consists of 6 dug wells and 1 bore well).

2.1.1 Andhakaranazhy Coastal Segment

Andhakaranazhy is a coastal village, situated in Pattanakkad Panchayath under Cherthala Taluk of Alappuzha District, Kerala. It lies between 09^o 44’ 50” N latitude and 76^o 17’ 07” E longitude. The eastern side is covered by the Vembanad Lake, one of the recognized Ramsar sites in Kerala. Pallithode and Thykkal regions are located at the north and south end of the Andhakaranzhy coast. The name also implies the peculiarity of the coast. A sand deposition (Azhy) is usually seen formed by the continuous action of scrolling waves, where backwaters merge into the sea. Two barges, having large mechanized shutters are constructed near the north and south end of the seasonally opened sand bar. These shutters prevent the flow of saline water entering into the neighboring paddy fields of Thuravoor, Pattanakkad, Ezhupunna & Kuthiathode panchayaths, which are connected to the extended backwater system. During monsoon, excessive rainfall occasionally creates flooding in these paddy fields. To control flood, these shutters are lifts up by government authorities and water flows into the sea. It is a low land region lies below the mean sea level (MSL). Andhakaranzhy is famous for its sandy beach which draws a number of domestic and international tourists every year. This beach is also known for the religious activities like paying last rites to departed nears one as per Hindu religious system. This coast devastated during the Indian Ocean Tsunami on 26th December 2004 and many reports are available [1-5]. These giant tsunami waves destructed many human lives and affected very most of the livelihoods of the people survived. The inhabitants mainly depend on fishing for their source of income and food. This place is highly populated, isolated with estuarine water bodies in the east and hence faces the shortage in fresh water availability. People depend on groundwater sources available on a large scale to meet their daily needs. However, there are fresh water available in some of the wells, placed near to the shoreline which are too very shallow in nature. Sand mining and coir retting activities are still common there. Coast is decorated with a tall, majestic light house near the canal, which acts as a signal tower for guiding the seamen during night.

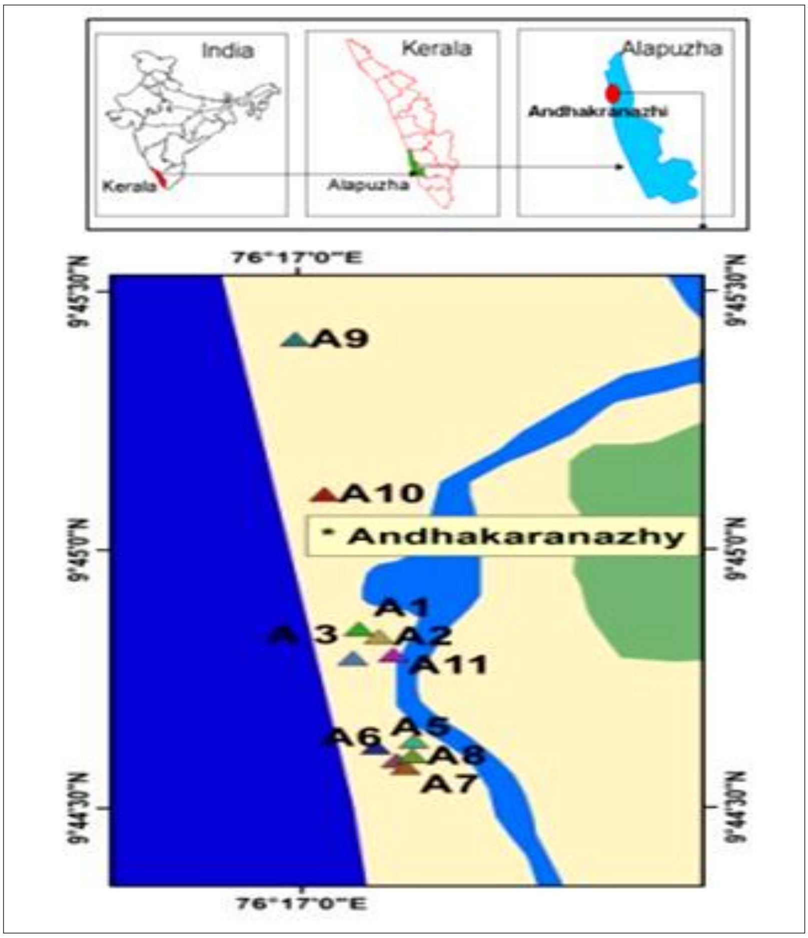


Figure 2.1: Location map of Andhakaranazhy, Alappuzha, Kerala, India, which has been subjected to inundation by 26th December 2004 Indian Ocean Tsunami

Figure 2.2: Barrage in the tidal canal at Andhakaranazhy coast, Alappuzha, Kerala, India

Figure 2.3: Sand mining near the estuary in Andhakaranazhy coast, Alappuzha, Kerala, India

(a) (b)

(c) (d)

Figure 2.4: Groundwater monitoring stations at Andhakaranazhy coast (a) & (b) dug wells (c) control well perennial fresh water source situated on the shoreline & (d) shallow open pond

Figure 2.5: Arial view of Andhakaranazhy coast from the light house

Figure 2.6: Chineese net used for fishing in backwater at Andhakaranazhy, Alappuzha, Kerala, India

2.1.2 Cherai Coastal Segment

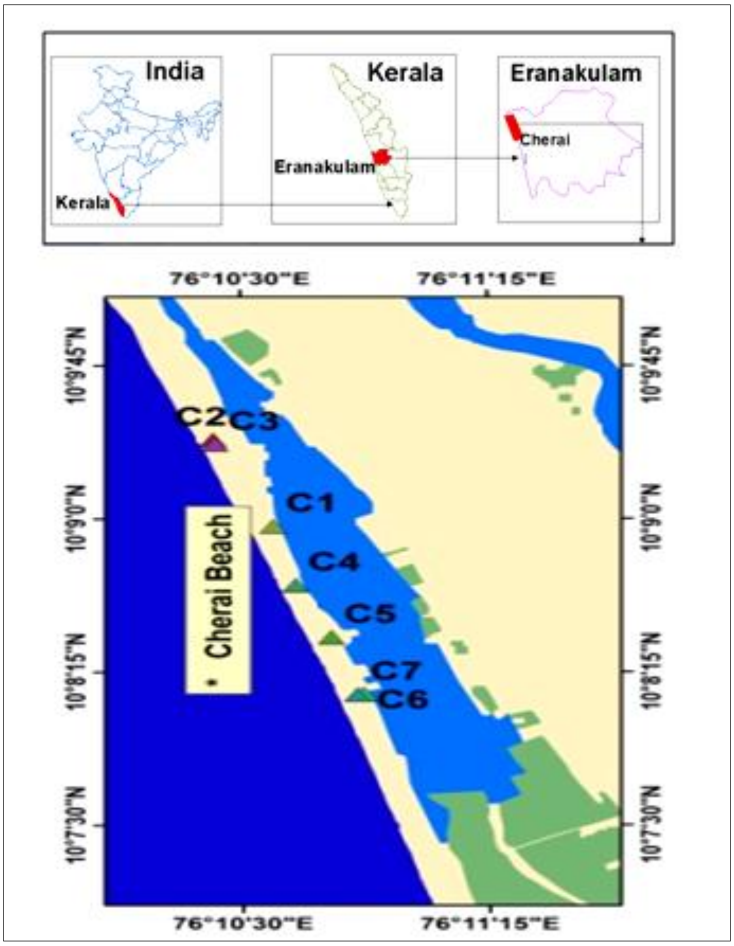


Figure 2.7: Location map of Cherai coast, Ernakulam, Kerala, India, which has been subjected to inundation by 26th December 2004 Indian Ocean Tsunami

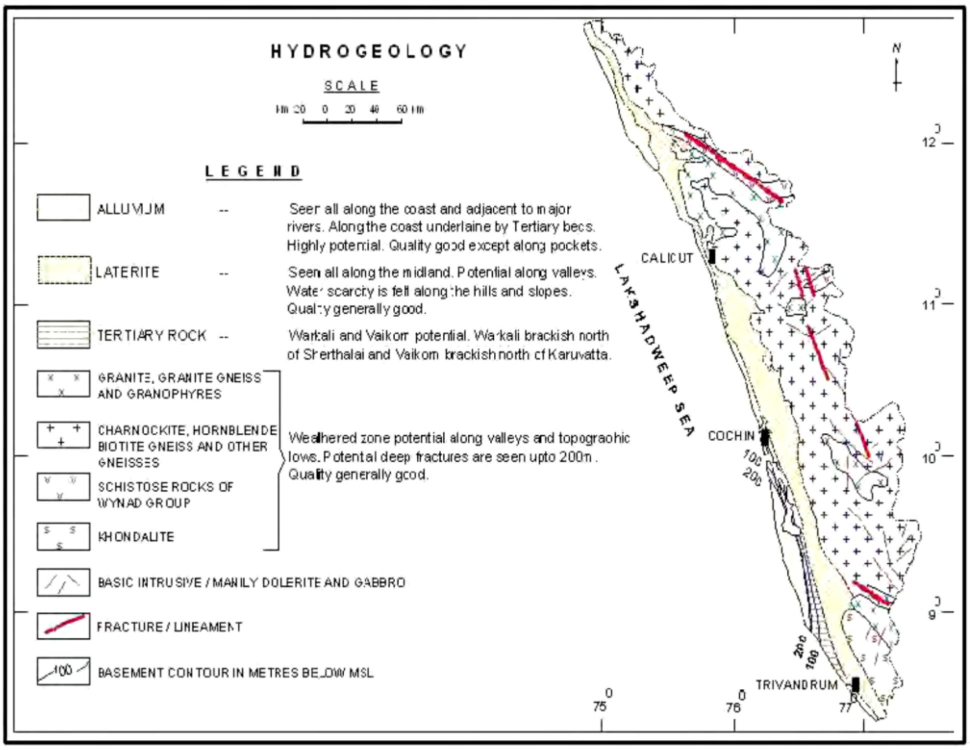
Cherai beach and nearby regions comes under Paravoor Taluk of Ernakulam District, Kerala. It lies between 10° 14' 22" N latitude and 76° 17' 82" E longitude. It is located 35 km away from Cochin under Cherai revenue village. This place is one of the Indian Ocean Tsunami affected coast of Kerala on 26th December 2004 [6,7]. This coastal area and its beach are emerged as one of the main tourist spots of Kerala, attracting many domestic and international tourists every day. This place is highly populated and fishing is their main source of income though tourism get flourished in the last decade. It is an island surrounded with backwater system of Cochin, mainly the extension of Vembanad Lake, largest lake system of Kerala. Cherai coastal region is slowly getting is under the threat of freshwater shortage, seasonally affected by salt water intrusion. The region lies below the mean sea level (MSL) and groundwater aquifers are phreatic in nature.


(a) (b)

Figure 2.8: Groundwater monitoring wells with brackish water at Cherai coast, Ernakulam, Kerala, India

2.2 Hydrogeology

The general geology of the study area indicate that recent unconsolidated alluvial deposits are underlain by the arkosic sediments and laterites of Warkalli Formation, followed by mixed chemical and clastic sediments of the Quilon Formation. These sedimentary formations are underlain by the rocks belonging to the Charnockite, Khondalite and Granites. Towards the coastal side (western part) of Alappuzha district, the Quaternary sedimentary sequence, consisting of alternate layers of sand and clay, has a total depth of 445 m at Arthungal (Lat. 09°39'32" N and Long. 76°17'59" E). Lithology of Quaternary sediments of Andhakaranazhy coast is composed of sand, clay, clay with lignite, limestone and gravel [8].



Source: CGWB Report, Faridabad

Figure 2.9: Hygrogeological map of Kerala [10]

A study conducted by Central Groundwater Board (CGWB) revealed that, Cochin and the western parts of Paravur and Aluva taluks encountered the coastal alluvium, composed of sand and clay [9]. This recent coastal alluvium is followed by Tertiary sediments. The upper most tertiary formation is Warkalli with thickness of about 80 m underlined by thick sequences of

Vaikom beds. These formation was overlayed the Precambrians of Charnockite, Khondalite and Granites. The geology and geomorphology of the study area control hydrogeochemistry of groundwater resources. Generally, the water table is very shallow. Hence, the aquifer system is phreatic and composed of coastal alluvium, which mainly constitutes with sand and clay. This coastal alluvium formation is developed from recent marine and estuarine deposits.

2.3 Geomorphology and Soil Type

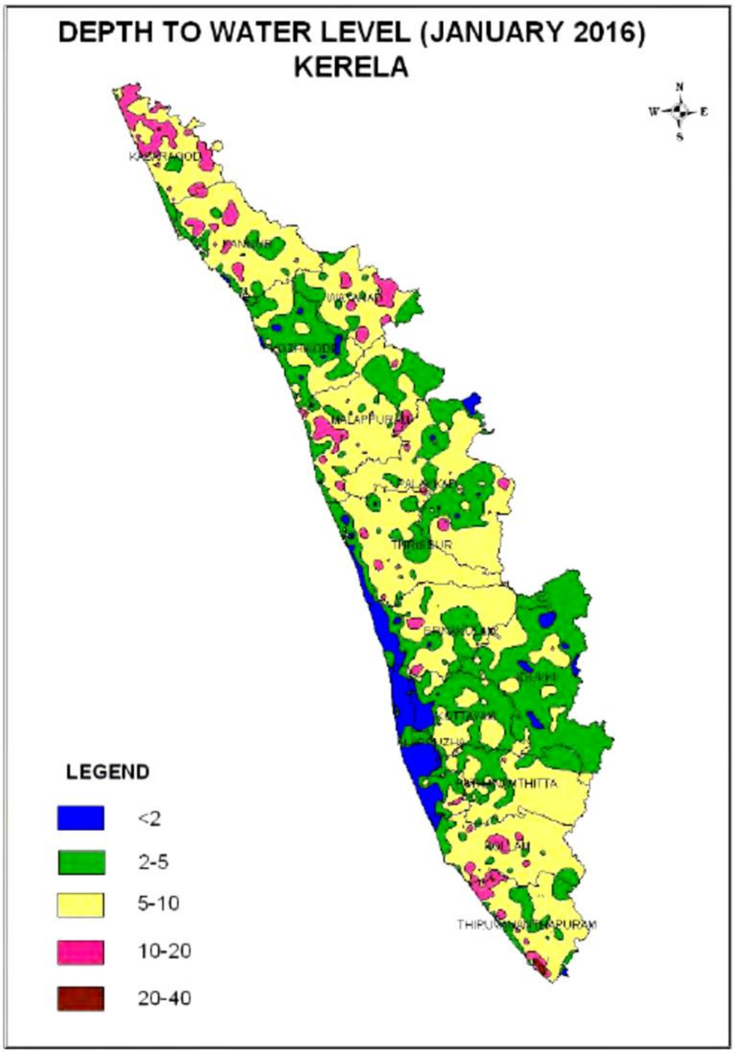
The study area lies in Alappuzha district, which is one of the well-developed and connected coastal districts in southern part of Kerala covering an area of 1,414 km^2 and is not having any reserved forests. The present study area, Andhakaranazhy lies below the mean sea level (MSL), falls under low land with soft, sedimentary rocks of origin. Typical coastal geomorphic features such as beaches, shore platforms and sand bars are the peculiarity of this region. Beach is very narrow and straight, noted for absence of extensive tidal plain and the intensive coastal erosion. Soil type of the Andhakaranazhy coast is composed of coastal alluvium, having low organic content and fertility level [8].

2.4 Climate and Rainfall

The study area experiences a humid tropical climate and the region receives two seasons of monsoon: southwest monsoon season (June–Sept); and northeast monsoon season (Oct–Dec). Annual average rainfall of Alappuzha district is 2965.4 mm [8].

2.5 Depth to Water Level

Groundwater level data recorded in the wells of Kerala were less than 2m below ground level (bgl) during the month of January 2016.



Source: National data Centre, CGWB, Faridabad

Figure 2.10: Map showing the Depth to water level in the state of Kerala (January 2016) [11]

2.6 Sample Collection and Preservation

Groundwater samples collected from 18 locations of Andhakaranazhy and Cherai; this includes fourteen (14) dug wells, three (3) bore wells and 1 open pond. The sample collection, preservation and analysis were done as per the standard procedures recommended by APHA as per standard [12].

Table 2.1: Standard analytical methods and instruments used for the analysis of groundwater quality samples

Water Quality Pareter	**Analytical method**	**Instrument Used/Method**
pH	pH (4500 H$^+$ B: APHA) : Electrometric Method	SCIENTIFIC TECH; model ST2025 Digital pH meter
Redox Potential (Eh)	(2580 B: APHA): Electrometric Method	SCIENTIFIC TECH; model ST2025 Digital pH meter
EC(mS/cm)	Digital conductivity meter	DELUX Conductivity Meter 601.
TA(mg/L)	Titrimetric method	Titrametry
DO(mg/L)	Azide modification method	Titrametry
BOD(mg/L)	Azide modification method	Incubator GAMBAK ENTERPRIES MADRAS 94
TH(mg/L)	EDTA titration	Titrametry
Ca^{2+}(mg/L)	EDTA titration	Titrametry
Mg^{2+}(mg/L)	EDTA titration	Titrametry
TDS(mg/L)	Gravimetric method	LABLINE Laboraory Oven.
Na^+(mg/L)	Flame photometric	ELICO CL378 Flame photometer.
K^+(mg/L)	Flame photometric	ELICO CL378 Flame photometer.
Cl^-(mg/L)	Argentometric titration	
SO_4^{2-}(mg/L)	Turbidimetric method	Varian model Cary 50 c UV
NO_3^-(mg/L)	UtravioletSreening method	Varian model Cary 50 c UV
PO_4^-(mg/L)	Ascorbic acid method	Varian model Cary 50 c UV
Total Iron(mg/L)	Phenanthroline method	Varian model Cary 50 c UV

Plastic cans of one (1) liter capacities were used to collect and stored the groundwater samples. For analyzing dissolved oxygen, DO and BOD bottles were used for collecting the groundwater samples. 100 mL plastic cans were used for the collection and storage of water samples for the analysis of iron (Fe). All the containers were washed thoroughly rinsed with distilled water and then with sample prior to the collection. The samples were collected using a water sampler. Groundwater samples were collected during every month of the year 2012 specifically, thereafter every month of December for the subsequent years 2013, 2014, 2015, 2016 and 2017. These results were compared with previous secondary data available for the period April 2001, 2005 and December 2008, being 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 [1-7, 13-16].

2.7 Experimental Procedure

Analytical procedures followed for the analysis of groundwater samples are precisely described.

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

Apparatus: pH meter with electrode (Digital pH meter 335 Systronics 1011). **Reagents and Solutions:1)** Buffer solution pH 4.60: Prepared by mixing 200mL acetic acid (1mol/L) is mixed with 100 mL sodium hydroxide (1 mol/L) and 700 mL water.2) Buffer solution, pH 7.0 a) 9.078 g potassium dihydrogen phosphate (AR) was dissolved in water and the volume made up to 1L. b) 11.88g disodium hydrogen phosphate (AR) were dissolved in water and the volume made up to 1L, 2 parts of solution **a** and 3 parts of solution **b** are mixed. Buffer solution pH=9.0 **a)** 12.40g of boric acid and 100mL sodium hydroxide, (1 mol/L) are dissolved in water and the volume made up to 1L.**b)** Hydrochloric acid, 0.1mol/L.8.5 parts of **a** and 1.5 parts of **b** are mixed.

Calibration and measurement: Before performing potentiometric pH measurements new or dry glass electrodes are allowed to stand in water or KCl solution, (3 mol/L), for several days. The calibration is carried out using two standard buffer solutions. The sample temperature is determined at the same time and is entered into the meter to allow for a temperature correction. The reading is taken after it has remained constant for about 1 minute. **Interfering factors:** At pH values above 10, alkali resistant electrodes must be used. Oil in the sample can impair sensitivity. In this case the electrode must be cleansed with soap, then with distilled water, dilute HCl and again with distilled water.

2.7.2 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). For most applications, a meter scale readable to ±1400 mV is sufficient.

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 measurement.

2.7.3 Electrical Conductivity (2510b: APHA): Conductivity method

Principle: Conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. Conversely molecules of organic solution that do not dissociate in aqueous solution conduct a current poorly. **Apparatus:** Digital conductivity meter (CENTURY CC 601-P N) is used for the analysis. **Reagents:** Standard potassium chloride solution 0.0100M: Dissolved 745.6mg of anhydrous potassium chloride (AR) in conductivity water and diluted to 1 litre at 25ºC.

Calibration and measurement: Before measurement begins, the container and the cell were rinsed several times with the solution to be tested. The measurements were carried out at 25^{o} C temperature correction has to be calculated otherwise. To check the instrument, the cell constant is measured from time to time using standard KCl. After measuring oil-containing samples, the electrode is cleaned thoroughly with acetone.

2.7.4 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 h and cool in a desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1litre volumetric flask, fill flask to the mark with distilled water, and dissolve and mix reagent. It is not allowed to keep longer than 1 week.

b. Hydrochloric acid*,* 0.1N*:* Prepare acid solution of approximate normality as indicated under

c. Methyl Orange indicator solution. **Procedure:** HCl solution was standardized using 0.05N Na_2CO_3 solution. 50 mL samples were taken in 250mL conical flask, and two drops of methyl orange indicator solution were added. The sample was titrated against standard HCl, the end point was the color change from yellow to red. **Calculation:** Alkalinity in mg $CaCO_3$/L = normality of HCl x volume of HCl consumed x 50,000/vol of sample.

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

Principle: DO depend on the physical chemical and biochemical activities in the water body. The iodometric test is the most precise and reliable titrimetric procedure. It is based on the addition of divalent manganese solution followed by a strong alkali. DO oxidizes $Mn(OH)_2$ to higher valency levels. In the presence of iodide ions in an acidic solution the oxidized Mn reverts to divalent state, with the liberation of iodine equivalent to original DO. Iodine is then titrated against standard sodium thiosulfate. Azide modification removes nitrite interference common in biological effluents. In cases of ferric ions exceeding 5mg/L added potassium fluoride or used 85% phosphoric acid instead of sulfuric acid. *Sampling:* Did not agitate the source. Let the water overflow three times the volume of the DO bottle. Recorded sample temperature. All chemicals were added together. Protected from sunlight thereafter. **Apparatus:** 300 mL capacity of BOD bottles with ground glass stoppers. Cleaned bottles with a good detergent rinsed thoroughly and drained before use. **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-Dissolved 500 g NaOH or 700 g KOH and 135 g NaI or 150 g KI in 1L. Added 10 g NaN_3 in 40 mL distilled water and transferred to the alkaline KI solution. b) Conc. H_2SO_4. c) Starch solution: added 2g starch to 100 mL of boiling distilled water. Added 0.2 g salicylic acid. d) Sodium thiosulfate: Dissolved 6.205 g $Na_2S_2O_3.5H_2O$ in distilled water. Added 0.4g solid NaOH and dilute to 1L. This solution was standardized by standard potassium dichromate solution. e) Standard potassium dichromate solution, 0.025N: Dried $K_2Cr_2O_7$ at 103°C for 2 hours. Dissolved 1.226 g dichromate in 1 L. 20 mL dichromate solution was taken in a conical flask, 10 mL of 5% KI is added to the same followed by 3mL conc. H_2SO_4. Titrated against thiosulphate and added a few drops of starch when the color fades. End point is the disappearance of color.

Procedure: To the sample collected in a BOD bottle of 300 mL capacity, add 1 mL of Winkler A, followed by Winkler B. The bottle was shaken well. 1mL of conc. Sulfuric acid was added liberating iodine. Iodine was estimated against standard thiosulfate. When the color faded to pale yellow, one or two drops of starch indicator is added. Disappearance of blue color was the end point.

DO/L = strength of thiosulfate*mL of thiosulfate*8*1000*298/ (300*300).

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

Principle: BOD determination is an empirical test in which standard laboratory procedures are used to determine the relative oxygen requirements of wastewaters effluents and polluted waters. BOD values cannot be compared unless the results have been obtained under identical test conditions. To reduce the change in oxygen demand between sampling and testing, keep the samples at or below 4°C and begin incubation not more than 24 hours after the sample is collected. **Apparatus:** a) Incubation bottles: 300 mL capacity of BOD bottles with ground glass stoppers. Cleaned bottles with a good detergent rinsed thoroughly and drained before use. b) Incubator: Labline Bacteriological Incubator set at 27°C. **Reagents:** 1) Distilled water, free of copper chloramines chlorine, caustic alkalinity and organic material. 2) Phosphate buffer solution: Dissolved 8.5g KH_2PO_4, 21.75g K_2HPO_4, 33.4g $Na_2HPO_4.7H_2O$ and 1.7 g NH_4Cl in about 500mL distilled water and dilute to 1L. The pH of this buffer should be 7.2 without adjustment. 3) Magnesium sulphate solution: Dissolved 22.5 g $MgSO_4$. $7H_2O$ in distilled water and diluted to 1L. 4) Calcium chloride solution: Dissolved 27.5g anhydrous $CaCl_2$ in distilled water and dilute to 1L. 5) Ferric chloride solution: Dissolved 0.25g $FeCl_3.6H_2O$ in distilled water and diluted to 1L. 6) Seeding: Seeding was unnecessary in natural water samples. 7) Acid and alkali solutions 1N.

Procedure: Preparation of dilution water: Saturated the dilution water with DO using aerators or by shaking. Placed the desired volume of dilution water in a suitable bottle and add 1mL each of phosphate buffer, magnesium, calcium and iron salt solutions per liter. 1) Pretreatment of sample: Acidic or alkaline samples were neutralized with 1N H_2SO_4 or NaOH . 2) Dilution:

Suitable amounts of sample were directly measured into the BOD bottle of known capacity with a large tip volumetric pipette and the bottles were filled with sufficient dilution water to permit the insertion of stopper without leaving air bubbles. Two bottles of the same dilution were prepared, one for incubation and the other for the determination of the initial DO in the mixture. Stoppered tightly and incubated for 5 days at 20°C, with water seal in the flared mouth of the bottle. 3) Glucose glutamic acid check: The BOD test is a bioassay procedure; hence the results obtained are influenced greatly by the presence of toxic substances or the use of poor seeding material. Distilled water is frequently contaminated with toxic substances, often with copper. The quality of the dilution water the effectiveness of the seed and the technique of the analyst should be checked from time to time by using pure organic compounds having a known BOD. Prepared a standard solution containing 150mg/L each of regent grade glucose and glutamic acid that have been dried at 103°C for 1 hour. Pipetted 5 mL of this mixture and fill with dilution water to the neck of the BOD bottles. Found the initial DO and incubated at 20°C for 5 days and final DO was evaluated. The value varies between 210 and 240 depending on the seed.

$$BOD_5\,(mgO_2/L) = \text{(initial DO-final DO) dilution factor}$$

2.7.7 Hardness (2340 C: APHA): EDTA Titrimetric Method

Principle: Ethylene diamine tetra acetic acid (EDTA) and its sodium salts form a chelated soluble complex when added to a solution of certain metal ions. If a small amount of a dye such as Erichrome Black T is added to an aqueous solution containing Ca and Mg ions at a pH of 10 the solution will become wine red. If EDTA is then added as a titrant Ca and Mg will be complexed. When sufficient amount of EDTA has been added the solution becomes blue, this is the end point of titration. A small amount of complexometrically neutral magnesium salt of EDTA is added to the buffer to yield a satisfactory end point of titration. A limit of 5 minutes is set for the duration of titration to minimize $CaCO_3$ precipitation. **Apparatus:** Pipettes-volumetric, Flasks-volumetric 250 mL, Burettes- borosilicate glass 50 mL. **Reagents:** a) Buffer solution was prepared by the methods. Dissolved 16.9g ammonium chloride in 143 mL conc. Ammonium hydroxide, added 1.35g of magnesium salt of EDTA and diluted to 250 mL with distilled water. (If the magnesium salt of EDTA was not available, dissolved 1.179g of disodium salt of EDTA and 780mg $MgSO_4$ $.7H_2O$ in 50mL distilled water. This solution was added to 16.9g NH_4Cl and 143 mL conc. NH_4OH and diluted to 250 mL with distilled water). b) Eriochrome Black-T indicator: Mixed together 0.5 g dye and 100g NaCl to prepare a dry powder mixture. c) Standard EDTA titrant; 0.01M Weighed 3.723g analytical reagent grade disodium salt of EDTA and dissolved in distilled water and made up to 1L.Store in polyethylene or Pyrex bottles. Compensated for gradual deterioration by periodic re-standardization. d) Standard Calcium solution for EDTA standardization: Weighed 1.0g anhydrous $CaCO_3$ pure of heavy metals alkalis and magnesium, into a 500mL Erlenmeyer flask. Place a funnel in the neck of the flask and add, a little at a time, 1:1 HCl (50% HCl) until $CaCO_3$ had dissolved. Added 200 mL distilled water and boiled to expel CO_2. Cooled and added a few drops of methyl red indicator and adjusted to the intermediate orange red color by adding 3N NH_4OH or 1N HCl. Transferred to a 1L volumetric flask and fill to the mark with distilled water. This contains 1.00mg $CaCO_3$/100mL.

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.

2.7.8 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. Prepared it by mixing 200mg murexide with 100g solid NaCl and grinding. Titrated immediately after adding the indicator because it is unstable under alkaline conditions. 2) Sodium hydroxide buffer, 1N.

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

Calculation: Hardness as mg $CaCO_3$ /L= Strength of EDTA x Vol of EDTA consumed x100x 1000/mL of sample taken.

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

Magnesium may be estimated as the difference between hardness and calcium as $CaCO_3$ if interfering metals are present in non interfering concentrations in the calcium titration (Section 3500-Ca.B) and suitable inhibitors are used in the hardness titration (Section 2340C). Mg/L = [total hardness (as mg $CaCO_3$/L) − calcium hardness (as mg $CaCO_3$/L)] × 0.243.

2.7.10 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. Minimum detectable concentration: Better flame photometers or atomic absorption spectrometers operating in the emission mode can be used to determine sodium levels approximating 5 μg/L. **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. **Reagents:** To minimize sodium contamination, store all solutions in plastic bottles. Use small containers to reduce the amount of dry element that may be picked up from the bottle walls when the solution is poured. Shake each container vigorously to wash accumulated salts from walls before pouring solution. *Reagent water:* Use reagent water to prepare all reagents and calibration standards, and as dilution water. Stock sodium solution: Dissolve 2.542 g NaCl dried at 140°C to constant weight and dilute 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). Use this intermediate solution to prepare calibration curve in sodium range of 1 to 10 mg/L. Standard sodium solution: Dilute 10.00 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: Because of differences between makes and models of instruments, it is impossible to formulate detailed operating instructions. Follow 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. b) Direct-intensity measurement: Prepare a blank and sodium calibration standards in stepped amounts in any of the following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Determine emission intensity at 589 nm. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Construct a calibration curve from the sodium standards. Determine sodium concentration of sample from the calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy.

Calculation: For direct reference to the calibration curve:
mg Na/L = (mg Na/L in portion) × D

Where, D = dilution ratio.

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

Principle: Trace amounts of potassium can be 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. **Reagents:** To minimize potassium pickup, store all solutions in plastic bottles. Shake each container thoroughly to dissolve accumulated salts from walls before pouring. a) Reagent water: See Section 1080. Use this water for preparing all reagents and calibration standards, and as dilution water. b) Stock potassium solution: Dissolve 1.907g KCl dried at 110°C and dilute to 1000 mL with water; 1 mL = 1.00 mg K. c) Intermediate potassium solution: Dilute 10.0 mL stock potassium solution with water to 100 mL; 1.00 mL = 0.100 mg K. Use this solution to prepare calibration curve in potassium range of 1 to 10 mg/L. 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: Because of differences between makes and models of instruments, it is impossible to formulate detailed operating instructions. Follow 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 in any of the following applicable ranges: 0 to 1.0, 0 to 10, or 0 to 100 mg/L. Determine emission intensity at 766.5 nm. Aspirate calibration standards and samples enough times to secure a reliable average reading for each. Constructed a calibration curve from the potassium standards. Determined potassium concentration of sample from the calibration curve. Where a large number of samples must be run routinely, the calibration curve provides sufficient accuracy.

Calculation: For direct reference to the calibration curve:
mg K/L = (mg K/L in portion) × D

Where: D = dilution ratio.

2.7.12 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: Dissolved 50g K_2CrO_4 in a little distilled water. Added silver nitrate solution until a definite red precipitate was formed. Let stand for 12 hours, filtered and diluted to 1L with distilled water. 2) Standard silver nitrate solution, 0.0141N. Dissolved 2.395 g $AgNO_3$ in distilled water and diluted to 1000mL. Standardized against 0.0141 N NaCl. Stored in a brown bottle. 3) Standard sodium chloride, 0.0141N: Dissolved 824.1 mg NaCl dried at 140^{o}C for 24 hrs. in chloride free water and dilute to 1000mL. 4) Special reagents for the removal of interference: a) Aluminiun hydroxide suspension: Dissolved 125g aluminium potassium sulfate in 1L distilled water. Warmed to 60^{o}C and added 5 mL con. NH_4OH slowly with stirring. Let stand for 1 hour. Washed the precipitate 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. If the sample was highly colored added 3 mL Al $(OH)_2$ suspension mixed, and let it settle. Filtered washed and combined filtrate and washing. If sulfide thiosulfate or sulfite was present, added 1mL H_2O_2 and stirred for 1 minute. Directly titrated the samples in the pH range 7 to 10. Adjusted the pH range if necessary. Added 1mL K_2CrO_4 indicator solution. Titrated with standard silver nitrate to a pinkish yellow end point. Standardized silver nitrate titrant and established the reagent blank using distilled water.

Calculation: Chloride, mg/L = strength of silver nitrate x mL. of silver nitrate x 35,450/mL. of sample.

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

Procedure: Measured 100mL sample into an Erlenmeyer flask. Added 20mL buffer solution and mixed by stirring apparatus. Added a spoonful of barium chloride crystals. After stirring the readings are taken in a spectrophotometer at 420 nm and measured turbidity at 5 ± 0.5 min.

2.7.14 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 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, for use at 220 nm and 275 nm with matched silica cells of 1-cm or longer light path. **Reagents:** a) Nitrate-free water: Use redistilled or distilled, deionized water of highest purity to prepare all solutions and dilutions. b) Stock nitrate solution: Dry potassium nitrate (KNO_3) in an oven at 105°C for 24 h. Dissolve 0.7218 g in water and dilute 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: Dilute 100 mL stock nitrate solution to 1000 mL with water; 1.00 mL 10.0 g NO_3^- -N. Preserve with 2 mL $CHCl_3$/L. This solution is stable for 6 months. d) Hydrochloric acid solution, HCl, 1N.

Procedure: Treatment of sample: To 50 mL clear sample, filtered if necessary, add 1 mL HCl solution and mix thoroughly. Preparation of standard curve: Prepare 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. Treat NO_3^- standards in same manner as samples.

Spectrophotometric measurement: Read absorbance or transmittance against redistilled water set at zero absorbance or 100% transmittance. Use 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.

2.7.15 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: 10 μg/L. **Apparatus:** Spectrophotometer with infra-red photo tube for use at 880 nm. **Reagents:** a) Sulfuric acid solution, 5N: Diluted 70 mL conc. H_2SO_4 with distilled water to 500 mL. b) Potassium antimonyl tartrate solution: Dissolved 1.3751g potassium antimonyl tartrate in 400 mL distilled water in a 500mL volumetric flask and diluted to volume. Store in a glass stoppered bottle. c) Ammonium molybdate solution: dissolved 20g ammonium molybdate tetra hydrate in 500mL distilled water. Stored in a plastic bottle at 4^oC. d) Ascorbic acid, 0.1M; Dissolved 1.76 g ascorbic acid in 100mL-distilled water. The solution is stable for about one week at 4^oC. e) Combined reagent: Mixed the above regents in the following proportions for 100mL of the combined regent. 50mLof 5N H_2SO_4, 5mL potassium antimonyl tartrate solution, 15mL ammonium molybdate solution and 30 mL ascorbic acid solution. Mixed well after the addition of each reagent. If turbidity forms 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 in distilled water 219.5g anhydrous potassium dihydrogen phosphate, KH_2PO_4 and diluted to 1000 mL. 1mL = 50micro gram PO_4-P. g) Standard phosphate solution: Diluted 50.0 mL stock phosphate solution to 1000 mL with distilled water. 1 mL= 2.50 micro gram.

Procedure: Treatment of the sample: Pipetted 50 .0 mL of the sample into an acid washed and dried 125mL Erlenmeyer flask. Added one drop of phenolphthalein indicator and if there is color development neutralize the pH with 5N H_2SO_4. Added 8 mL combined reagent and mixed well. After at least 10 minutes and not longer than 30 minutes measured the color absorbance at 880 nm. Used a distilled water blank with combined reagent.

2.7.16 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. Washed all glassware with concentrated HCl and rinse with distilled water. 3) Separating funnels 125 mL with ground glass or Teflon stopcocks and stoppers. **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 800mL distilled water. 5) Phenanthroline solution: Dissolved 100mg 1, 10 phenanthroline monohydrate in 100 mL distilled water. Add 2 mL of conc. HCl. 6) Stock iron solution: Added slowly 20mL conc. H_2SO_4 to 50mL distilled water and dissolve 1.404g Fe $(NH_4)_2(SO_4)_2.6H_2O$. Add 0.1N $KMnO_4$ drop wise until a faint pink color persists. Dilute to 1000 mL with iron free distilled water. Each 1mL will contain 200 micro grams Fe. 7) Standard iron solution: Pipette 50mL stock solution into a 1L volumetric flask and diluted to the mark with iron free distilled water. 1mL contains 10 micro grams Fe.

Procedure: Preparation of calibration curve. Pipetted 10.0, 20.0, 30.0, 40.0 and 50.0 mL of standard iron solution into 100 mL volumetric flasks. Mixed the sample thoroughly and measure 50.0mL into a 125 mL flask. Added 2 mL conc. HCl and 1mL hydroxylamine solution. Added a few glass beads and heated to boiling. Continued boiling until the volume was reduced to 15 to 20 mL. Cooled to room temperature and transferred to a100 mL volumetric flask. Added 10 mL ammonium acetate solution and 4mL phenanthroline solution and diluted to the mark with distilled water. Mixed and waited for 10 to 15 minutes for maximum color development.

2.7.17 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 (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.The filtrate from the total suspended solids determination (Section 2540D) may be 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- 60 µm) fritted disk as filter support.

Procedure: *a. Preparation of evaporating dish:* The total dissolved solids can be measured by heating clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use. *b. Sample analysis:* Stirr sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 hour in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less.

Calculation:

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

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

2.8 TOC Analysis

There are various methods available for determination of organic carbon content of sample to be analyzed. The analyses are based on the principle of oxidation of the carbon in the sample to carbon dioxide. Elementar Vario TOC Cube (made in Germany, Model No.38092033) was used for the detection of total organic carbon content in the groundwater samples [12].

2.9 Microbiology Analysis

Microbiology of groundwater contains a broad spectrum of microorganisms, which includes bacteria, fungi, and protozoa and are representative of most physiological types. These microorganisms are harmful to humans as well as livestock, when it consumes the water. Total coliform bacteria are generally considered as the potential indicator of faecal contamination. It can be determined by the method of most probable number (MPN) [12].

2.10 Trace Metal Analysis

Determination of trace metals were done by inductively coupled plasma/mass spectrometry (ICP/MS) method. Sample material is introduced into an argon-based, high-temperature radio-frequency plasma, usually by pneumatic nebulization. Energy transfer from the plasma to the sample stream causes desolvation, atomization, and ionization of target elements. Ions generated by these energy-transfer processes are extracted from the plasma through a differential vacuum interface, and separated on the basis of their mass-to-charge ratio by a mass spectrometer. The mass spectrometer usually is of the quadrupole or magnetic sector type. The ions passing through the mass spectrometer are counted, usually by an electron multiplier detector, and the resulting information processed by a computer-based data-handling system. Elements analyzed are 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) [17].

2.11 Irrigation Water Quality

Irrigation suitability of the groundwater sources can be determined by calculating the sodium percent (Na %), sodium adsorption ratio (SAR), Kelly’s ratio (KR), permeability index (PI) and magnesium ratio (MR). The agricultural suitability was also explained by the diagrams such as USSL and Wilcox.

2.11.1 Sodium Adsorption Ratio (SAR)

The sodium adsorption ratio (SAR) is an indicator of the relative proportion of sodium ions to that of calcium and magnesium in a groundwater source. It can be used to predict the sodium hazard, calculated from the ratio of sodium to calcium and magnesium. If high amount of sodium present in the groundwater, can have the tendency to replace the adsorbed calcium or magnesium in the aquifer, which cause damage to soil structure and the soil becomes compact and impermeable [18]. SAR can be obtained by using the following equation:

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

The SAR values are grouped into four classes-Low, Medium, High and Very High according to the hazard caused by sodium. High sodium levels can contribute to salinity problems, which can interfere with magnesium and calcium availability. According to Richardm (1954), irrigation water is classified into four categories based on SAR- excellent (0-10), good (10-18), fair (18-26) & poor (>26). The Pollution Control Board has prescribed 26 as the maximum tolerance limit value of SAR [19].

2.11.1.1 USSL Diagram

USSL diagrams are used to find the suitability of water for agriculture, constructed by plotting SAR (sodium hazard) against EC (salinity hazard). SAR is divided into four categories-low (S1), medium (S2), high (S3) and very high (S4) sodium water. EC is classified into four based on the hazard. They are < 250 µmho-low salinity water (C1), 250-750 µmho-medium salinity water (C2), 750-2250 µmho-high salinity water (C3) & > 2250 µmho-very high salinity water (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.

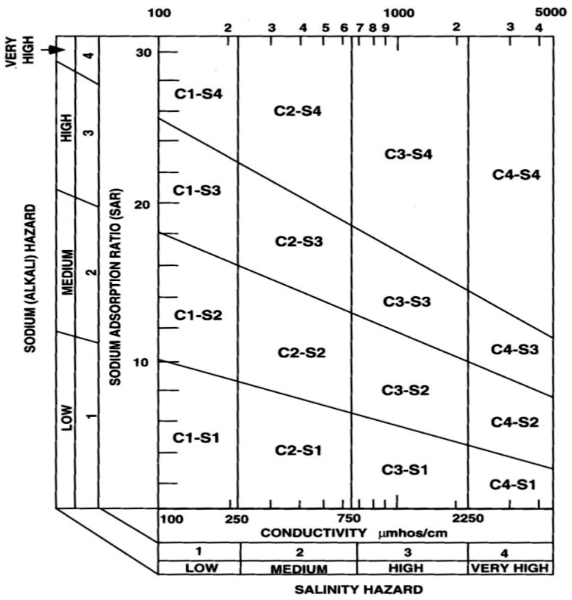


Figure 2.11: USSL Diagram for classification of water based on SAR and EC [19]

2.11.2 Sodium Percent (Na %)

Sodium in irrigation water usually expressed as percent sodium. According to Wilcox (1955) [20] Na% is a common parameter in all natural water, to obtain the suitability of irrigation use. It is determined by following the formula

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

Irrigation water classified based on Na% are excellent (<20), good (20-40), permissible (40-60), doubtful (60-80) & unsuitable (>80).

2.11.3 Wilcox Diagram

Wilcox diagrams are also used to determine the irrigation suitability, prepared by plotting the graph EC vs Na%. It is divided into five classes-

excellent to good, good-permissible, permissible to doubtful, doubtful to unsuitable and unsuitable quality of water [21].

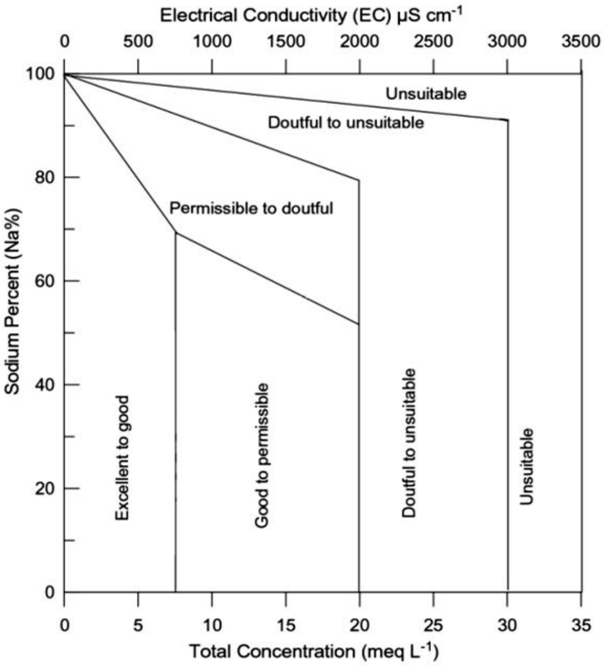


Figure 2.12: Wilcox Diagram for classification of water based on Na% and EC [20]

2.11.4 Permeability Index (PI)

Doneen (1964) [22] developed a classification for water irrigation suitability based on PI. It can be calculated by following equation.

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

Accordingly, water can be classified as Class I, Class II and Class III. Class I and II are suitable for irrigation purposes with 75% or more of maximum permeability and Class III water is unsuitable for irrigation with 25% of maximum permeability.

2.11.5 Kelley's Ratio (KR)

Kelley ratio is used for the classification of water for irrigation purposes. Sodium measured against calcium and magnesium was considered by Kelley (1951) for calculating Kelley's ratio. All the ions are expressed in meq/l. The values of KR is below one, water is suitable for irrigational practice. But, the ratio <1 indicates unsuitability of water for agricultural use. It is calculated by using the formula [23]

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

2.11.6 Magnesium Adsorption Ratio (MAR)

Generally, calcium and magnesium maintain equilibrium in most waters [24]. However, the excess of Mg^{2+} in waters will adversely affect crop yield [25]. The hazard caused by magnesium in irrigated water can be expressed as magnesium hazard [26].

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

2.12 Corrosion Indices

The indices used for predicting the corrosion and scaling potential of groundwater are Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI).

2.12.1 Langelier Saturation Index (LSI)

The Langelier saturation index (LSI) [27], a measureof ability of a solution to dissolve or deposit calcium carbonate, is often used as an indicator of the corrosivity of water. In 1936 Dr. Langelier has introduced this equilibrium model. This index is derived from the theoretical concept of saturation. It is not related directly to corrosion, but is related to the deposition of a calcium carbonate film or scale; this covering can insulate pipes, boilers and other components of a system from contact with water. When no protective scale is formed, water is considered to be aggressive and corrosion can occur. Highly corrosive water can cause system failures or result in health problems because of dissolved lead and other heavy metals. An excess of scale can also damage water systems, necessitating repair or replacement. LSI may be positive, negative or zero depending upon the nature of the water as shown in the Table 2.2.

$$\boldsymbol{LSI = pH - pH_s} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

$$\boldsymbol{pH_s = pK_2 - pK_s + pCa^{2+} + pHCO_3^-} \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

Where pH = actual pH of water

pH_s = pH of saturation for $CaCO_3$

pCa^{2+} = equilibrium calcium content

pK_2 = Second protolysis constant for H_2CO_3

pK_s = solubility product constant for $CaCO_{3(s)}$

$pHCO_3^-$ = total alkalinity when pH>9.5

Table 2.2: Classification of groundwater based on Langelier saturation index (LSI)

Range	Water Tendency
$< {}^{-}2$	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)

2.12.2 Ryznar Stability Index (RSI)

The Ryznar stability index (RSI) [28] is an empirical method used for predicting the scale forming tendencies of water. John Ryznar (1944) has developed a modification of the LSI in 1944, called Ryznar Stability Index (RSI). It is useful for both low and high hardness waters having same LSI. Value of RSI will be always a positive number. It is determined by using the following formula

$$\boldsymbol{RSI = 2pH_s - pH} \text{ .... (3)}$$

According to RSI, groundwater can be classified into five types. They are heavy scale forming water (HS), little scale (LS), little scale or corrosive water (LSC), corrosion significant type (CS) and heavy corrosion type water (HC).

Table 2.3: Classification of groundwater based on Ryznar stability index (RSI)

Range	Water Tendency
4.0 – 5.0	Heavy scale(HS)
5.0 – 6.0	Light scale(LS)
6.0 – 7.0	Little scale or corrosion(LSC)
7.0 – 7.5	Corrosion significant(CS)
7.5 – 9.0	Heavy corrosion(HC)

2.12.3 Aggressive Index (AI)

The Aggressive Index (AI), originally developed for monitoring water in asbetose pipe, sometimes is substituted for LSI as an indicator of the corrosivity of water. The AI is derived from the actual pH, calcium hardness and total alkalinity. It is usually applicable as it is simpler and more convenient than the LSI. Because the AI does not include the effects of temperature or dissolved solids, it is less accurate as an analytical tool than the LSI [29].

$$AI = pH + log\ (AH) \quad \text{..........} (4)$$

Where ‘**A**’ is the total alkalinity and ‘**H**’ is calcium hardness in mg/L as $CaCO_3$

Table 2.4: Classification of groundwater based on aggressiveness index (AI)

Range	Water Tendency
< 10.0	Highly aggressive(HA)
10.0-11.9	Moderately aggressive(MA)
> 12.0	Non-aggressive(NA)

2.13 Hill-Piper-Trilinear plot and Hydrochemical Facies

Piper diagrams [19] are made up of two triangles, that are supposed to share a common base line and each side are separated by an angular distance of 60^o apart. These two are interlocked by a diamond shaped portion. Cations and anions are plotted on separate triangle as percentages and the concentrations are expressed in milli equivalent per litre. The area of the diamond portion represents the TDS present in the groundwater of the region. The diagram provides very valuable knowledge on the water type, precipitation or solution behavior, mixing character and ion exchange phenomena. Water is classified into mainly four different facies based on the data positions in diamond portion of Piper diagram. They 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)*

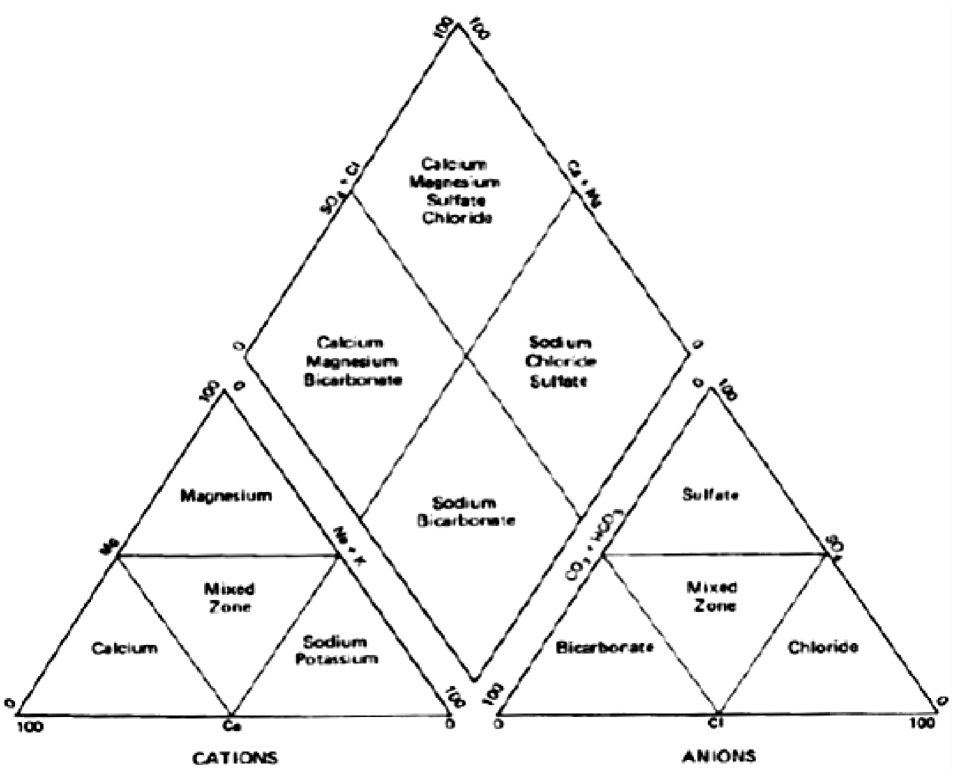


Figure 2.13: Classification of water types based on Piper diagram [15]

2.14 Gibb's Diagrams

Chemical composition of the groundwater is mainly controlled by many processes such as rock-water interaction, evaporation, precipitation etc. It can be explained with the help of Gibb's diagrams [30]. The total dissolved solids were plotted against the ratio of sodium and sum of sodium and calcium constitutes the cationic part. The anionic plot was constructed by ratio of chloride and sum of chloride and bicarbonate against TDS. Gibb's diagram was very much helpful to identify the source of dissolved ions present in groundwater. TDS was between 100-1000 mg/l constitutes the precipitation dominance region. Rock-water interaction is contributing many of the mineral ions into the groundwater and the TDS between 1000-10000 mg/L can be attributed by weathering of rocks. Evaporation process was also enhanced the dissolved solids concentration in groundwater. When the TDS value exceeds 10000 mg/L, the ion chemistry was controlled by evaporation process.

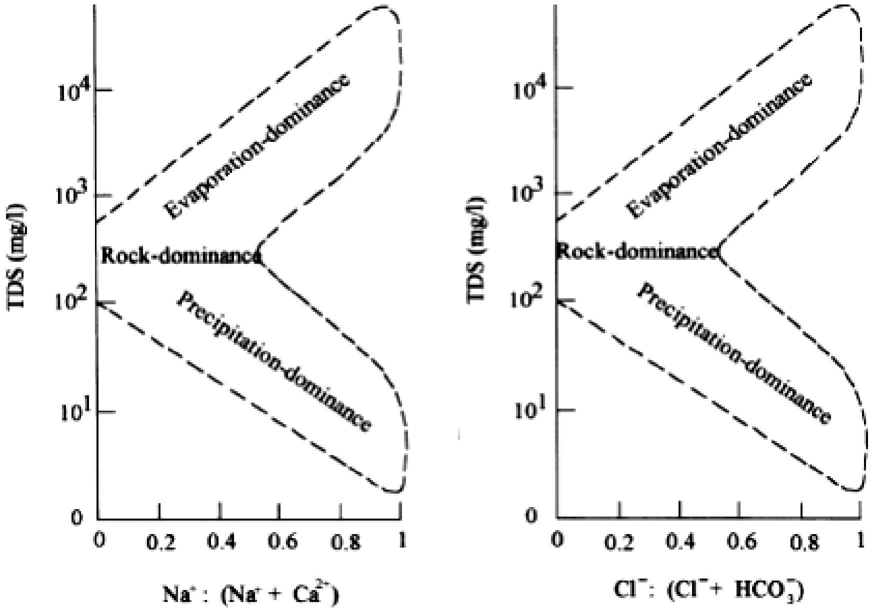


Figure 2.14: Chemical composition of groundwater explained in Gibb's diagrams [16]

2.15 Study of Ionic Ratios

2.15.1 Sodium - Chloride Ratio

It gives us an idea about the ion exchange or reverse ion exchange processes taking place in groundwater. If the *Na/Na+Cl* ratio is greater than 0.5 and *Na/Cl* > 1.0, the process taking place is ion exchange and reverse to that (*Na/Na+Cl*< 0.5 and *Na/Cl* < 1.0) reverse ion exchange may occurs [7].

2.15.2 (Ca^{2+}+Mg^{2+}) / (HCO_3^-+SO_4^{2-}) Scatter Diagram

The ionic concentrations falls below the 1:1 equiline of (Ca+Mg) vs (HCO_3+SO_4) scatter diagram, resulting from the silicate weathering process. The ionic concentrations lies above the 1:1 line indicates dissolution of calcite, dolomite and gypsum supported by (Ca + Mg) vs (HCO_3+SO_4) scatter [31].

2.15.3 Na^+ / Ca^{2+} Scatter Diagram

In Na vs Ca scatter, the ionic concentrations fall on above the equline, indicates the ion exchange process. If the concentrations are lies below the equiline, indicates the dissolution of carbonate mineral [32].

2.15.4 Na^+ /Cl^- Scatter Diagram

The concentrations of ions are plotted above the equiline of Na vs Cl scatter, indicate the silicate weathering process. There is halite dissolution occurs when ratio less than one [33].

2.15.5 (TZ^+) / (Na^+ + K^+) Scatter Diagram

Silicate weathering is one of the main geochemical processes, which controls the major ions chemistry of the groundwater. This process can be understood from the total cations (TZ^+) vs Na + K scatter diagram. The relationship between Na + K and total cations (TZ^+) indicates the involvement of silicate weathering in the geochemical processes, which contributes mainly sodium and potassium ions to the groundwater [34].

2.16 Water Quality Index (WQI)

Water quality index is a single number that express overall water quality of the region, used multiple water quality parameters for its calculation. Weighted arithmetic index method has been used for the calculation of WQI. Andhakaranazhy coast groundwater quality depends on number of physico - chemical parameters such as pH, EC, alkalinity, TDS, DO, BOD, TH,Ca^{2+}, Mg^{2+}, Na^{+}, $K^{+,}$ Cl^{-}, SO_4^{2-} and total iron. Hence, we chosen these important parameters and the BIS & WHO standards have been considered for the further calculation [35-37]. The overall quality of water can be assessed by using following the equation given below,

$$\text{Water quality index (WQI)} = \frac{\Sigma W_i q_i}{\Sigma W_i}$$

Where $q_i = 100[V_o - V_i] / [S_i - V_i]$; $W_i = K/S_i$; Where q_i is the quality rating for the i^{th} 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 relative unit weight (W_i) of any parameter is proportional to K/S_i. Where S_i= standard permissible value of particular parameter. K= proportionality constant. For the sake of simplicity K is taken as 1.

Groundwater classification according to the WQI has been given in Table 2.5.

Table 2.5: Classification of groundwater on the basis of Water Quality Index

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

2.17 CPCB Classification for Designated Best Use

Central Pollution Control Board (CPCB), Ministry of Environment and Forest, Government of India has been recognized the water quality requirements known as primary water quality criteria [38]. CPCB classified the water into five categories-A, B, C, D & E according to their designated best use (DBU) of water and it has been arranged in the increasing order of deterioration in quality of water starting from A to E.

Table 2.6: 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**

2.18 Statistical Analysis

Statistical analysis used for the evaluation of the data are correlation, t-Test and two factor ANOVA [13]. Data collected for the study were compiled and analyzed statistically using the following tests:

t-test

For the determination of each parameter limited set of data is obtained by representative sampling. In statistical analysis, mean and standard deviation are first determined for parameters. Student's t-test method is a statistical tool used most frequently to express confidence intervals and to compare results from different experiments. As regards to 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

$$\mu = \bar{x} \pm ts/\sqrt{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

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

The *t*-test is used to compare one set of measurements with another for water quality measurement to decide whether or not they are "the same". It is called testing the null hypothesis, which states that the mean values from two sets of measurements are not different.

Correlation

Correlation is one of a broad class of statistical relationships involving dependence. It refers to the extent to which two variables have a linear relationship with each other. But it does not provide evidence for causal relationship between the two variables. There are several correlation coefficients measuring the degree of correlation. The most common of these is the Pearson correlation coefficient. The Pearson correlation is +1 in the case of a perfect direct (increasing) linear relationship (correlation), −1 in the case of a perfect decreasing (inverse) linear relationship. As it approaches zero there is less of a relationship (closer to uncorrelated). The closer the coefficient is to either −1 or +1, the stronger the correlation between the variables. SPSS software is used in correlation matrix calculation. The formula for r

$$r = \frac{1}{n-1}\Sigma^{n}{}_{i=1}\left(\frac{x_i-\bar{x}}{s_x}\right)\left(\frac{y_i-\bar{y}}{s_y}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

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 2.3

Table 2.7: 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

The primary data generated as a result of groundwater analysis of the samples collected from Andhakaranazhy and Cherai coastal segment are critically analysed and interpreted and are presented in the subsequent chapters to come out with most valuable inference as outcome of this study.

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Chapter 3

EVALUATION OF GROUNDWATER CHEMISTRY AND QUALITY ALONG THE ANDHAKARANAZHY COAST, ALAPPUZHA, KERALA DURING THE YEAR 2012

3.1 Introduction

Andhakaranazhy coast is one of the northern coastal segments of Alappuzha district, lies between 09^{o} 44’ 50” N latitude and 76^{o} 17’ 07” E longitude. This coast was vulnerable to many natural and anthropogenic stresses, was seriously affected by 26th December 2004 Indian Ocean Tsunami. Proximity to sea, salt water intrusion into the tidal canals in the lean months make this coastal islet vulnerable to many social and ecological issues. Sand mining and coir retting activities lead to the quality deterioration of groundwater resources, is being noticed as a issue in this place. Because of this reason, the contamination of groundwater is now a great concern. The quality of groundwater in Andhakaranazhy is known to depend on hydrological, physical, chemical and biological factors. Study of tsunami induced water quality variation and its assessment has been a major research work focused by researchers with respect to post tsunamic situation [1-5]. This research has many significances.

(1) it is essential to have a good primary data base to evaluate the hydrogeochemistry of the region for over a period of time to come out with salient changes brought in the groundwater chemistry in a changing climatic and environmental scenario.

(2) To generate more research initiatives on available sources of drinking water with respect to quality, extraction and source protection in one of the coastal region of Kerala known for growing water scarcity and a recorded history of coastal hazard and disaster.

The major work presented in the following section of the thesis comprises the major results and discussions on the water quality parameters of the groundwater sources of the Andhakaranazhy coast during the year 2012. The original data obtained from the physico-chemical analysis of water samples, are evaluated for its drinking water quality and designated use as well as for irrigation and industrial suitability based on the indices evaluated. The groundwater chemistry and quality was interpreted using the standard methods [6] and statistical tools. Water samples collected from eleven(11) shallow groundwater sources consists of eight(8) dug wells, two(2) bore wells and one (1) open shallow pond were presented in the Table 3.1. Location map of Andhakaranazhy coast, the designated study area (Alappuzha) representing the sampling locations during the year 2012 are shown in Figure 3.1.

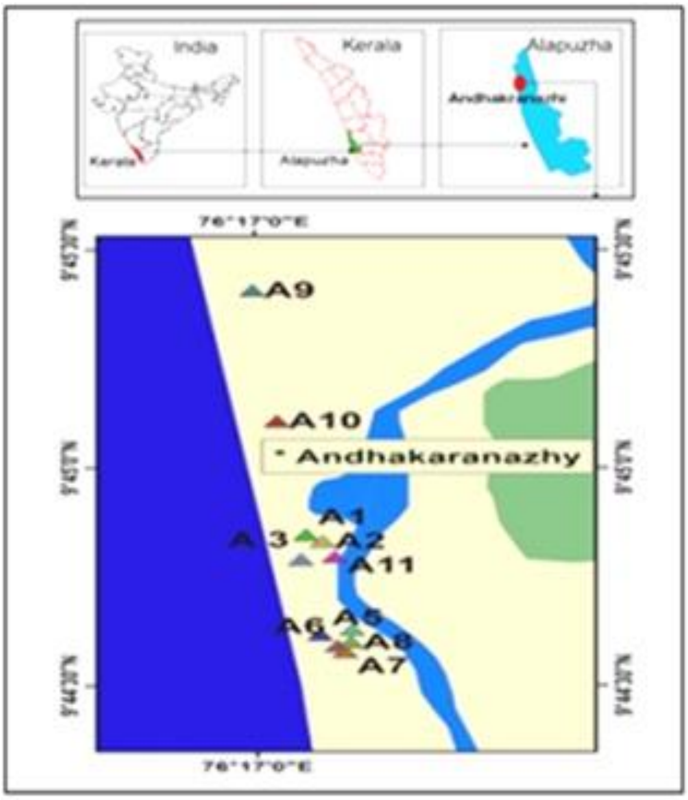


Figure 3.1: Location map of Andhakaranazhy coast, Alappuzha, Kerala, India, which has been subjected to inundation by 26th December 2004 Indian Ocean Tsunami.

Table 3.1: Water quality sampling stations of Andhakaranazhy coast (Alappuzha) during the year 2012

Station	Remarks	Water table	Location
1. Dug well-canal side	Dug well (DW1)	5ft	09° 44’ 50N, 76° 17’ 07E
2. Mariamma-house owner	Dug well (DW2)	3ft	09° 44’ 50N, 76° 17’ 05E
3. Maniyan- house owner (Control)	Dug well (DW3)	2ft	09° 44’ 48N, 76° 17’ 04E
4. James- house owner	Dug well (DW4)	2ft	09° 44’ 37N, 76° 17’ 08E
5. Pius- house owner	Dug well (DW5)	3ft	09° 44’ 37N, 76° 17’ 07E
6. Sebastian- house owner	Dug well (DW6)	3ft	09° 44’ 35N, 76° 17’ 07E
7. Devdas- house owner	Bore well (BW1)	5ft	09° 44’ 35N, 76° 17’ 07E
8. Babu- house owner	Open Pond (OP1)	5ft	09° 44’ 36N, 76° 17’ 08E
9. Purushothaman- house owner	Bore well (BW2)	6ft	09° 45’ 25N, 76° 17’ 00E
10. George- house owner	Dug well (DW7)	3ft	09° 75’ 17N, 76° 28’ 37E
11. Sabu-house owner	Dug well(DW8)	2ft	09° 74’ 66N, 76° 28’ 49E

3.2 Evaluation of Physico-Chemical Parameters

Water quality parameters of the Andhakaranazhy coast evaluated and reported in this study during the period 2012, is being obtained as mean of 12 monthly sampling events starting from January - December 2012. Physico-chemical parameters of groundwater analysed were temperature, pH, Eh, EC, TA, TH, Ca^{2+}, Mg^{2+}, TDS, Na^{+}, K^{+}, Cl^{-} , SO_4^{2-}, NO_3^{-}, PO_4^{3-} & total Iron. The basic data generated for the shallow groundwater are compared with control well during the period 2012.

3.2.1 Temperature

Groundwater usually maintains a fairly constant temperature, normally close to the average annual air temperature for surficial aquifers [7]. It recorded an annual mean of temperature 28.3±0.93°C in shallow groundwater sources with confidence interval (CI) of 27.7-28.8 °C at 95% significant level. In January 2012, temperature was 26.4±1.58°C and gradually it increases and reaches at 29.8±0.81°C in May 2012, due to the summer effect.

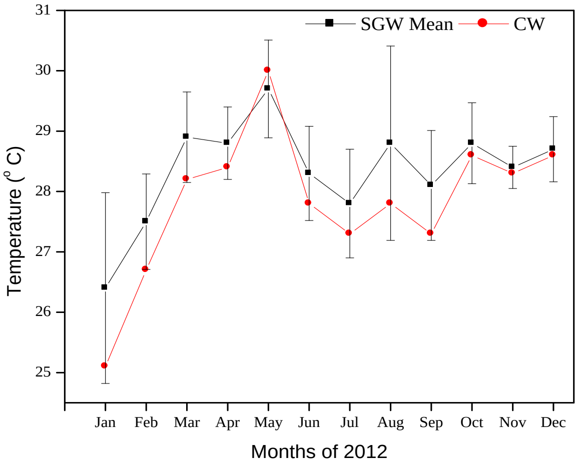


Figure 3.2: Monthly variation of temperature of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

There was a slight decrease in water temperature in June (28.3±0.78°C) and July months (27.8±0.90°C) of the year 2012. From August, 2012 (28.8±1.61°C) onwards, it is seen that a small fluctuation in groundwater temperature and attains 28.7±0.54°C in December, 2012. Same trend was observed in the case of control well. It shows an annual mean of groundwater temperature 27.8±1.2 °C with a range of 25.1-30°C. The lowest temperature was observed during the month January and highest in May, 2012 (Figure 3.2). But June, 2012 (27.8°C) onwards, the temperature was quite steady and reaches 28.6°C in December, 2012. Since, the monsoon, it reduces the atmospheric temperature as well as groundwater temperature.

3.2.2 pH

pH may vary diurnally and seasonally due to the changes in photosynthetic activity. It actually indicates the hydrogen ion concentration. The groundwater sources of Andakaranazhy coast showed an alkaline behaviour throughout the period. It may be due to the presence of bicarbonate in the groundwater source. pH records an annual mean of 7.6±0.25 with confidence intervel (C I) of 7.4-7.8 at 95% significant level in the case of shallow groundwater sources. In January, 2012 the pH was 7.7±0.32 and reaches the maximum of 8.0±0.18 during the month August, 2012, but within the standard limits [8]. After that the pH showed a decreasing trend and attains 7.4±0.22 in December, 2012. The control well also showed an annual mean of pH 7.6±0.27. The lowest temperature was observed during the month November (7.2) and highest in March (8.1) as shown in the Figure 3.3.

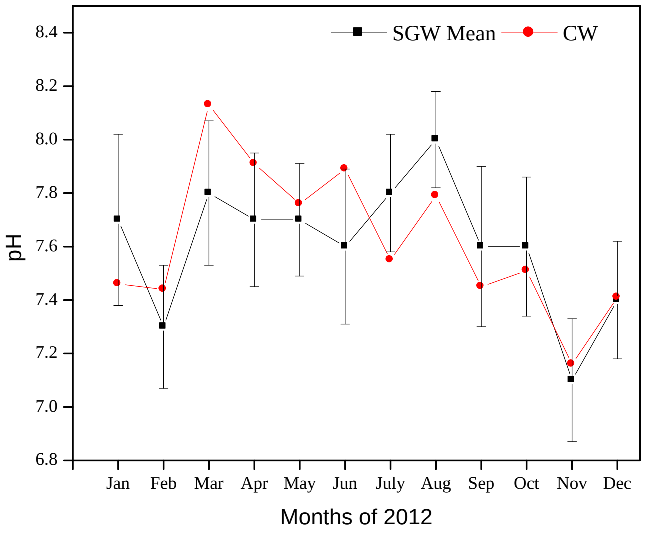


Figure 3.3: Monthly variation of pH of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.3 Redox Potential (Eh)

The redox potential (Eh) is used to find out the oxidation-reduction state of natural waters, characterised by Eh value, determined potentiometrically. Some factors are depends on the Eh are oxygen, iron and sulphur as well as some organic systems. Groundwaters containing dissolved oxygen are usually characterised by a Eh value between +100 mV and +500 mV. As Eh depends on the dissolved gas content of the water, it can be changed when the water is in contact with air [7].

Eh showed an annual mean of -36±14.57 mV with CI of -45 to -27 mV at 95% significant level for shallow groundwater sources during the year 2012. It showed, water exists in reduced state throughout the period and reported a maximum of $^{-}$7.5±12.92 mV during November 2012. Control well also exhibited a reducive nature during the year 2012 with an annual mean of -37 ±14.43 mV (Figure 3.4).

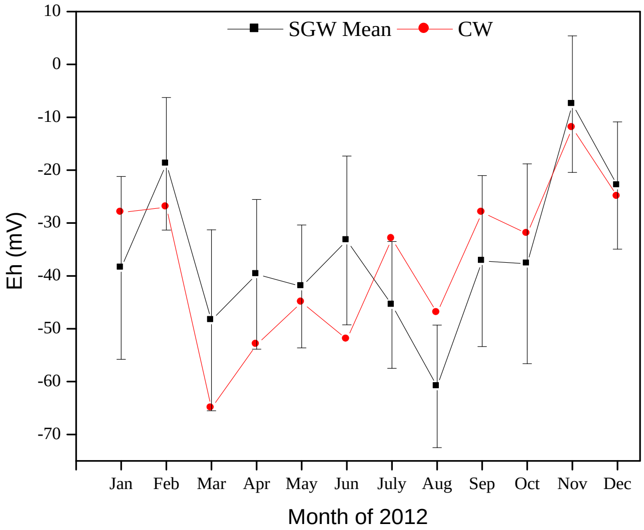


Figure 3.4: Monthly variation of Eh of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.4 Electrical Conductivity (EC)

Electrical conductivity (EC) is the measure of capability of a substance or solution to conduct electric current. It is depends on the amount of total dissolved solids, mainly mineral salts. EC of shallow groundwater sources showed an annual mean of 809.4±618.38 µS, with CI of 428.5-1190.3 mS/cm at 95% significant level. In January 2012, the groundwater maintains with low EC (327.3±127.21 µS). It fluctuates throughout the year but within the standard limits [9]. During the summer month of March, 2012 have recorded a high EC (1190.9±985.35) value (Figure 3.5). December, 2012 also noted with very high EC (1293.6±1395.06). During summer season, the mineral ion concentration is enhanced in the aquifer and it will leads to the increased concentration of EC. Control well has an annual EC of 831.7±304.66 µS showed a varying trend.

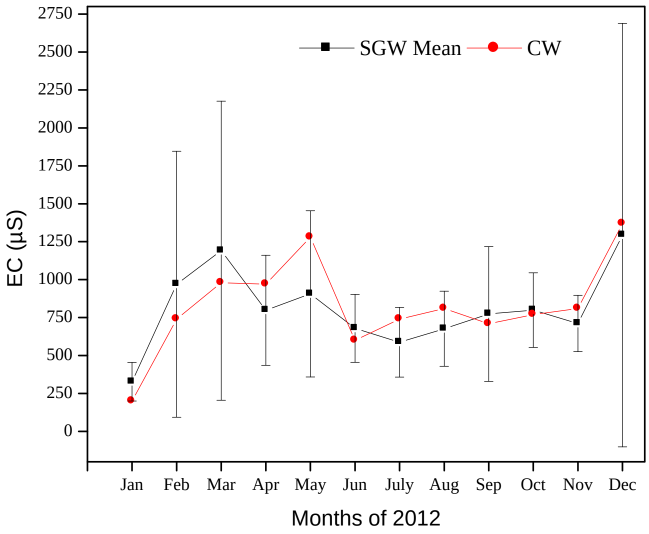


Figure 3.5: Monthly variation of electrical conductivity (EC) of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Large variations in electrical conductivity was contributed by many of the geochemical processes such as ionic exchange, reverse exchange, evaporation, silicate weathering, rock water interaction, sulfate reduction and oxidation processes, and anthropogenic activities [10].

3.2.5 Alkalinity

Alkalinity is defined as the acid-neutralising ability of water, which is controlled by ions such as carbonates, bicarbonates and hydroxides, but the other ions, may also contribute to alkalinity includes borates, phosphates and silicates. However, most of the natural alkalinity in water is due to the bicarbonate ions produced by the action of groundwater with limestone. Andhakaranazhy coast maintains a constant alkalinity throughout the period. Annual mean of alkalinity recorded is 330.2±117.23 mg/L with CI of 258.0-402.4 mg/L at 95% significant level in the case of shallow groundwater sources. The highest alkalinity is reported during the month of February, 2012 (418.8±211.14 mg/L) and lowest in August, 2012 (273.6±107.70 mg/L), because of the monsoonal dilution (Figure 3.6). Control well has same trend with shallow groundwater and an annual mean of 317.9±44.41 mg/L. An increase in the free CO_2 may be a probable reason for the increase in alkalinity [11].

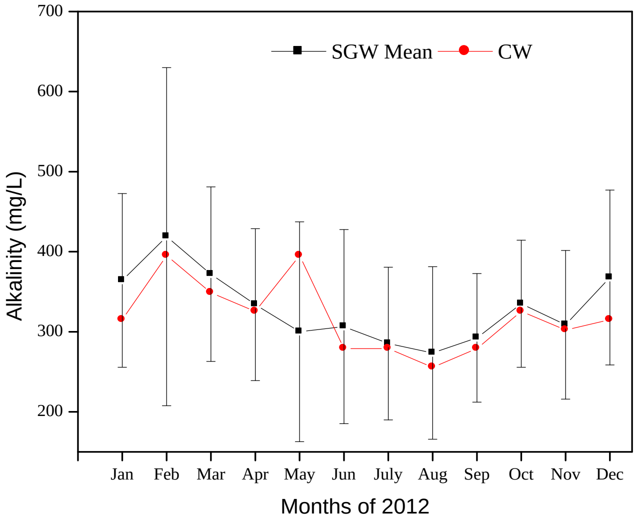


Figure 3.6: Monthly variation of alkalinity of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.6 Total Hardness (TH)

Hardness is the characteristics of the water with excess Mg^{2+} and Ca^{2+} ions which prevents the lather formation with soap and enhances the boiling point of water. The ions responsible for the hardness are calcium, magnesium and anions such as bicarbonates, chlorides & sulphides [12].

The annual mean of total hardness (TH) of shallow groundwater sources are 290±108.93 mg/L, with CI of 222.9-357.1 mg/L at 95% significant level. We can observe a slight variation in TH, always higher during summer months (Figure 3.7). The control well also shows same trend in TH with an annual mean of 282.6±57.97 mg/L. The long term usage of very high hard water may cause adverse effects on health such as urolithiasis, anencephaly, prenatal mortality, some type of cancer, and cardiovascular disorders [13]. But some extent, it may be advantageous, which prevents the corrosion in the pipes by forming a thin layer of scale and reduces the entry of heavy metals from the pipe to the water [14].

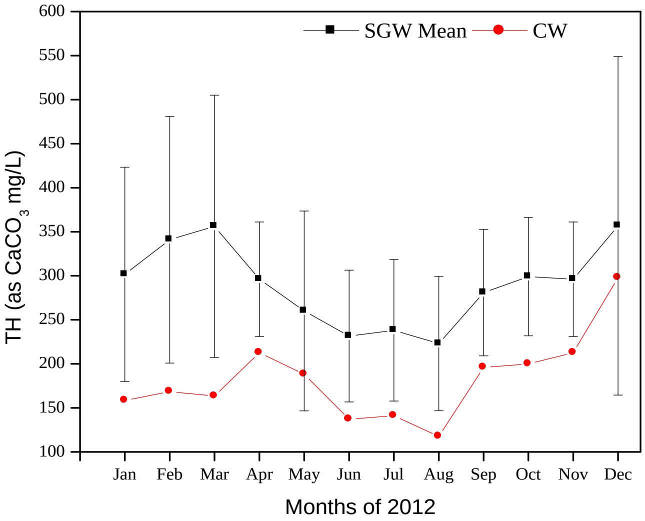


Figure 3.7: Monthly variation of Total Hardness of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

In the hardness-alkalinity relationship alkalinity may be 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 TH and TeH [15]. According to Vescilind (2004), [16] water is classified into six categories based on water hardness- If hardness is in the range 0-45 mg/L, water type is *extremely soft to soft* (ESS), *46-90 mg/L-soft to moderately hard* (SMH), 91-130 mg/L *-moderately hard to hard* (MHH), 131-170 mg/L-*hard to very hard* (HVH), 171-250 mg/L-*very hard to excessively hard* (VHEH) and >250 mg/L-*too hard for ordinary domestic use* (THODU) [16]. Table 3.2 shows the comparison of TA, TH, TeH of shallow groundwater sources of Andhakaranazhy coast during the year 2012.

Table 3.2: Comparison of TA, TH, TeH in mg/l $CaCO_3$ of shallow groundwater sources of Andhakaranazhy Coast, Alappuzha, Kerala, India during the year 2012

Period	TA(mg/L)	TH(mg/L)	TeH (mg/L)	Inference
Jan 2012	367.8±109.16	301.6±121.62	301.6±121.62	THODU
Feb 2012	418.8±211.14	341.0±140.08	341.0±140.08	THODU
Mar 2012	372±109.05	356.2±148.91	356.2±148.91	THODU
Apr 2012	334±94.88	296.1±65.03	296.1±65.03	THODU
May2012	300.1±137.33	260.2±113.43	260.2±113.43	THODU
Jun 2012	306.5±121.18	231.6±74.86	231.6±74.86	VHEH
Jul 2012	285.3±95.35	238.1±80.34	238.1±80.34	VHEH
Aug 2012	273.6±107.7	223.1±76.36	223.1±76.36	VHEH
Sep 2012	292.5±80.28	280.8±71.75	280.8±71.75	THODU
Oct 2012	335±79.34	299.0±67.24	299.0±67.24	THODU
Nov 2012	308.8±92.85	296.1±65.03	296.1±65.03	THODU
Dec 2012	367.8±109.16	356.7±192.14	356.7±192.14	THODU
$\bar{x}\pm\sigma$	330.2± 117.23	290.03±108.93	290.03±108.93	THODU
μ	330.2± 72.20	290.03±67.09	290.03±67.09	THODU
CI	258.0-402.4	222.9-357.1	222.9-357.1	THODU

It is clear that, total alkalinity (TA) is greater than TH for the entire sampling period. Hence, we consider the TH as *temporary hardness* (TeH) and PeH is taken as zero throughout the year 2012. Total hardness of Andhakaranzhy coast groundwater reported an annual mean of 290.03±108.93 mg/L as $CaCO_3$ and comes under THODU type of water. Most of the months, water type is *too hard for ordinary domestic use* (THODU) except in June, July and August 2012, which is *very hard to excessively hard* (VHEH).

3.2.7 Dissolved Oxygen (DO)

Oxygen is very essential for most of the biological life. It can be available for living things in water for respiration. DO is depleted by the oxygen demanding wastes, determined by Winkler’s method. The presence of chloride content reduces solubility of dissolved oxygen (DO) in water. The DO concentration in groundwater below 3 mg/L is hazardous to human consumption [17]. The shallow groundwater sources of Andhakaranazhy coast showed an annual mean of 4.1±1.95 mg/L of DO, with confidence intervel (CI) of 2.9-5.3 mg/L at 95% significant level. In the case of control well, DO reported an annual mean is 5.7±0.93 mg/L (Figure 3.8). It reveals that, groundwater sources of study area is having low DO value, because of the presence of oxidisable organic matter through contamination.

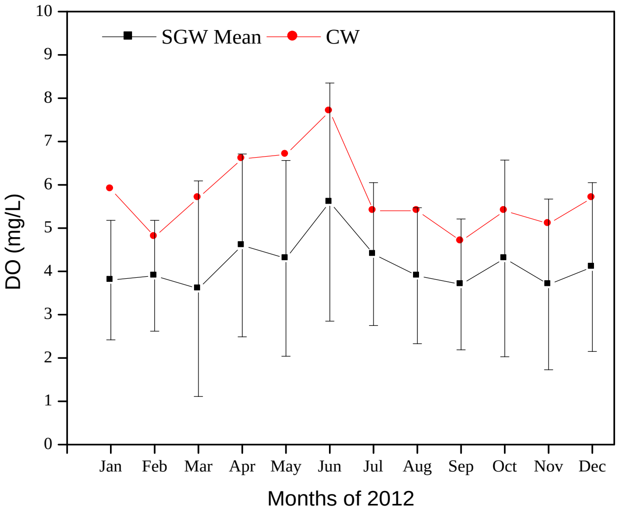


Figure 3.8: Monthly variation of dissolved oxygen (DO) of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.8 Biological Oxygen Demand (BOD)

Biological oxygen demand is the amount of oxygen required for microorganisms to degrade the oxydisable organic matter. It is an indicator of pollution in water, determined after three days incubation at 27°C.

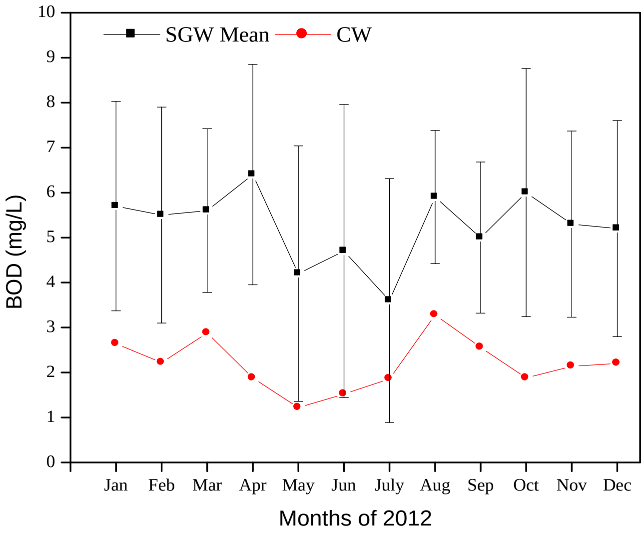


Figure 3.9: Monthly variation of biological oxygen demand (BOD) of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Andhakaranazhy coast recorded an annual mean of 5.2±2.40 mg/L with CI of 3.7-6.7 mg/L at 95% significant level in shallow groundwater sources during the year 2012, exceeding the permissible limit for BOD is 5 mg/l prescribed by WHO. This is because of high organic matter present in the aquifer. However, the control well having low BOD values compared to shallow groundwater sources. An annual mean of 2.2±0.61 mg/L of BOD was reported in control well as shown from the Figure 3.9. Very high BOD was reported during summer months[18].

3.2.9 Calcium (Ca^{2+})

Calcium is present in groundwater as Ca^{2+} and its the source is calcium rich minerals such as limestone and gypsum. These minerals react with water containing atmospheric carbondioxide, liberate the calcium and magnesium ions into the soil. It is one of the principal cation, which causes hardness of water. The maximum concentration can be reaching up to 30-100 mg/L waters associated with carbonate-rich rocks. Shallow groundwater sources of Andhakaranazhy coast showed an annual mean of 83.2±26.46 mg/L of calcium concentration during the year 2012, with CI of 66.9-99.5 mg/L at 95% significant level. In January, 2012 the reported calcium concentration is 86.6±20.90 mg/L. It is attained at high concentration during the month of February, 2012 (103.3±36.76 mg/L). The evaporation rate is very high during this period. Thus enhances the amount of calcium ion in groundwater. The concentration is gradually decreased from April, 2012 onwards (85.8±23.84 mg/L) and reached a minimum of (64.0±23.55) mg/L by August, 2012 (Figure 3.10). The quantity was reduced due to monsoonal dilution and ion exchange. Again its amount increased and get stabilised till December 2012 (86.5±20.91 mg/L). The control well revealed, the concentration of calcium was high during the month of November, 2012 (109.76 mg/L) with an annual mean of 85.7±15.47 mg/L. Lithology of the study area is composed of sand, clay, clay with lignite, limestone and gravel [19].

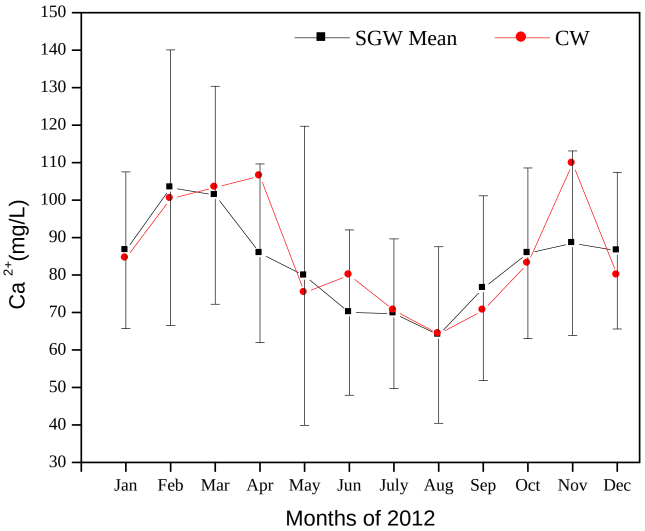


Figure 3.10: Monthly variation of calcium (Ca^{2+}) ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.10 Magnesium (Mg^{2+})

Magnesium is an essential element for living things, present as Mg^{2+} in natural waters. It is also a main contributor of water hardness along with calcium. The natural sources of magnesium are, the rocks containing limestone, gypsum and ferromagnesium minerals. Organic matter also contains some amount of magnesium. The source of magnesium is different but finally it reached in water in many ways [20]. Fresh waters may contain 1-100 mg/L of magnesium. In Andhakaranazhy coast, the concentration of Mg^{2+} is very less compared to calcium ion. The shallow groundwater reported an annual mean of 18.5±11.39 mg/L of magnesium in groundwater, with CI of 11.5-25.5 mg/L at 95% significant level. The shallow groundwater sources showed magnesium content of 14.6±9.40 mg/L in January, 2012 and increased during the summer season with a highest quantity in March, 2012 (25.0±22.25 mg/L). Rain water dilutes its concentration. Again the quantity (21.1±12.96 mg/L) was increased from September, 2012 onwards and reached (20.8±10.27) mg/L in December, 2012 (Figure 3.11). Control well showed an annual mean of 16.6±7.86 mg/L magnesium. It is attained a highest peak in December, 2012 (29.52 mg/L), indicates the sea water intrusion during the month. Calcium and magnesium are found in groundwater because of the dissolution of limestone. Limestone dissolves when it reacts with acidic rainwater through a reaction with carbon dioxide. These minerals react with atmospheric carbon dioxide and liberate the calcium and magnesium ions into the soil.

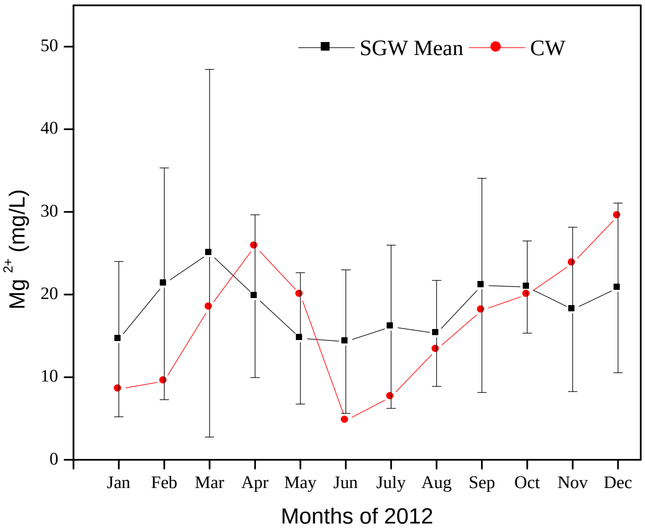
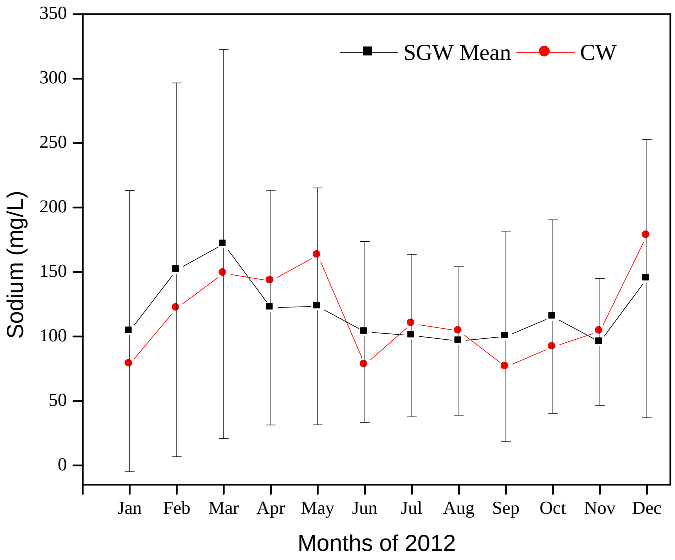


Figure 3.11: Monthly variation of magnesium ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.11 Sodium (Na^+)

All natural waters contain some amount of sodium and sea water intrusion may result the higher concentration of sodium in groundwater.

Andhakaranazhy coast has an annual (2012) mean 119.2±96.21 mg/L of sodium concentration, with CI of 59.9-178.5 mg/L at 95% significant level for the shallow groundwatersources where as 116.5±34.72 mg/L for control well. The highest concentration was observed during March, 2012 (171.7±151.03 mg/L). But after monsoonal dilution, the concentration of sodium is decreased, finally reaches at 144.9±108.03 mg/L in December, 2012. Control well also reveals a very high concentration of sodium during the year 2012, equal to 116.5±34.72 mg/L. Same trend was observed in the case of control well. The highest sodium content is 178.3 mg/L during December 2012 (Figure 3.12). Fluctuations in sodium was due to the evaporation process and monsoonal dilution. High sodium content in groundwater may cause hypertension, congenial heart disease, and kidney problems while consumption [21].



Figur 3.12: Monthly variation of sodium ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.12 Potassium (K^+)

Potassium is usually found in low concentrations in natural waters, less than 10 mg/L, whereas concentration exceeds that limit shows the sea water contamination [22].

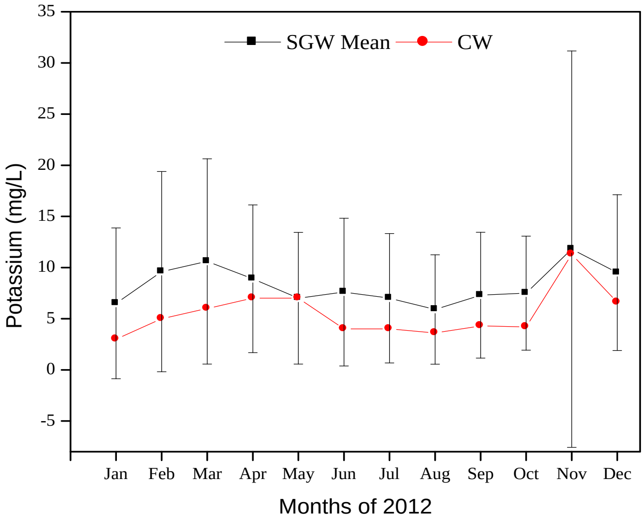


Figure 3.13: Monthly variation of potassium ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Shallow groundwater sources exhibits an annual mean of 8.3±8.98 mg/L potassium, with CI of 2.8-13.8 mg/L at 95% significant level highest during the month November, 2012 (11.8±19.37 mg/L).Control well also exhibits same trend with shallow groundwaterwith an annual mean of 5.5±2.28 mg/L (Figure 3.13).

3.2.13 Chloride (Cl^-)

Chlorides are responsible for the brackish nature of the water, which is an indicator of sewage pollution. The permissible limit of chloride in drinking water is 250 mg/L according to BIS [8]. In natural waters, chloride content was fairly low, usually less than 100 mg/L, except for brackish or saline water [23].

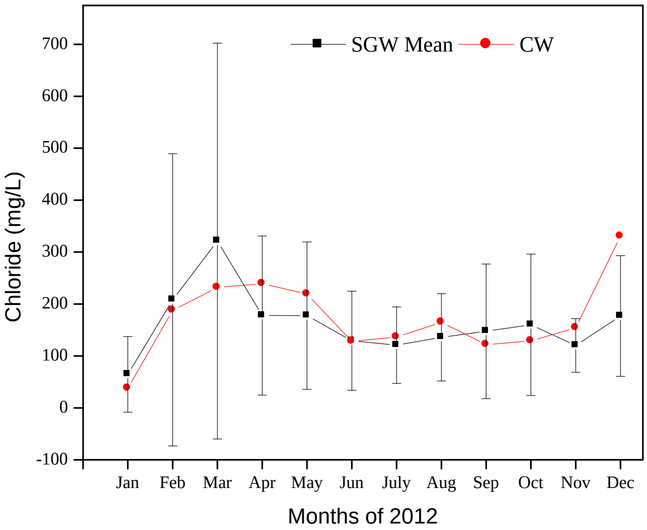


Figure 3.14: Monthly variation of chloride ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

The groundwater showed an annual mean of 161.6±169.9 mg/L of chloride in shallow groundwater sources. However, the control well has an increased concentration of chloride with an annual mean of 173.4±74.87 mg/L with CI of 57.0-266.2 mg/L at 95% significant level compared to shallow groundwater sources, because of the proximity to sea. In January 2012 shallow groundwater sources exhibits 64.6±72.81 mg/L of chloride whereas for control well it is 37.78 mg/L (Figure 3.14). This month shows the lowest chloride content both for shallow groundwater and control well. But afterwards, the concentration is increasing gradually and comes at 321.2±381.05 mg/L in March, 2012 highest amount of chloride in shallow groundwater. It may be the summer season enhances the evaporation rate thus by increasing the chloride content in groundwater. After March, 2012 the concentration is decreased and shows not much variability in chloride. Control well has a varying trend in the case of chloride, was high concentration in March, April & May 2012. After June, 2012 onward the water get stabilized with chloride. But in December 2012, the concentration of chloride attained a very high amount (330.54 mg/L).

3.2.14 Sulphate (SO_4^{2-})

Sulphate is naturally present in groundwater as SO_4^{2-}. It arises from the weathering of sulphate bearing minerals originated from sedimentary rocks. In natural water its concentration ranges from 2-80 mg/L. Under anaerobic conditions, the sulphate ion is reduced to sulphide ion by microorganisms and form hydrogen sulphide. This hydrogen sulphide leads to corrosion of pipes [24].

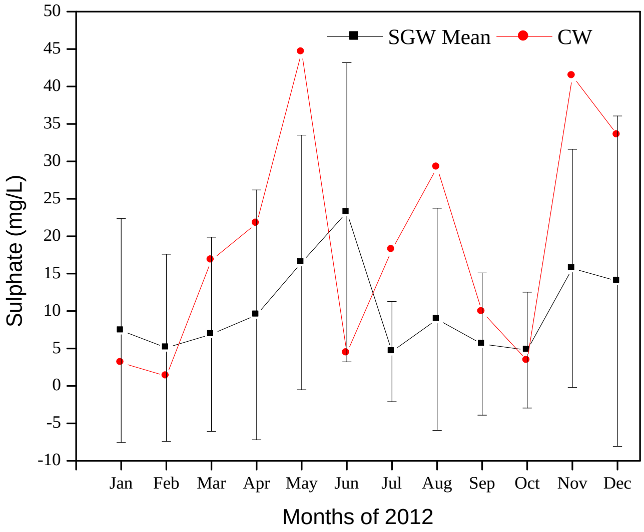


Figure 3.15: Monthly variation of sulphate ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Annual mean of sulphate for shallow groundwater sources was 10.2±14.91 mg/L with CI of 1.0-19.4 mg/L at 95% significant level. In January, 2012, its concentration is 7.4±14.95 mg/L. After that the concentration shows a decreasing trend and reached at its peak in June, 2012, (23.2±19.98 mg/L). But decline to 4.6±6.70 mg/L in July, 2012. Thereafter, gradually increases up to 15.7±15.90 mg/L in November, 2012 and then decreases (14.0±22.06 mg/L) as shown in Figure 3.15. The amount of sulphate in the control well is very high compared to shallow groundwaters, but within the recommended limit [8]. Though the highest concentration is known in May (44.6 mg/L) with an annual mean of 19.0±15.34 mg/L of sulphate.

3.2.15 Nitrate (NO_3^-)

Nitrate is an essential nutrient for the growth of all living organisms. Sewage and other organic matter rich soil produce the nitrate in groundwater [25]. Nitrates can be toxic to children especially under the six months of age, which cause blue-baby syndrome. Nitrate recorded an annual mean of 1.3±1.41 mg/L, with CI of 0.4-2.2 mg/L at 95% significant level in shallow groundwater and a fairly constant nitrate over the period 2012. Control well showed an annual mean of 0.5±0.11 mg/L, remains a steady state throughout the period (Figure 3.16).

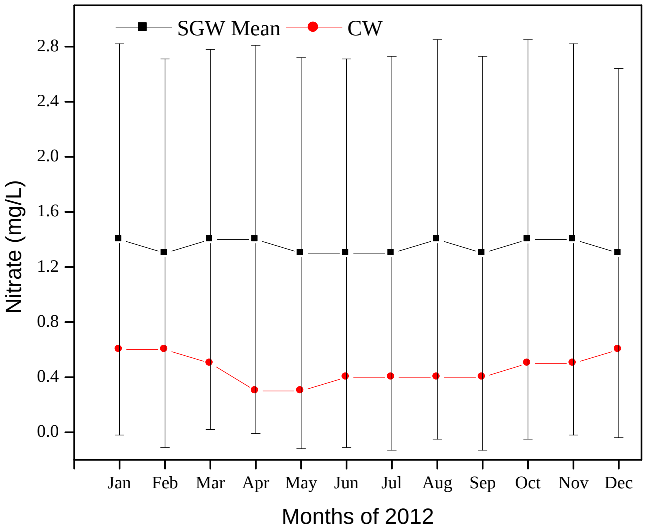


Figure 3.16: Monthly variation of nitrate ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.16 Phosphate (PO_4^{3-})

Phosphorus is very necessary for living organisms but its high concentration indicates the pollution load in groundwater sources. Average groundwater levels of phosphorus is about 0.02 mg l/L as PO_4^{3-}. Andhakaranazhy coast groundwater reported an annual mean of 0.2 ± 0.18 mg/L of phosphate in shallow groundwater sources with CI of 0.1-0.3 mg/L at 95% significant level (Figure 3.17).

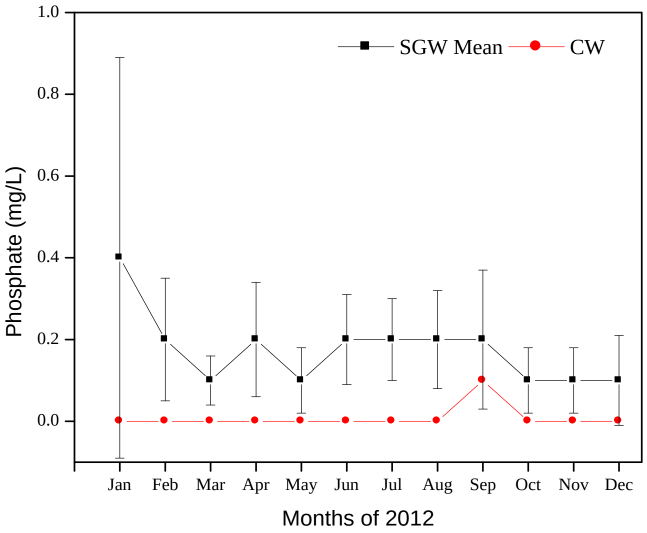


Figure 3.17: Monthly variation of phosphate ion of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

In January, 2012 showed its very high concentration, 0.4±0.49 mg/L. After January the phosphate concentration gradually decreases and maintains a steady state. The control well having no phosphate concentration except the September month of the year 2012 (0.1 mg/L). The excess presence of phosphate in groundwater is a result of domestic sewage and detergents [26].

3.2.17 Total Iron

Iron is a common constituent in soil as well as groundwaters. It is present in water as two states-soluble ferrous (Fe^{2+}) iron and insoluble ferric (Fe^{3+}) iron. Water having ferrous iron is clear and colourless because the iron is completely dissolved. When it is exposed to air, the water turns cloudy and reddish brown colour due to oxidation of ferrous (Fe^{2+}) iron into reddish brown ferric oxide (Fe_2O_3). The permissible limit of iron in drinking water is 0.3 mg/L. Shallow groundwater sources reported an annual mean of 0.8±0.84 mg/L of total iron during the year 2012 with CI of 0.3-1.3 mg/L at 95% significant level. Entire period of 2012, iron exceeds the permissible limits of BIS with a maximum of 1.3±1.02 mg/L during the month of June, 2012 (Figure 3.18). Control well also reported the iron contamination during the period 2012 with an annual mean of 0.5±0.46 mg/L. If groundwater with more amount of iron is tapped during rock formation process, it quickly oxidizes to ferric state in the form of insoluble ferric hydroxide [27]. Natural condition, that have been produces high levels of iron in groundwater is aquifers with alluvial sediments [28].

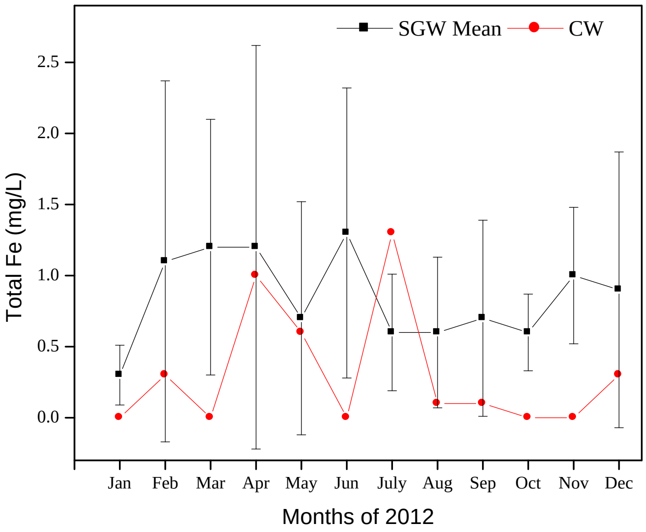


Figure 3.18: Monthly variation of total iron of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.2.18 Total Dissolved Solids (TDS)

The presence of Calcium, Magnesium, Sodium, Potassium, Bicarbonate, Chloride and Sulphate ions are responsible for the TDS in groundwater. As permissible limit of TDS for drinking water is 2000 mg/L. TDS reported an annual mean of 576.3±398.92 mg/L for shallow groundwater sources during the year 2012 with CI of 330.6-822.0 mg/L at 95% significant level. During January TDS was observed at a minimum of 269.5±72.20 mg/L and gradually increases to 828.2±637.90 mg/L in March, 2012. Afterwards, the TDS decreases and reaches at 642.0±345.87 mg/L during May 2012 (Figure 3.19). During monsoon season, the TDS was very low and it attains a maximum of 890.9±902.88 mg/L at the end of December, 2012. The control well also showed an annual mean of 583.6±198.81 mg/L of TDS during the year 2012. Higher concentrations of TDS in the groundwater sources is due to the leaching of fractions from soil and also domestic sewage, which percolate into the groundwater [29].

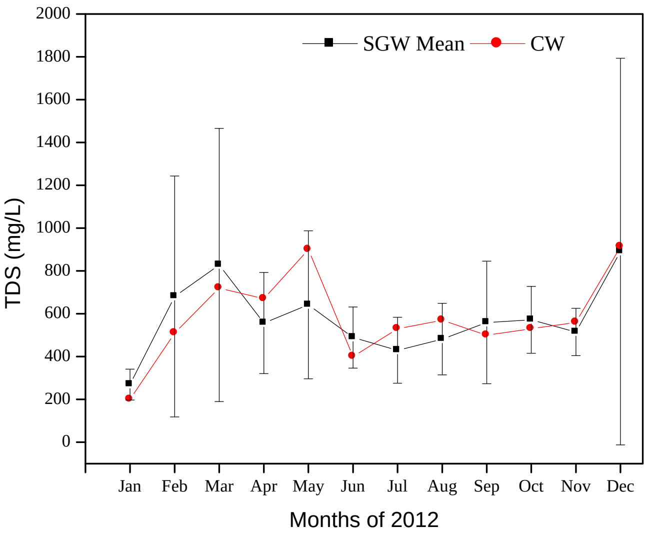


Figure 3.19: Monthly variation total dissolved solids (TDS) of control well (CW) and shallow groundwater (SGW) sources along the Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3. 3 Irrigation Water Quality

Irrigation suitability of groundwater was measured by using the sodium percent (Na %), sodium adsorption ratio (SAR) and Kelley's ratio (KR), permeability index (PI), magnesium ratio (MR), USSL and Wilcox diagrams.

3.3.1 Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio can be used to find out the degree to which irrigation water tends to enter into cation exchange reactions, undergo within the soil. High amount of sodium present in the groundwater, can have the tendency to replace the adsorbed calcium or magnesium in the aquifer, cause damage to soil structure and the soil becomes compact and impermeable. SAR can determined by using the following equation:

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

According to Richard's (1954) irrigation water is classified into four categories [30] based on SAR- excellent (0-10), good (10-18), fair (18-26) & poor (>26). Table 3.3 shows the monthly variation of SAR of SGW and CW of Andhakaranazhy coast during the year 2012. The SAR reported an annual mean of 3.0±2.09 during the year 2012. Entire period (January-December 2012) SAR maintains an *excellent* (0-10) quality of water for irrigation purposes. In the case of control well, SAR becomes 3.0±0.79, confirms it excellent for irrigation.

Table 3.3: Monthly variation of sodium adsorption ratio (SAR) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	Parameters			
	CW		SGW	
	SAR	Water Quality	SAR	Water Quality
Jan 2012	2.2	E	2.6±2.59	E
Feb 2012	3.1	E	3.3±2.45	E
Mar 2012	3.5	E	3.6±2.55	E
Apr 2012	3.2	E	3.0±2.08	E
May 2012	4.3	E	3.2±2.13	E
Jun 2012	2.3	E	2.8±1.72	E
Jul 2012	3.3	E	2.8±1.66	E
Aug 2012	3.1	E	2.9±1.71	E
Sep 2012	2.1	E	2.5±1.89	E
Oct 2012	2.3	E	2.9±2.02	E
Nov 2012	2.3	E	2.4±1.04	E
Dec 2012	4.3	E	3.6±2.63	E
$\bar{x} \pm \sigma$	3.0±0.79	E	3.0±2.09	E
μ	3.0±0.49	E	3.0±1.29	E
CI	2.5-3.5	E	1.7-4.3	E

E-Excellent

3.3.1.1 USSL Diagram

USSL diagrams are used to find the suitability of water for agriculture, constructed by plotting SAR (sodium hazard) against EC (salinity hazard). SAR is divided into four categories-low (S1), medium (S2), high (S3) and very high (S4) sodium water. EC is classified into four based on the hazard. They are < **250** µmho-low salinity water (C1), **250-750** µmho-medium salinity water (C2), **750-2250** µmho-high salinity water (C3) & > **2250** µmho-very high salinity water (C4). In USSL diagram, we can see three regions of water quality- *good, moderate* and *bad.* If the points are fall in the *C1S1* and *C2S1* regions, water quality is considered as *good*. The points in the *C3S2* region are come under moderate quality. But the points are placed beyond the *C3S2* is termed as *bad water quality*. Figure 3.20 shows the USSL diagram of groundwater sources of Andhakaranzhy coast during the period 2012. Water is having *medium salinity hazard and low sodium hazard* during the months January, June, July, August and November 2012 and comes under the class of *C2S1* range. However, during February, March, April, May, September, October and December 2012, water is in the range of C3S1 with moderate water quality due to the increased EC concentration as a result of salt water intrusion [31].

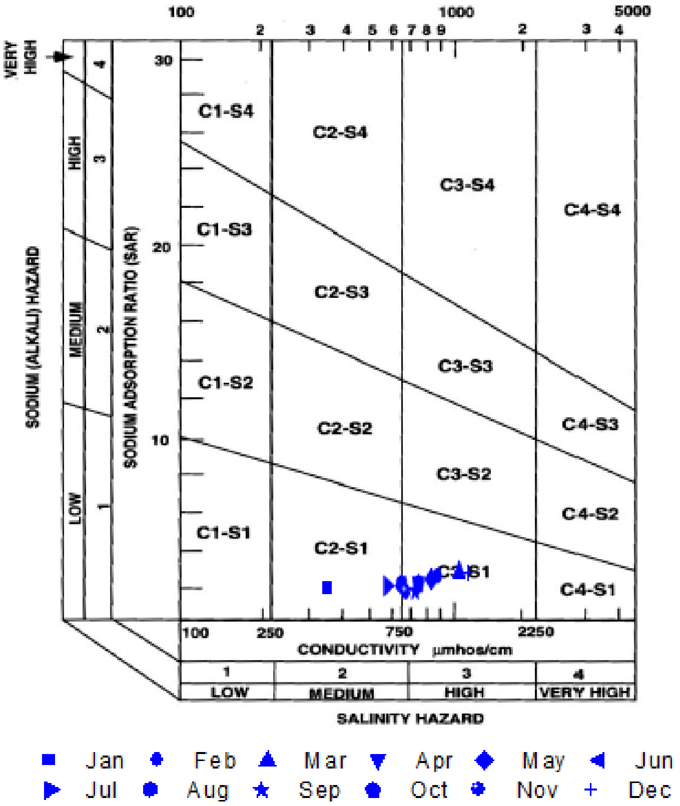


Figure 3.20: USSL Diagram of shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

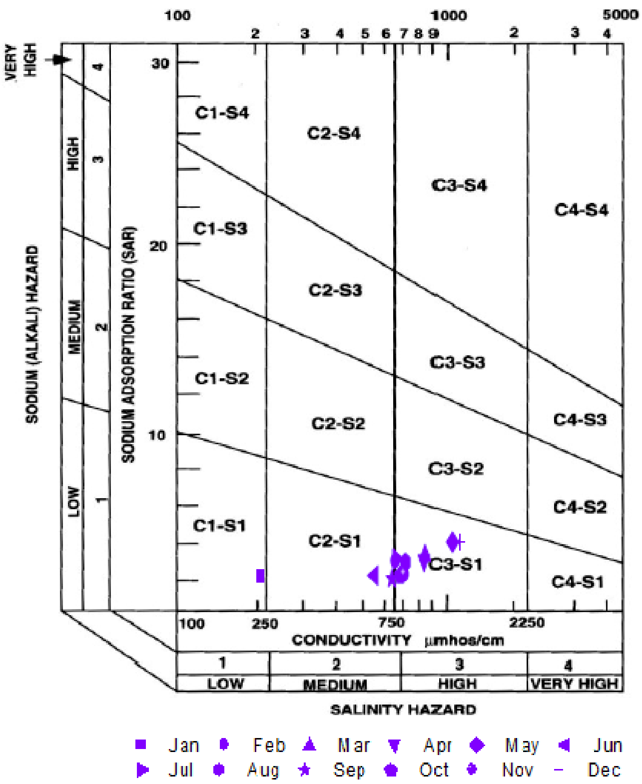


Figure 3.21: USSL Diagram of control well (CW) of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Control well falls under *C1S1* during the month January 2012. But during the months February, June, July and Septrember 2012, it belongs to *C2S1* type of water. The remaining months groundwater comes under *C3S1* with high salinity and low sodium hazard region (Figure 3.21).

3.3.2 Sodium Percent (Na%)

Sodium in irrigation water usually expressed as percent sodium. According to Wilcox (1955) Na% is a common parameter in all natural water, to obtain the suitability of irrigation use. It can be determined by following the formula [32]

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

Irrigation water classified based on Na% are excellent **(<20)**, good **(20-40)**, permissible **(40-60)**, doubtful **(60-80)** & unsuitable **(>80)**. Andhakaranazhy coast shallow groundwater possess an annual mean of 43.8±14.3 of Na% during the year 2012, water is permissible for irrigation. Most of the period Na% is in the range of 40-60, suitable for agricultural uses as they are noted as January (37.8±18.07) and September (39.7±11.27) 2012 groundwater is *good* for irrigation. The control well exhibits Na% of 47.5±6.20 during the year 2012, comes under the category *permissible* as per the classification (Table 3.4).

Table 3.4: Monthly variation of sodium percent (Na%) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	Na%	**Water Quality**	**Na%**	**Water Quality**
Jan 2012	41.5	P	37.8±18.07	G
Feb 2012	48.4	P	42.9±8.07	P
Mar 2012	49.8	P	45.5±12.35	P
Apr 2012	46.2	P	43.8±10.28	P
May 2012	57.4	P	46±10.76	P
Jun 2012	44.4	P	45.8±7.42	P
Jul 2012	54.1	P	45.9±15.37	P
Aug 2012	51.8	P	47.7±14.54	P
Sep 2012	40.7	P	39.7±11.27	G
Oct 2012	41.5	P	42.7±28.89	P
Nov 2012	39.3	G	40.8±12.12	P
Dec 2012	55.2	P	47.4±9.44	P
$\bar{x} \pm \sigma$	47.5±6.20	P	43.8±14.3	P
M	47.5±3.82	P	43.8±8.81	P
CI	43.7-51.3	P	35.0-52.7	G-P
E- Excellent		*G-Good*	*P-Permissible*	

3.3.2.1 Wilcox Diagram

Wilcox diagrams are also used to determine the irrigation suitability, prepared by plotting the graph of EC vs Na%. It is divided into five classes-*excellent to good, good-permissible, permissible to doubtful, doubtful to unsuitable and unsuitable* quality of water. Most of the months groundwater of Andhakaranazhy coast fall in the range of *good to permissible* except January and July 2012, which keeps *excellent to good* quality of water for agriculture as shown from the Figure 3.22 [33].

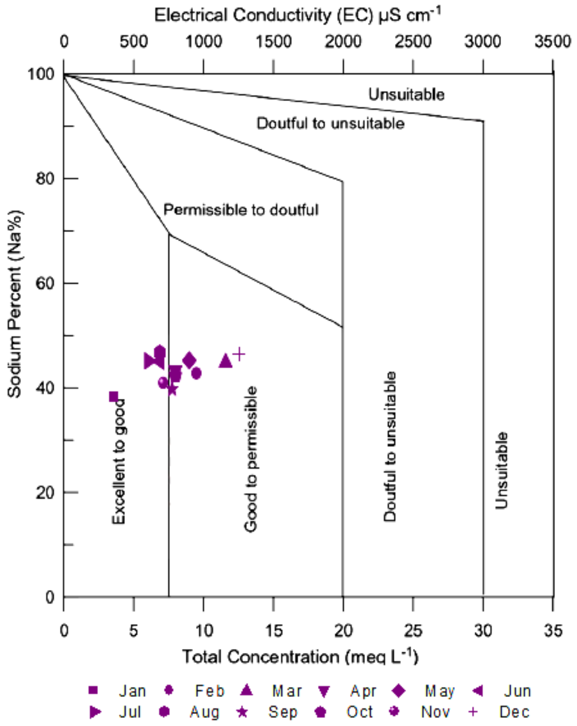


Figure 3.22: Wilcox Diagram of shallow groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

During January and July, 2012 groundwater of control well possess excellent to good quality. The remaining months, water quality becomes good to permissible (Figure 3.23).

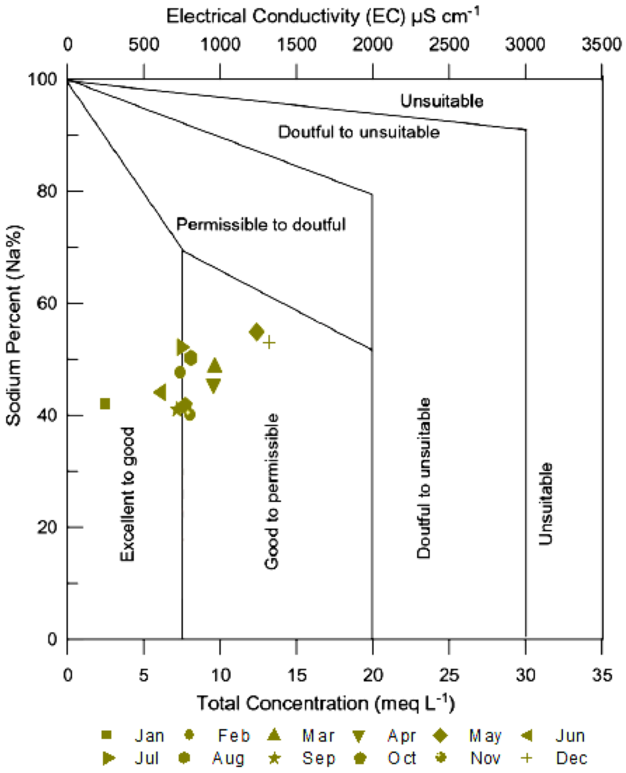


Figure 3.23: Wilcox Diagram of control well (CW) of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.3.3 Permeability Index (PI)

Doneen (1964) developed a classification for water irrigation suitability based on PI. It is calculated by following equation [34]

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

Accordingly, water can be classified as C*lass I, Class II and Class III. Class I and Class II* are suitable for irrigation purposes with 75% or more of maximum permeability and *Class III* water is unsuitable for irrigation with 25% of maximum permeability. Permeability Index (PI) showed an annual mean of 70.1±7.74 during the year 2012, reveals groundwater of andhakaranazhy coast is *marginally safe (Class II)* for irrigation. Most of the months, water is having 25-75% of maximum permeability, belongs to the C*lass II.* Groundwater occupies under C*lass I* with more than 75% maximum permeability during August 2012, water is safe for irrigation uses. Table 3.5 shows the monthly variation of permeability index of shallow groundwater and control well of Andhakaranazhy coast, indicates suitability of groundwater sources for irrigation [35]. PI exhibits an annual mean of 70.1±7.74 in the case of shallow groundwater. In most of the months groundwater was comes under *Class II, marginally safe for irrigation* except in August 2012. During August, PI of groundwater becomes *safe for irrigation* and comes under *Class I*. However, the control well showed a PI of 71.2±6.29, indicates the groundwater suitability for irrigation purposes during the year 2012.

Table 3.5: Monthly variation of permeability index (PI) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	PI	**Water Quality**	**PI**	**Water Quality**
Jan 2012	71.1	Class II	68.7±7.46	Class II
Feb 2012	73.1	Class II	68.7±6.64	Class II
Mar 2012	69.3	Class II	69.2±4.67	Class II
Apr 2012	64.2	Class II	68.4±7.77	Class II
May 2012	79.3	Class II	73.0±8.73	Class II
Jun 2012	74	Class II	74.9±4.66	Class II
Jul 2012	80	Class II	73.6±10.19	Class II
Aug 2012	76.9	Class I	75.2±9.40	Class I
Sep 2012	68.2	Class II	66.1±7.97	Class II
Oct 2012	66.9	Class II	67.5±8.26	Class II
Nov 2012	58.4	Class II	65.2±5.90	Class II
Dec 2012	73.3	Class II	70.6±8.96	Class II
$\bar{x} \pm \sigma$	71.2±6.29	Class I	70.1±7.74	Class II
μ	71.2±3.87	Class I	70.1±4.77	Class II
CI	67.3-75.1	S-MS	65.3-74.8	Class II

Class I- Safe for Irrigation (S) *Class II-Marginally Safe for Irrigation(MS)*

3.3.4 Kelley's Ratio (KR)

The concentration of sodium measured against calcium and magnesium is known as Kelley's ratio [36]. The irrigation water is classified into two categories based on KR. The Kelley's ratio <1 indicates suitability of water for agricultural use. But KR>1, water is unsuitable for irrigation.

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

KR of shallow groundwater recorded an annual mean of 0.9±0.61 during the period 2012. Throughout the year, groundwater sources were suitable for irrigation according to Kelley's ratio, except for May 2012 (KR is 1.0±0.7), August 2012 (KR is 1.1±0.9) and December 2012 with a KR of 1.1±0.9, may be due to the excess sodium concentration (Table 3.6). Control well having a KR of 1.0±0.74 during the year 2012, revealed the suitability of groundwater for agricultural uses.

Table 3.6: Monthly variation of Kelley's ratio (KR) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	KR	**Water Quality**	**KR**	**Water Quality**
Jan 2012	0.7	S	0.7±0.7	S
Feb 2012	0.9	S	0.8±0.52	S
Mar 2012	1	US	0.9±0.49	S
Apr 2012	0.8	S	0.9±0.56	S
May 2012	1.3	US	1±0.7	US
Jun 2012	0.8	S	0.9±0.47	S
Jul 2012	1.2	US	0.9±0.51	S
Aug 2012	1.1	US	1.1±0.9	US
Sep 2012	0.7	S	0.7±0.53	S
Oct 2012	0.7	S	0.9±0.65	S
Nov 2012	0.6	S	0.7±0.26	S
Dec 2012	1.2	US	1±0.74	US
$\bar{x} \pm \sigma$	0.9±0.23	S	0.9±0.61	S
μ	0.9±0.14	S	0.9±0.38	S
CI	0.8-1.0	S	0.5-1.3	S-US

S-Suitable *US-Unsuitable*

3.3.5 Magnesium Adsorption Ratio (MAR)

In most of the water, calcium and magnesium keeps an equilibrium state. But if the concentration of magnesium exceeds over calcium, it creates adverse effects on crop yield. Excess magnesium enhances the soil pH and affects its quality. The magnesium ratio was calculated using following formula

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

If the ratio less (MAR<50) means, water is suitable for irrigation. But if the value exceeds 50, water is unsuitable for agriculture purposes [37]. MAR of shallow groundwater exhibits an annual mean of 26.5±12.24 during the period 2012.

Table 3.7: Monthly variation of magnesium adsorption ratio (MAR) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	MAR	**Water Quality**	**MAR**	**Water Quality**
Jan 2012	14.3	S	21.3±10.56	S
Feb 2012	13.5	S	23.8±8.83	S
Mar 2012	22.8	S	25.8±11.63	S
Apr 2012	28.6	S	27.8±15.31	S
May 2012	30.5	S	25.6±14.26	S
Jun 2012	8.9	S	24.6±10.38	S
Jul 2012	15.1	S	25.8±10.86	S
Aug 2012	25.5	S	29.0±8.80	S
Sep 2012	29.7	S	30.8±14.88	S
Oct 2012	28.4	S	29.1±7.08	S
Nov 2012	26.3	S	25.5±15.80	S
Dec 2012	37.8	S	28.4±14.49	S
$\bar{x} \pm \sigma$	23.5±8.64	S	26.5±12.24	S
μ	23.5±0.18	S	26.5±7.54	S
CI	18.2-28.8	S	18.9-34.0	S

S-Suitable *US-Unsuitable*

Throughout the year, the ratio is found as below 50, assures suitability of agricultural usage (Table 3.7). Control well also showed a magnesium adsorption ratio of 23.5±8.64 during the year 2012, further indicates suitability of groundwater.

3.4 Corrosion Indices

The indices used for predicting the industrial suitability are Langelier Saturation Index (LSI), Ryznar Stability Index (RSI) and Aggressiveness Index (AI), measures the corrosion and scaling potential of groundwater.

3.4.1 Langelier Saturation Index (LSI)

Langelier saturation index (LSI) can be used to predict the tendency of water to form or dissolve calcium carbonate scale. Dr. Langelier (1936) has introduced this equilibrium model. It is an indication of calcium carbonate scale formation tendency of water. This index is derived from the theoretical concept of saturation leading to scale formation, corrosiveness and equilibrium conditions. Means that, in equilibrium condition there is neither scale formation nor dissolution of scale. But undersaturated water dissolves the existing calcium carbonate scale and supersaturated water will precipitate the calcium carbonate leading to scales. LSI may be positive, negative or zero depending upon the nature of the water [38-39].

$$\boldsymbol{LSI = pH - pH_s \ldots\ldots\ (1)}$$

$$\boldsymbol{pH_s = pK_2 - pK_s + pCa^{2+} + pHCO_3^-} \quad \ldots\ldots\ldots(2)$$

Where pH = actual pH of water
pH_s = pH of saturation for $CaCO_3$
pCa^{2+} = equilibrium calcium content
pK_2 = second protolysis constant for H_2CO_3
pK_s = solubility product constant for $CaCO_{3(s)}$
$pHCO_3^-$ = total alkalinity when pH>9.5

Table 3.8 shows the monthly variation of Langelier saturation index (LSI) of shallow groundwater and control well of Andhakaranazhy coast. SGW showed an annual mean of 0.5±0.39 during the year 2012, indicates the groundwater of Andhakaranazhy coast is slightly scale forming and corrosive (SSFC). In January 2012, LSI is 0.6±0.48, *scale forming but non corrosive (SFNC)* behaviour and it becomes *slightly scale forming and corrosive* (SSFC) during February 2012 (0.4±0.30). Again the LSI was enhanced during the month of March, 2012 and reached at a maximum of LSI (0.9±0.36). But in June 2012, the groundwater reported an LSI of 0.3±0.49 and becomes SSFC. After that there was a gradual increase in LSI and reached 0.7±0.53 in August, 2012. During September, the LSI found 0.4±0.44. However, there is a pit corrosion taking place in November. Finally, the LSI reached at 0.3±0.18 in December, 2012. In the case of control well reported the LSI of 0.5±0.30 during the year 2012, *slightly scale forming and corrosive (SSFC)* behavior.

Table 3.8: Monthly variation of Langelier saturation index (LSI) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	LSI	**Tendency of water**	**LSI**	**Tendency of water**
Jan 2012	0.4	SSFC	0.6±0.48	SFNC
Feb 2012	0.5	SSFC	0.4±0.30	SSFC
Mar 2012	1.2	SFNC	0.9±0.36	SFNC
Apr 2012	0.9	SFNC	0.6±0.30	SFNC
May 2012	0.7	SFNC	0.5±0.48	SSFC
Jun 2012	0.7	SFNC	0.3±0.49	SSFC
Jul 2012	0.3	SSFC	0.5±0.50	SSFC
Aug 2012	0.5	SFNC	0.7±0.53	SFNC
Sep 2012	0.2	SSFC	0.4±0.44	SSFC
Oct 2012	0.5	SFNC	0.5±0.15	SSFC
Nov 2012	0.2	SSFC	0.0±0.22	SSFC
Dec 2012	0.3	SSFC	0.3±0.18	SSFC
$\bar{x} \pm \sigma$	0.5±0.30	SFNC	0.5±0.39	SSFC
μ	0.5±0.23	SFNC	0.5±0.24	SSFC
CI	0.3-0.7	SSFC-SFNC	0.3-0.7	SSFC

SSFC- Slightly scale forming and corrosive *SFNC- Scale forming and non-corrosive*

3.4.2 Ryznar Stability Index (RSI)

John Ryznar (1944) has developed a modification of the LSI, called Ryznar Stability Index (RSI). It is useful for both low and high hardness waters having same LSI. Value of RSI will be always a positive number [38-39].

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

Shallow groundwater sources of Andhakaranazhy coast reported an annual mean of (6.6±0.68) of RSI during the period 2012, having *little scale forming or corrosive* (LSC) behaviour. Most of the months in 2012 showed a LSC character except in November 2012. During November, 2012 the RSI was 7.1±0.48, indicates the corrosive nature of groundwater. Control well recorded an annual mean of 6.5±0.37 during the year 2012 (Table 3.9).

Table 3.9: Monthly variation of Ryznar stability index (RSI) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	RSI	**Tendency of water**	**RSI**	**Tendency of water**
Jan 2012	6.7	LSC	6.4±0.68	LSC
Feb 2012	6.4	LSC	6.6±0.51	LSC
Mar 2012	5.8	LSC	6.1±0.56	LSC
Apr 2012	6.0	LSC	6.5±0.53	LSC
May 2012	6.3	LSC	6.8±1.05	LSC
Jun 2012	6.4	LSC	6.9±0.91	LSC
Jul 2012	6.9	LSC	6.7±0.82	LSC
Aug 2012	6.8	LSC	6.6±0.94	LSC
Sep 2012	7.0	CS	6.7±0.64	LSC
Oct 2012	6.6	LSC	6.5±0.29	LSC
Nov 2012	6.8	LSC	7.1±0.48	CS
Dec 2012	6.8	LSC	6.7±0.26	LSC
$\bar{x} \pm \sigma$	6.5±0.37	LSC	6.6±0.68	LSC
μ	6.5±0.18	LSC	6.6±0.42	LSC
CI	6.3-6.7	LSC	6.2-7.0	LSC

LSC- Little Scale Forming *CS-Corrosion Significant*

3.4.3 Aggressive Index (AI)

The Aggressive Index (AI) was originally developed for monitoring the corrosion in asbestos pipes [38]. But it can be used as a substitute for LSI to draw more knowledge on aggressiveness based on simple calculations. The AI is derived from the actual pH, calcium hardness and total alkalinity. It is simple and more convenient than the LSI. Because the AI does not include the effects of temperature or dissolved solids, it is less accurate as an analytical tool than the LSI [40].

$$\boldsymbol{AI = pH + log\ (AH)} \text{ ....} (4)$$

Where '**A**' is the total alkalinity and '**H**' is calcium hardness in mg/L as $CaCO_3$

AI of shallow groundwater of Andhakaranazhy coast was found to be 12.4±0.41 during the year 2012. Throughout the period, the AI of groundwater shows non-aggressive character (NA) except in November (11.9±0.23) as shown from the Table 3.10.

Table 3.10: Monthly variation of aggressiveness index (AI) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	AI	**Tendency of water**	**AI**	**Tendency of water**
Jan 2012	12.3	NA	12.5±0.47	NA
Feb 2012	12.4	NA	12.3±0.32	NA
Mar 2012	13.1	NA	12.8±0.39	NA
Apr 2012	12.8	NA	12.5±0.32	NA
May 2012	12.6	NA	12.3±0.52	NA
Jun 2012	12.6	NA	12.2±0.49	NA
Jul 2012	12.2	NA	12.4±0.51	NA
Aug 2012	12.4	NA	12.6±0.56	NA
Sep 2012	12.1	NA	12.3±0.44	NA
Oct 2012	12.3	NA	12.4±0.16	NA
Nov 2012	12.1	NA	11.9±0.23	MA
Dec 2012	12.2	NA	12.2±0.18	NA
$\bar{x} \pm \sigma$	12.4±0.30	NA	12.4±0.4	NA
μ	12.4±0.18	NA	12.4±0.25	MA
CI	12.2-12.6	NA	12.1-12.7	MA

NA-Non-aggressive *MA-Moderately Aggressive*

During November month, AI shows slightly corrosive behaviour, may be due to the presence of reactive hydrogen ion species. In the case of control well, AI reported 12.4±0.30 during the year 2012.

3.5 Hill-Piper-Trilinear plot and Hydrochemical Facies

Piper diagrams are made up of two triangles, that are supposed to share a common base line and each side are separated by an angular distance of 60° apart. These two are interlocked by a diamond shaped portion. Cations and anions are plotted on separate triangle as percentages and the concentrations are expressed in milliequivalent per litre. Piper diagram provides very valuable knowledge on the water type, precipitation or solution behaviour, mixing character and ion exchange phenomena. The diamond-shaped portion of piper diagram is mainly classified into four hydrochemical facies based on the dominance of major cations and anions:

(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)*

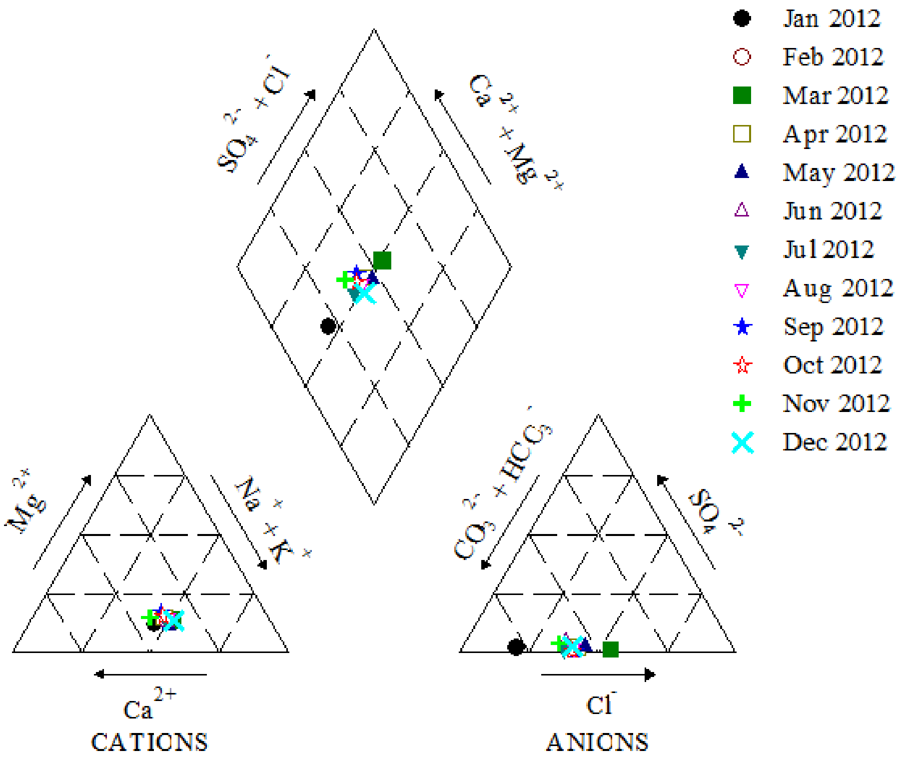


Figure 3.24: Piper Diagram of groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Figure 3.24 showed the piper diagram of shallow groundwater sources of Andhakaranazhy coast during the year 2012. In most of the months groundwater sources were fall in Facies I (Ca^{2+}-Mg^{2+}-HCO_3^-) and followed by Facies III (Na^+-K^+-Cl^--SO_4^{2-}) during the month March. The dissolution of carbonate minerals are the main source of calcium, magnesium and bicarbonate in the groundwater [29]. Due to the combined effect of sea water intrusion and ion exchange process, calcium and magnesium ions reach their super saturation,leads to precipitation during March, 2012 as observed by earlier researchers [41].

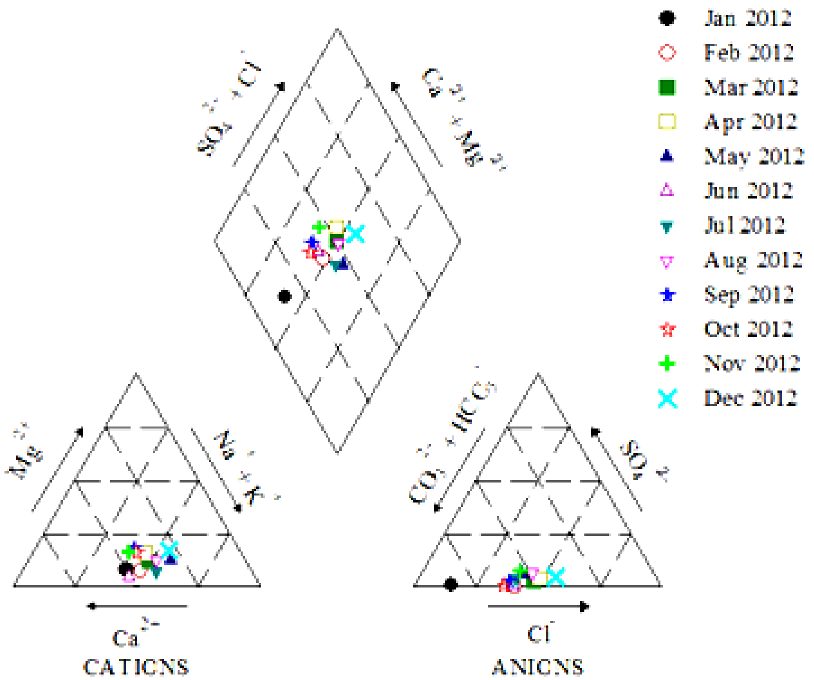


Figure 3.25: Piper Diagram of control well (CW) of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Piper diagram of control well showed temporary hardness behaviour during most of the months. However, during April, May, June and July, 2012 groundwater is having non-dominance type of ions. But December 2012, groundwater becomes saline type, indicates salt water intrusion (Figure 3.25).

3.6 Gibb’s Diagrams

Chemical composition of the groundwater is mainly controlled by many processes such as rock-water interaction, evaporation, precipitation etc. It can be explained with the help of Gibb’s diagrams [42]. The total dissolved solids were plotted against the ratio of sodium and sum of sodium and calcium constitutes the cationic part. The anionic plot was constructed by ratio of chloride and sum of chloride and bicarbonate against TDS. Gibb’s diagram was very much helpful to identify the source of dissolved ions present in groundwater. TDS was between 100-1000 mg/l constitutes the precipitation-dominance region. Rock-water interaction is contributing many of the mineral ions into the groundwater and the TDS between 1000-10000 mg/L can be attributed by weathering of rocks. Evaporation process was also enhanced the dissolved solids concentration in groundwater. When the TDS value exceeds 10000 mg/L, the ion chemistry was controlled by evaporation process. Groundwater quality of Andhakaranazhy coast is mainly controlled by weathering of rock forming minerals, clearly shown from the Figure 3.26 and figure 3.27. Throughout the year 2012, the TDS of shallow groundwater and control well is observed between 1000-10000 mg/L and the points were fall in the rock dominance region. This means the chemical composition of the groundwater is affected by rock-water interaction.

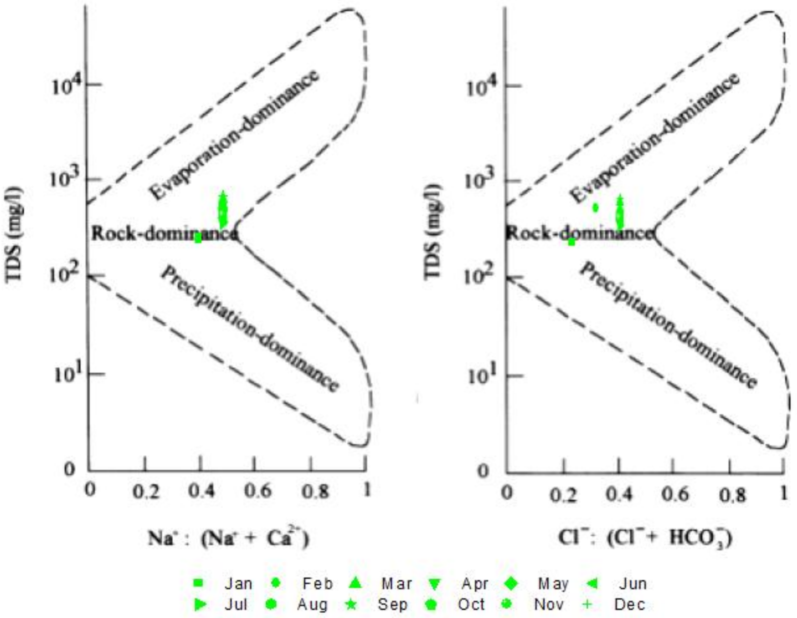


Figure 3.26: Gibb's Diagram of shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

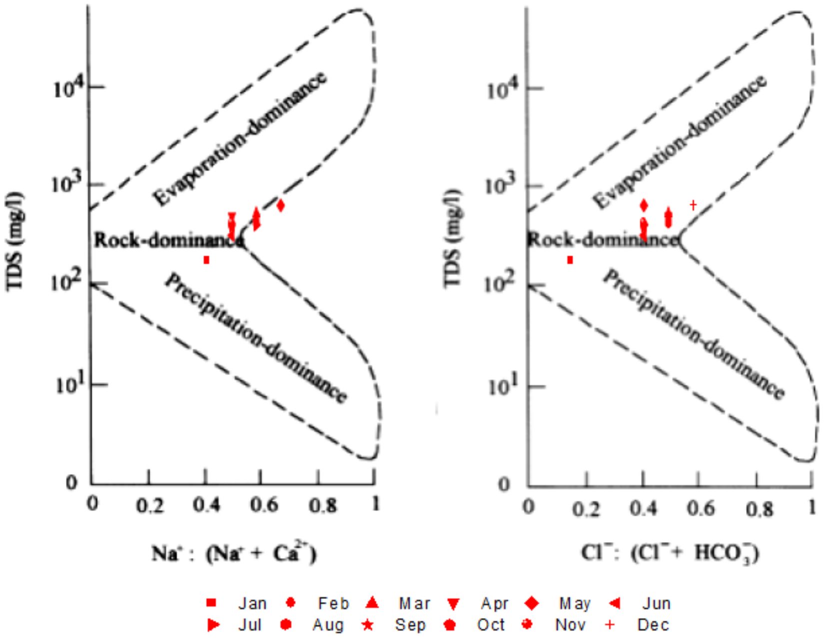


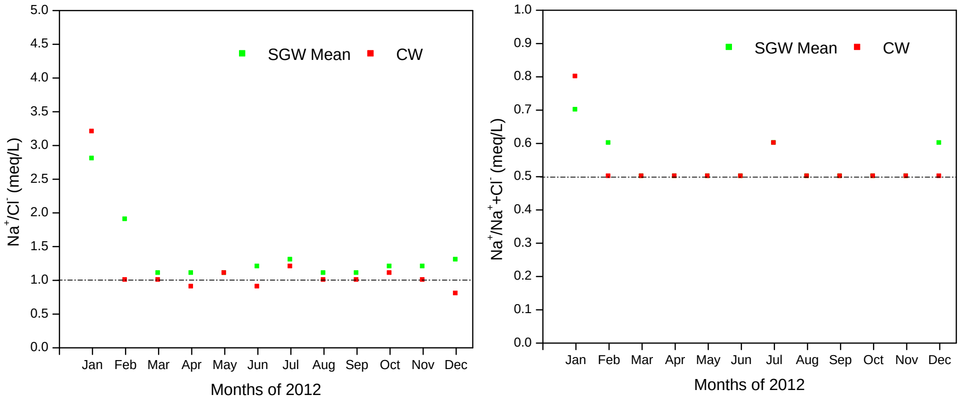
Figure 3.27: Gibb's Diagram of control well (CW) of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.7 Study of Ionic Ratios

Various processes controlling the groundwater chemistry of the coast such as weathering of rock forming minerals, ion exchange, reverse ion exchange, evaporation, sea water intrusion, dissolution, precipitation. The ionic concentrations of the groundwater are responsible for the occurrence of the above mentioned processes.

3.7.1 Sodium-Chloride Ratio

Sodium chloride ratio gives us an idea about the ion exchange or reverse ion exchange processes taking place in groundwater. If $Na/Na+Cl>$ 0.5 and $Na/Cl > 1.0$, the process taking place is ion exchange and reverse to that ($Na/Na+Cl< 0.5$ and $Na/Cl < 1.0$) reverse ion exchange may occurs [15].



(a) (b)

Figure 3.28: (a) Na^+/Cl^- ratio (b) Na^+/Na^++Cl^- ratio of shallow groundwater sources (SGW) of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Shallow groundwater sources of Andhakaranazhy coast showed an annual mean of 1.4 ±0.63 of Na^+/Cl^- ratio. Throughout the year 2012, indicates the ion exchange process is prevalent in the region. Na^+/Na^++Cl^- ratio also noted that ion exchange process was occurring in the groundwater with an annual mean of 0.6 ±0.02. This means, calcium ion replaces the sodium ions from the clay layer of aquifer. It will produce high sodium content in groundwater. Table 3.11 shows the monthly variation of Na^+/Cl^- ratio and Na^+/Na^++Cl^- ratio of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast. The scatter diagrams were clearly indicated, the ion exchange process (Figure 3.28) was dominated in the study area. Throughout the period, shallow groundwater characterised an ion exchange behaviour. Same trend was observed in the case of control well, except April and May 2012, which indicates reverse ion exchange character of groundwater.

Table 3.11: Monthly variation of Na^+/Na^++Cl^- and Na^+/Cl^- ratios of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	CW			SGW		
	Na/Na+ Cl	**Na/Cl**	**Inference**	**Na/Na+ Cl**	**Na/Cl**	**Inference**
Jan 2012	0.8	3.2	IE	0.7 ±0.05	2.8 ±0.82	IE
Feb 2012	0.5	1.0	IE	0.6 ±0.13	1.9 ±1.73	IE
Mar 2012	0.5	1.0	IE	0.5 ±0.09	1.1 ±0.46	IE
Apr 2012	0.5	0.9	RIE	0.5 ±0.06	1.1 ±0.27	IE
May 2012	0.5	1.1	RIE	0.5 ±0.06	1.1 ±0.28	IE
Jun 2012	0.5	0.9	IE	0.5 ±0.07	1.2 ±0.31	IE
Jul 2012	0.6	1.2	IE	0.6 ±0.07	1.3 ±0.40	IE
Aug 2012	0.5	1.0	IE	0.5 ±0.05	1.1 ±0.25	IE
Sep 2012	0.5	1.0	IE	0.5 ±0.05	1.1 ±0.22	IE
Oct 2012	0.5	1.1	IE	0.5 ±0.06	1.2 ±0.33	IE
Nov 2012	0.5	1.0	IE	0.5 ±0.08	1.3 ±0.39	IE
Dec 2012	0.5	0.8	IE	0.6 ±0.07	1.3 ±0.37	IE
$\bar{x} \pm \sigma$	0.5± 0.08	1.2±0.64	IE	0.6 ±0.02	1.4 ±0.63	IE
μ	0.5±0.05	1.2±0.39		0.6 ±0.01	1.4 ±0.39	
CI	0.45-0.55	0.8-1.6		0.54-0.56	1.01-1.79	

IE- Ion Exchange RIE-Reverse Ion Exchange

3.7.2 $(Ca^{2+}+Mg^{2+})$ vs $(HCO_3^-+SO_4^{2-})$ Scatter Diagram

Data falls above the equiline of $(Ca^{2+}+Mg^{2+})$ vs $(HCO_3^-+SO_4^{2-})$ scatter diagram, resulting from the carbonate dissolution process. However, the ionic concentrations lies below the 1:1 line, indicates the silicate weathering process. Shallow groundwater having silicate weathering character throughout the period. In the case of control well points fall above the equiline during the months of April and November 2012 indicates carbonate dissolution behavior [43]. The remaining months groundwater showed the dominance of silicate weathering process.

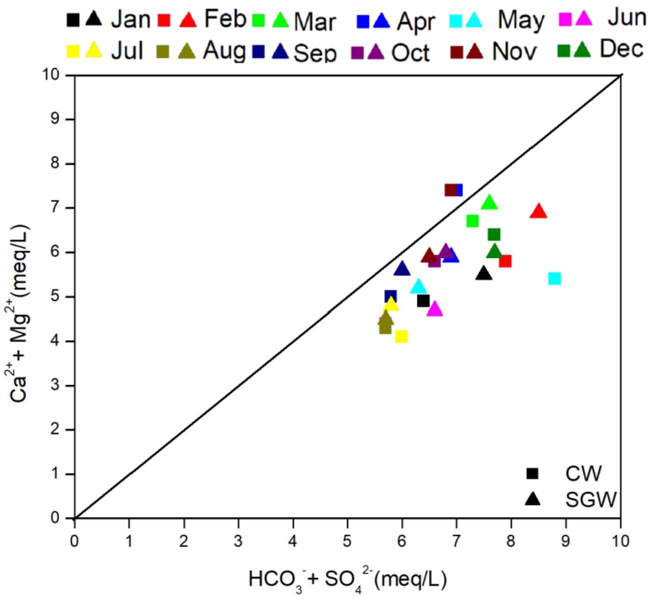


Figure 3.29: (Ca+Mg) / (HCO3+SO4) scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.7.3 Na / Ca Scatter Diagram

In Na vs Ca scatter, points falls below the 1:1 line indicates the ion exchange process. In shallow groundwater sources, ion exchange behaviour was prominent. However, during January and November 2012, concentrations lies along the equiline indicates the occurrence of both ion exchange and carbonate weathering processes [44].

Control well showed ion exchange to occur in most of the months. Instances where the ionic concentrations fall above the equiline, indicates the dissolution of carbonate mineral during the months of January, June & November 2012. However, the months of September & October both processes are dominating in the study area.

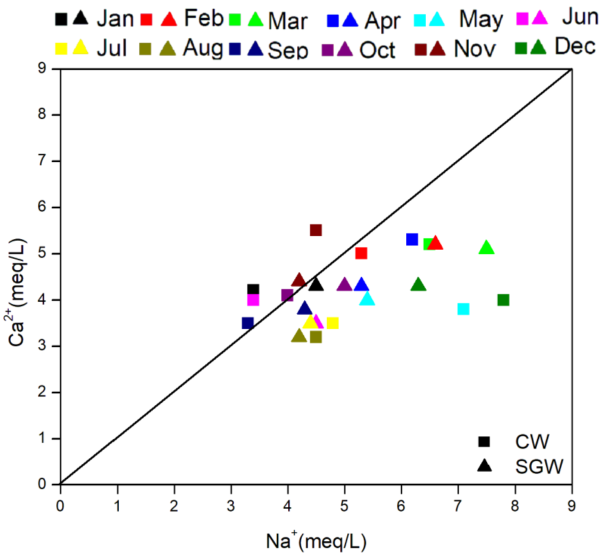


Figure 3.30: Na / Ca scatter diagram scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.7.4 Na vs Cl Scatter Diagram

The scatter diagram of Na vs Cl indicate that, ionic concentrations lies above the equiline indicates the dissolution of halite. But, the sodium ions are originating from silicate weathering process as the data falls below the equiline [45]. Most of the months shallow groundwater showed silicate weathering except during March 2012. During March we can see the occurrence of halite dissolution, because of the invasion of sea water into the groundwater aquifer. However, groundwater showed both silicate weathering and halite dissolution during the month of September 2018.

In the case of control well, water exhibits both silicate weathering and halite dissolution processes during the months February, March, June, August, September & November 2012. During months of April & December 2012, control well showed halite dissolution. However, the remaining months showed the prevalence silicate weathering processes.

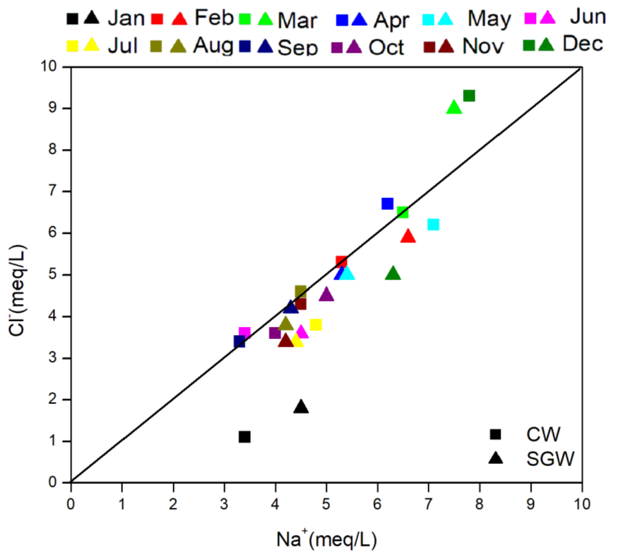


Figure 3.31: Na / Cl scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

3.7.5 (TZ^+) vs (Na + K) Scatter Diagram

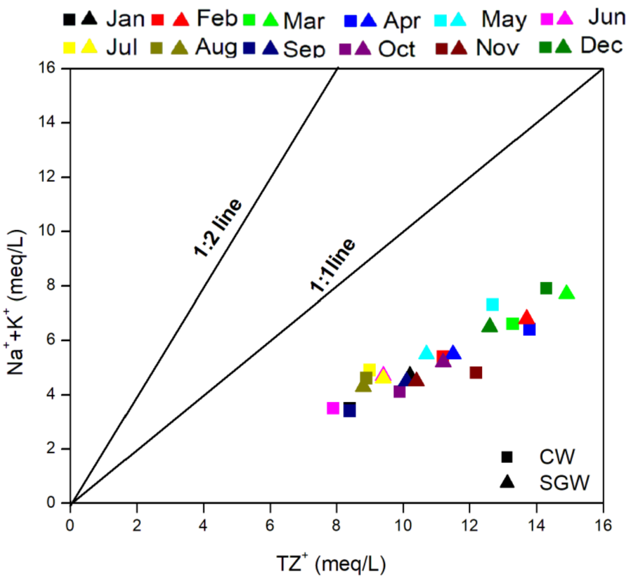


Figure 3.32: (TZ+) /(Na + K) scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Silicate weathering can be understood from the total cations (TZ^+) vs (Na + K) scatter diagram. If the points are falls below the equiline indicates silicate weathering process. Throughout the study period shallow groundwater sources was characterized by silicate weathering process. In the case of control well, all the ionic concentrations are lies below the 1:1 line, indicate the occurrence of silicate weathering process [46].

3.8 Water Quality Index (WQI)

Water quality index is a single number that express overall water quality of the region, used multiple water quality parameters for its calculation. Weighted arithmetic index method [47] has been used for the calculation of WQI. Groundwater quality Andhakaranazhy coast depends on number of physico - chemical parameters such as pH, EC, TA, TDS, DO, BOD, TH,Ca^{2+}, Mg^{2+}, Na^+, $K^{+,}$ Cl^-, SO_4^{2-} and total Fe. Hence, we chosen these important parameters and the BIS & WHO standards have been considered for the further calculation [8-9]. Monthly variation of groundwater sources of Andhakaranazhy coast are shown from the Table 3.12. According to WQI, shallow groundwater sources were *unfit for drinking purpose* (UDP) during the study period (2012). This means, we cannot use this water for human consumption before subjected to the treatment methods. Control well also showed variations in WQI during every month of 2012. In most of the time, its quality comes under *excellent class*, but it is also affected by the processes occurring in the groundwater system of the study area. Increased concentrations of ions in groundwater leads to the fluctuations in WQI of control well.

Table 3.12: Monthly variation of water quality index (WQI) of control well (CW) and shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	WQI	**Water Quality**	**WQI**	**Water Quality**
Jan 2012	5.0	E	81.7±62.24	UDP
Feb 2012	84.4	VP	244.9±326.59	UDP
Mar 2012	7.9	E	241.6±251.18	UDP
Apr 2012	274.1	UDP	253.0±357.01	UDP
May 2012	164.5	UDP	185.4±215.42	UDP
Jun 2012	3.8	E	236.0±273.33	UDP
Jul 2012	352.0	UDP	142.6±121.43	UDP
Aug 2012	34.2	G	139.0±140.76	UDP
Sep 2012	31.5	G	170.2±184.57	UDP
Oct 2012	3.4	G	124.6±96.31	UDP
Nov 2012	4.8	G	178.1±168.66	UDP
Dec 2012	89.6	E	188.5±246.23	UDP
$\bar{x} \pm \sigma$	87.9±117.05	VP	182.1±221.58	UDP
μ	87.9±72.09	VP	182.1±136.47	UDP
CI	15.8-160.0	E-UDP	45.6-318.6	P-UDP

E – Excellent G - Good VP - Very poor UDP - Unfit for drinking purposes;

3.9 Trace Metal Study

Some metals occurring in groundwater are important for the physiological functions of living tissue, which control many biochemical processes. However in trace amount they were required, known as trace metals. It is present naturally in fresh water through weathering of rocks and soils but, within the standard limits. In groundwater, the availability of these metals are very much important, because its increased concentrations can leads to harmful effects on humans as well as living things. It is used as an indicator of pollution by anthropogenic sources. For the determination of trace metals in groundwater, we used inductively coupled plasma/mass spectrometry (ICP/MS).

Table 3.13: Trace element analysis in groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the month of December 2012

Trace Metals	DW1	DW2	DW3	DW4	DW5	DW6	BW1	OP	BW2	DW7	DW8	$\bar{x} \pm \sigma$	BIS
Li (µg/l)	11.8	3.1	4.1	5.8	5.1	5.6	5.1	3.8	10.4	6.4	7.1	6.3±2.84	
Al (µg/l)	56.6	13	9.6	8.7	7.5	9.1	7.6	6.7	9.5	10	33.9	16.4±16.24	200
V (µg/l)	1.1	1.2	1.7	1.4	0.5	0.5	1.1	0.4	2	0.3	3.1	1.2±0.88	
Cr (µg/l)	0.2	0.4	0.2	0.3	0.2	0.3	0.4	0.2	1	0.2	0.4	0.4±0.25	50
Mn (µg/l)	96.9	16.3	11.7	51	72.8	49	59.7	49	146.9	101.5	15.5	61.9±43.75	300
Ni (µg/l)	3.7	0.9	1.2	4	1.7	2.2	3.4	2	4.5	3	0.7	2.3±1.28	20
Co (µg/l)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1±0.00	
Cu (µg/l)	1.4	1.1	1.4	2.7	0.9	1	0.7	0.7	2.7	0.7	0.7	1.1±0.62	1500
Zn (µg/l)	1.5	1.4	3.3	3	2.1	2.2	1.9	1	7.3	2.1	1.8	2.5±1.81	15000
Ga (µg/l)	0.7	1.5	1	3.2	2.6	3.2	2.4	3.2	2.9	1.9	2.2	2.2±0.88	
As (µg/l)	6.7	1.9	9.9	1.2	0.9	0.3	0.3	0.9	0.1	1.6	0.2	2.3±3.32	50
Se (µg/l)	1.9	2.5	2.9	2.7	3.7	3.4	3.5	3.7	3.5	3.7	3.5	3.2±0.61	10
Rb (µg/l)	5.8	9.6	6.3	7.1	1.7	3.3	6.5	8.1	3.2	1.6	10.9	5.7±3.23	
Sr (µg/l)	628.6	252.2	375	398	594.4	396.9	563.7	341.8	575.9	599.4	482.8	481.1±131.04	
Ag (µg/l)	0.1	0	0.4	3.5	0.1	0.1	0	4.4	0.1	0.1	0.4	0.6±1.35	100
Cd (µg/l)	0	0	0	0	0	0	0	0	0.1	0	0	0.01±0.03	3
In (µg/l)	0	0	0	0	0	0.1	0	0	0.1	0	0	0.02±0.04	
Cs (µg/l)	0.1	0	0	0	0	0	0	0	0	0	0	0.01±0.03	
Ba (µg/l)	5	8.4	4.9	17.2	12.3	15.7	11.9	15.4	15.5	9.9	12.3	11.1±4.04	700
Pb (µg/l)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.4	0.2	0.1	0.2±0.07	10
Bi (µg/l)	1.7	0.8	0.4	1.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.4±0.51	

The trace metals analyzed for the present study includes 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). Table 3.15 shows the results of trace element analysis of groundwater sources of Andhakaranazhy coast in the month of December, 2012 and found that all trace elements were within the standard limits of BIS [48].

3.10 Total Organic Carbon (TOC) Analysis

Organic matter present in the water can be measured as total organic carbon (TOC). It originates from the decaying vegetation, bacterial growth, and metabolic activities of living organisms or chemicals. Total organic carbon consists of dissolved and particulate material. Therefore, the fluctuations in suspended solids will affect the TOC. It is very much useful in detecting contaminants in drinking water. Organic carbon present in the water will reacts with disinfection chemicals such as chlorine and forms disinfection byproducts (DBP), which may cause cancer. Hence the reduction of organic carbon prior to disinfection can significantly decrease harmful DBP exposure to the public.TOC analysis measures both the total carbon and inorganic carbon by subtracting the TIC from the TC. Low TOC value indicates the absence of potentially harmful organic chemicals in water. The results of TOC analysis revealed that, groundwater sources of Andhakaranazhy coast exhibits a mean of 2.1±1.87 mg/L of TOC. This means, the carbon present in the groundwater is mainly composed of inorganic carbon (Table 3.16) [6].

Table 3.14: Total organic carbon (TOC) analysis in shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the month of February 2012

Station	TCmg/l	TICmg/l	TOCmg/l
DW1	7.522	6.081	1.441
DW2	4.93	3.789	1.141
DW3	4.32	3.039	1.281
DW4	15.662	8.972	6.69
DW5	4.62	3.99	0.63
DW6	4.186	3.919	0.267
BW1	6.492	5.687	0.805
OP	13.668	9.467	4.201
BW2	5.142	3.134	2.008
DW7	9.016	6.335	2.681
DW8	10.897	8.535	2.362
$\bar{x}\pm\sigma$	7.9±4.0	5.7±2.39	2.1±1.87

3.11 Designated Best Use

Central Pollution Control Board (CPCB), Ministry of Environment and Forest, Government of India has classified the water into A, B, C, D & E categories according to their designated best use (DBU) of water [Chapter 2.17].

Table 3.15: Classification of shallow groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India based on designated best use by CPCB during the period December 2012

Station	Total coliforms MPN/100ml	E. Coli	pH	EC (mS/cm)	DO (mg/L)	BOD (mg/L)	SAR	Boron (mg/L)	Class
DW1	120	Present	7.4	860	4.1	2.46	3.2	0.1	C
DW2	75	Present	7.3	5440	3.3	4.82	10.5	0.5	Below E
DW3	2	Absent	7.4	1370	4.7	2.88	4.3	0.3	C
DW4	870	Present	7.3	1120	0.8	9.9	5.1	0.2	E
DW5	97	Present	7.3	880	1.2	3.9	2.3	0.2	E
DW6	140	Present	7.3	740	3.7	3.1	2.2	0.3	E
BW1	2	Absent	7.3	500	4.3	3.0	1.3	0.1	C
OP	245	Present	7.5	650	4.0	3.1	1.5	0.1	C
BW2	128	Present	7.0	940	4.9	2.6	2.8	0.1	C
DW7	20	Present	7.3	740	4.5	2.5	1.8	0.2	C
DW8	35	Present	7.9	990	1.7	7.4	4.7	0.1	E

Table 3.17 showed the classification of shallow groundwater (SGW) sources based on designated best use (DBU) by CPCB of Andhakaranazhy coast during the period December 2012. Presence of E.Coli was reported in most of the groundwater aquifers, which indicates the faecal contamination. However, pH showed slightly alkaline character due to the presence of bicarbonate ions, but within the standard limits. Electrical conductivity and SAR were slightly high in some water samples because of the enhanced concentration of dissolved ions. Boron values are within the limits of 2 mg/L. Hence, DW1, DW3, BW1, OP, BW2 & DW7 shallow groundwater sources comes under *class C* and the water can be used as drinking water source after the conventional treatment & disinfection. The groundwater sources such as DW4, DW5 & DW6 used for irrigation and industrial cooling purposes because of the slight increase in DO and BOD. DW2 having very high EC values and which is in below E category.

3.12 Statistical Analysis

3.12.1 Pearson Correlation Matrix

Correlation is a broad class of statistical relationship between two or more variables. It is used to find the strength and statistical significance of water quality parameters. The correlation matrix of shallow groundwater sources of Andhakaranazhy coast during year 2012 are shown in Table 3.13, prepared using the XLSTAT software [50]. pH showed strong negative correlation with K, reveales acidic pH was favourable for the weathering of potassium bearing minerals. Correlation between EC & Na^+, EC & Cl^-, EC & Mg^2, EC & TH and EC & TDS indicate that conductivity of groundwater was mainly produced by the ions such as Ca, Mg, Na and Cl. Alkalinity was strongly correlated with hardness, calcium and sodium ions indicates, bicarbonate ions are produced from weathering of silicate as well as carbonate minerals. Very good correlations could be observed between TH & Ca^{2+} , TH & Mg^{2+} , TH & TDS, TH & Na^{+}, TH & K^{+} . This means Ca, Mg, Na and K ions are main contributers of hardness to groundwater of the region. Correlation between Ca^{2+} & Mg^{2+} Ca^{2+} & Na^{+}, Mg^{2+} & Na^{+} reveales that, these ions were originated from carbonate and silicate weathering. Strong correlations are noticed between the parameters such as Ca^{2+} & K^{+}, Mg^{2+} & K^{+}, Mg^{2+} & Cl^{-} indicates, some amount of Ca, Mg and K enters into the groundwater system as a result of salt water intrusion. TDS was mainly contributed by magnesium, sodium and chloride ions, clearly shown from the correlations of Mg^{2+} & TDS, TDS & Na^{+} and TDS & Cl^{-}. Na^{+} and Cl^{-} ions very strongly correlated with each other, indicates salt water intrusion was occurring in the study area (Table 3.18). Control well showed strong positive correlation with following parameters - EC & TDS, EC & Mg^{2+}, EC & Na^{+}, EC & Cl^{-}, EC & SO_4^{2-}, TH & Mg^{2+}, TH & Ca^{2+}, TH & K^{+}, Mg^{2+} & Cl^{-}, Mg^{2+} & TDS, TDS & Na^{+}, TDS & Cl^{-}, TDS & SO_4^{2-} and K^{+} & SO_4^{2-} , produced from the same source by salt water intrusion. A very strong positive correlation was found between Na^{+} & Cl^{-}, related to the incursion of sea water. Carbonate weathering is the main source of Ca^{2+} and Mg^{2+} ions in groundwater (Table 3.19).

Table 3.16: Pearson's correlation matrix of shallow groundwater (SGW) sources of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Variables	pH	EC	Alk	DO	BOD	TH	Ca	Mg	TDS	Na	K	Cl	SO_4	NO_3	PO_4	Fe(t)
pH	1															
EC	-0.190	1														
Alk	-0.407	0.410	1													
DO	0.176	-0.358	-0.359	1												
BOD	-0.116	0.301	0.468	-0.360	1											
TH	-0.456	**0.645**	**0.855**	-0.630	0.549	1										
Ca	-0.483	0.488	**0.879**	-0.462	0.389	**0.903**	1									
Mg	-0.194	**0.700**	0.530	-0.489	0.451	**0.784**	**0.700**	1								
TDS	-0.200	**0.999**	0.418	-0.373	0.293	**0.656**	0.499	**0.705**	1							
Na	-0.080	**0.811**	**0.760**	-0.342	0.316	**0.794**	**0.771**	**0.706**	**0.814**	1						
K	**-0.684**	0.552	0.464	-0.323	0.274	**0.678**	**0.711**	**0.619**	0.556	0.510	1					
Cl	0.108	**0.812**	0.424	-0.225	0.195	0.569	0.591	**0.765**	**0.811**	**0.876**	0.506	1				
SO4	-0.286	0.066	-0.246	0.473	-0.160	-0.270	-0.268	-0.467	0.062	-0.168	0.132	-0.164	1			
NO3	-0.153	-0.312	-0.061	-0.177	0.272	0.062	0.236	0.232	-0.307	-0.242	0.297	-0.052	-0.319	1		
PO4	0.024	-0.533	0.380	-0.181	0.166	0.127	0.125	-0.259	-0.525	-0.131	-0.320	-0.465	-0.280	-0.048	1	
Tfe	-0.311	0.507	0.219	0.363	0.092	0.232	0.306	0.363	0.496	0.439	0.626	0.549	0.448	-0.133	-0.458	1

Table 3.17: Pearson's correlation matrix of control well (CW) of Andhakaranazhy coast, Alappuzha, Kerala, India during year 2012

Variables	pH	EC	Alk	DO	BOD	TH	Ca^{2+}	Mg^{2+}	TDS	Na^{+}	K^{+}	Cl^{-}	SO_4^{2-}	NO_3^{-}	PO_4^{3-}	Fe(t)
pH	**1**															
EC	0.175	**1**														
Alk	0.079	0.349	**1**													
DO	0.625	-0.093	0.034	**1**												
BOD	-0.126	0.151	-0.283	-0.607	**1**											
TH	-0.074	0.423	0.400	-0.157	0.092	**1**										
Ca^{2+}	-0.001	0.035	0.448	0.009	-0.111	**0.850**	**1**									
Mg^{2+}	-0.131	**0.716**	0.182	-0.293	0.298	**0.776**	0.326	**1**								
TDS	0.212	**0.994**	0.382	-0.089	0.154	0.424	0.041	**0.711**	**1**							
Na^{+}	0.250	**0.881**	0.545	-0.058	0.223	0.498	0.231	0.616	0.903	**1**						
K^{+}	-0.260	0.496	0.259	-0.094	-0.092	**0.794**	0.635	0.663	0.490	0.441	**1**					
Cl^{-}	0.234	**0.920**	0.345	-0.123	0.335	0.530	0.223	**0.684**	**0.907**	**0.917**	0.452	**1**				
SO_4^{2-}	-0.071	**0.697**	0.056	-0.035	0.088	0.338	0.008	0.596	**0.711**	0.598	**0.703**	0.533	**1**			
NO_3^{-}	-0.491	-0.246	0.152	-0.550	0.550	0.132	0.241	-0.051	-0.253	-0.046	-0.066	-0.050	-0.337	**1**		
$PO4^{3-}$	-0.197	-0.126	-0.276	-0.334	0.096	-0.172	-0.308	0.059	-0.132	-0.364	-0.166	-0.217	-0.186	-0.170	**1**	
Fe(t)	0.121	0.278	0.073	0.114	-0.322	-0.039	-0.082	0.029	0.286	0.364	0.029	0.252	0.221	-0.490	-0.150	**1**

3.12.2 Analysis of Co-Variance (ANOVA)

ANOVA tests were conducted to check the various hypotheses, suggested in the chapter 1. The results are following:

a) Whether there is any significant difference between mean values of various parameters in control well at different months of 2012

Table 3.18: ANOVA table for the comparison of water quality parameters between different months of control well of Andhakaranazhy coast during the year 2012

Source	SS	df	ms	F	p- value
Total	5756071.7264	215			
Parameters	5180569.7034	17	304739.3493	112.692	p<0.001
Month	69820.9891	11	6347.3626	2.347	p<0.01
Residual	505681.0339	187	2704.1767		

Inferences

1) There is very high significant difference between parameters ($p < 0.001$). TDS is significantly very high followed by Alkalinity, TH, Cl^-, and Na^+ ($p < 0.001$). Eh is significantly very low followed by PO_4^{3-}, NO_3^-, and Iron.

2) Months also exhibited a significant difference between them ($p < 0.01$) November and December showed significantly higher values for the parameters and January, June, July, August, September, and October registered significantly lower values for the parameters ($p < 0.001$).

b) Whether there is any significant difference between mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the each month of year 2012

Table 3.19: ANOVA table for the comparison of water quality parameters between different months of shallow groundwater sources of Andhakaranazhy coast during the year 2012

Source	SS	df	ms	F	p- value
Total	5587046.0266	215			
Parameters	5174150.2808	17	304361.7812	162.653	P < 0.001
Months	62975.4616	11	5725.0420	3.060	P < 0.01
Residual	349920.2842	187	1871.2315		

Inference

1) There is very high significant difference between parameters ($p < 0.001$). TDS showed significantly very high value followed by Alkalinity and TH, Eh was significantly lower among all the parameters followed by PO_4^{3-} and total Iron.
2) Months also showed a significant difference between them ($p < 0.01$) March exhibited significantly higher values for the parameters followed by February and December. Significantly lower values of the parameters are observed during January, June, July, August, September, October and November ($p < 0.01$).

c) Whether there is any significant difference between water quality index of control well (CW) and shallow groundwater sources of Andhakaranazhy coast during the year 2012.

Table 3.20: ANOVA table for the comparison of WQI between different months of control well and shallow groundwater sources of Andhakaranazhy coast during the year 2012

	SGW	**CW**
n	12	12
Mean	182.13	87.93
S^2		8327.6863
T		2.529
Df		22
p-value		$p < 0.05$

Inference

There is significant difference in the mean WQI of shallow groundwater (SGW) sources and control well (CW) ($p < 0.05$). WQI in SGW is significantly higher than that of CW ($p < 0.05$).

Table 3.21: Physico- chemical characteristics of shallow ground water sources of thee Andhakaranazhy coastal area during each month of year 2012

2012		Temp (^{0}C)	pH	Eh	EC (µS/cm)	TDS (mg/L)	TA (mg/L)	TH (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	HCO$_3$ (mg/L)	Cl (mg/L)	SO$_4^{3-}$ (mg/L)	PO$_4^{2-}$ (mg/L)	NO$_3$ (mg/L)	Fe (mg/L)	DO (mg/L)	BOD (mg/L)
Jan	$\bar{x}\pm\sigma$	26.38±1.6	7.65±0.3	-38.55±17.3	0.33±0.1	269.55±72.2	367.84±109.2	301.6±121.6	86.6±20.9	14.6±9.4	104.2±109.2	6.46±7.4	448.8±133.2	64.64±72.8	7.4±15	0.12±0.3	1.35±1.4	0.12±0.3	3.8±1.4	5.7±2.3
	CI	25.3-27.4	7.4- 7.9	-50.2- -26.9	0.2-0.4	221.0-318.0	294.5-441.2	219.9-383.3	72.6-100.6	8.3-20.9	30.9-177.5	1.5-11.4	359.3-538.2	15.7-113.6	221.0-318.0	-2.6-17.5	-0.1-0.3	0.4-2.3	2.8 -4.7	4.1 -7.3
Feb	$\bar{x}\pm\sigma$	27.52±0.8	7.3±0.2	-18.82±12.5	0.97±0.9	680.9±562.4	418.75±211.1	341.04±140.1	103.35±36.8	21.3±14	151.67±145	9.58±9.8	510.88±257.6	207.97±281.4	5.13±12.5	0.06±0.1	1.33±1.4	0.06±0.1	3.9±1.3	5.5±2.4
	CI	27.0-28.1	7.1-7.5	-27.2- -10.4	0.4-1.6	303.1-1058.7	276.9-560.6	246.9-435.1	78.6-128.0	11.9-30.7	54.3-249.1	3.0-16.2	337.8-683.9	19.0-397.0	303.1-1058.7	-3.3-13.5	0.0-0.2	0.4-2.3	3.0 -4.7	3.8 -7.1
Mar	$\bar{x}\pm\sigma$	28.92±0.8	7.82±0.3	-48.36±17.1	1.19±1	828.18±637.9	372±109.1	356.16±148.9	101.29±29.1	25±22.3	171.73±151	10.65±10	453.84±133	321.17±381	6.85±13	0.04±0.1	1.36±1.4	0.04±0.1	3.6±2.5	5.6±1.8
	CI	28.4-29.4	7.6-8.0	-59.9- -36.9	0.5-1.9	399.7-1256.7	298.7-445.3	256.1-456.2	81.8-120.8	10.1-40.0	70.3-273.2	3.9-17.4	364.5-543.2	65.2-577.1	399.7-1256.7	-1.9-15.6	0.0-0.1	0.4-2.3	1.9 -5.3	4.4 -6.9
Apr	$\bar{x}\pm\sigma$	28.8±0.6	7.7±0.3	-39.7±14.2	0.8±0.4	557.1±236.2	333.95±94.9	296.1±65	85.8±23.8	19.8±9.8	122.36±91.1	8.9±7.2	407.43±115.8	177.76±153.2	9.46±16.7	0.07±0.1	1.35±1.4	0.07±0.1	4.6±2.1	6.4±2.5
	CI	28.4-29.2	7.5-7.8	-49.2- -30.2	0.6-1.0	398.4-715.8	270.2-397.7	252.4-339.7	69.8-101.8	13.2-26.4	61.2-183.6	4.1-13.8	329.7-485.2	74.8-280.7	398.4-715.8	-1.7-20.7	0.0-0.2	0.4-2.3	3.2 -6.0	4.7 -8.0
May	$\bar{x}\pm\sigma$	29.67±0.8	7.7±0.2	-42±11.6	0.9±0.5	642±345.9	300.14±137.3	260.15±113.4	79.8±39.9	14.7±7.9	123.27±91.8	7.±6.4	366.17±167.5	177.74±142	16.52±17	0.08±0.1	1.29±1.4	0.08±0.1	4.3±2.3	4.2±2.8
	CI	29.1-30.2	7.6-7.9	-49.8- -34.2	0.5-1.3	409.7-874.3	207.9-392.4	183.9-336.3	53.0-106.6	9.4-20.1	61.6-185.0	2.7-11.3	253.6-478.7	82.4-273.1	409.7-874.3	5.1-27.9	0.0-0.1	0.3-2.2	2.7 -5.8	2.2 -6.1
Jun	$\bar{x}\pm\sigma$	28.26±0.8	7.56±0.3	-33.27±16	0.68±0.2	489.1±142.7	306.48±121.2	231.64±74.9	69.1±22.1	14.28±8.7	103.55±70.1	7.55±7.2	373.9±147.8	129.3±95.3	23.24±20	0.1±0.1	1.29±1.4	0.1±0.1	5.6±2.7	4.7±3.3
	CI	27.7-28.8	7.4-7.8	-44.0- -22.6	0.5-0.8	393.2-584.9	225.1-387.9	181.3-281.9	55.2-84.8	8.5-20.1	56.4-150.7	2.7-12.4	274.6-473.2	65.3-193.3	393.2-584.9	9.8-36.7	0.0-0.2	0.3-2.2	3.8 -7.5	2.5 -6.9
Jul	$\bar{x}\pm\sigma$	27.8±0.9	7.78±0.2	-45.55±12	0.59±0.2	429.4±154.0	285.34±95.3	238.05±80.3	69.7±19.9	16.1±9.9	100.7±63.1	6.98±6.3	348.12±116.3	120.84±73.7	4.6±6.7	0.06±0.1	1.3±1.4	0.05±0.1	4.4±1.7	3.6±2.7
	CI	27.2-28.4	7.6-7.9	-53.6- -37.5	0.4-0.7	326.0-532.8	221.3-349.4	184.1-292.0	56.3-83.1	9.5-22.7	58.3-	2.7-11.2	270.0-426.3	71.3-170.3	326.0-532.8	0.1-9.1	0.0-0.1	0.3-2.3	3.3 -5.5	1.8 -5.5
Aug	$\bar{x}\pm\sigma$	28.76±1.6	8±0.2	-60.9±11.6	0.7±0.2	481.8±167.2	273.55±107.7	223.1±76.4	64±23.5	15.32±6.4	96.5±57.6	5.9±5.3	333.7±131.4	135.8±84.0	8.9±14.8	0.05±0.1	1.35±1.5	0.05±0.1	3.9±1.6	5.9±1.5
	CI	27.5-28.7	7.4-7.8	-48.1- -26.3	0.5-1.1	367.2-751.8	238.6-346.5	232.6-329.0	59.9-93.0	12.4-29.8	45.2-154.9	3.2-11.4	291.1-422.7	60.2-234.5	367.2-751.8	-0.7-12.0	0.0-0.3	0.4-2.3	2.9 -5.0	4.9 -6.9
Sep	$\bar{x}\pm\sigma$	28.1±0.9	7.6±0.3	-37.18±16.2	0.77±0.4	559.5±286.3	292.53±80.3	280.8±71.8	76.48±24.7	21.12±13	100±81.7	7.28±6.1	356.9±97.9	147.36±129.8	5.64±9.5	0.15±0.2	1.35±1.4	0.15±0.2	3.7±1.5	5.0±1.7
	CI	27.5-28.7	7.4-7.8	-48.1- -26.3	0.5-1.1	367.2-751.8	238.6-346.5	232.6-329.0	59.9-93.0	12.4-29.8	45.2-154.9	3.2-11.4	291.1-422.7	60.2-234.5	367.2-751.8	-0.7-12.0	0.0-0.3	0.4-2.3	2.7 -4.7	3.8 -6.1
Oct	$\bar{x}\pm\sigma$	28.8±0.7	7.6±0.3	-37.7±18.9	0.8±0.2	571.8±156.3	335±79.3	298.99±67.2	85.8±22.8	20.86±5.6	115.35±75	7.54±5.6	408.74±96.8	160±136.2	4.85±7.7	0.08±0.1	1.4±1.5	0.08±0.1	4.3±2.3	6.0±2.8
	CI	28-29.5	7.3-7.9	-56- -18.8	0.6-1	4.15-728.1	255.7-14.3	231.8-366.2	63-108.6	15.3-26.5	40.4-190.4	1.94-13.1	311.9-505.5	23.8-296.2	-2.85-12.55	-0.0-0.18	-1-2.9	2-6.6	3.22 -8.8	3.8 -8.9
Nov	$\bar{x}\pm\sigma$	28.36±0.4	7.1±0.2	-7.55±12.9	0.7±0.2	515±110.8	308.8±92.9	296.05±65	88.5±24.6	18.16±10	95.65±49.2	11.8±19.4	376.74±113	120.1±51.5	15.7±15.9	0.08±0.1	1.44±1.4	0.08±0.1	3.7±2.0	5.3±2.1
	CI	27.7-29.8	7.9-8.1	-68.7- -53.1	0.5-0.8	369.5-594.1	201.2-345.9	171.8-274.4	48.2-79.8	11.0-19.6	57.8-135.2	2.3-9.5	245.5-422.0	79.4-192.3	369.5-594.1	-1.1-18.8	0.0-0.1	0.4-2.3	2.4 -5.0	3.9 -6.7
Dec	$\bar{x}\pm\sigma$	28.72±0.5	7.37±0.2	-22.91±12.0	1.29±1.4	890.86±902.9	367.84±109.2	356.7±192.1	86.5±20.9	20.8±10.3	144.86±108	9.5±7.6	451.26±99.4	176.9±116.2	14.01±22.1	0.06±0.1	1.25±1.3	0.06±0.1	3.4±1.5	4.2±2.4
	CI	28.4-29.3	7.4-7.8	-50.4- -25.0	0.6-0.9	466.8-676.8	281.7-388.3	253.8-344.2	70.5-101.1	17.1-24.6	65.0-165.7	3.8-11.3	343.7-473.8	68.6-251.5	466.8-676.8	-0.4-10.0	0.0-0.1	0.4-2.4	2.4 -4.4	2.5 -5.8

Table 3.22: Physico-chemical characteristics of shallow groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2012

Sl No	Parameter	Mean ($\bar{x}$)± SD (σ)	True Value (µ)	Confidence Interval (CI)	Drinking water standards as per IS 10500: 2012		WHO 2011	
					Acceptable	Permissible	Most desirable	Max. allowable
1	Temperature °C	28.3±0.93	28.3±0.57	27.7-28.8	-	-	-	
2	pH	7.6±0.25	7.6±0.15	7.4-7.8	6.5-8.5	No relaxation	6.5-8.5	No relaxation
3	Eh mV	-36±14.57	-36±8.97	¯45 - ¯27	-	-	1.5	-
4	EC (mS/cm)	809.4±618.38	809.4±380.86	428.5-1190.3	-	-	-	-
5	TA(mg/l)as$CaCO_3$	330.2±117.23	330.2±72.20	258.0-402.4	200	600	-	-
6	TH(mg/l)as $CaCO_3$	290.0±108.93	290.0±67.09	222.9-357.1	300	600	100	500
7	DO (mg/l)	4.1± 1.95	4.1± 1.20	2.9-5.3				
8	BOD (mg/l)	5.2±2.40	5.2±1.48	3.7-6.7				
9	Ca (mg/l)	83.2± 26.46	83.2± 16.30	66.9-99.5	75	200	75	200
10	Mg (mg/l)	18.5±11.39	18.5±7.02	11.5-25.5	30	100	50	150
11	Na (mg/l)	119.2±96.21	119.2±59.26	59.9-178.5	-	-	-	200
12	K (mg/l)	8.3± 8.98	8.3± 5.53	2.8-13.8	-	-	-	12
13	Cl^- (mg/l)	161.6±169.9	161.6±104.64	57.0-266.2	250	1000	250	600
14	SO_4^{2-} (mg/l)	10.2±14.91	10.2±9.18	1.0-19.4	200	400	250	400
15	NO_3^- (mg/l)	1.3± 1.41	1.3± 0.87	0.4-2.2	45	No relaxation	50	-
16	PO_4^{3-} (mg/l)	0.2± 0.18	0.2± 0.11	0.1-0.3				
17	Total Iron (mg/L)	0.8± 0.84	0.8± 0.52	0.3-1.3	0.3	No relaxation	0.1	-
18	TDS(mg/l)	576.3 ± 398.92	576.3 ± 245.69	330.6-822.0	500	2000	500	1500
Trace Elements								
19	Li (µg/l)	6.3±2.84	6.3±1.75	4.6-8.0				
20	Al (µg/l)	16.4±16.24	16.4±10.0	6.4-26.4	-	-	-	
21	V (µg/l)	1.2±0.88	1.2±0.54	0.7-1.7	-	-	-	
22	Cr (µg/l)	0.4±0.25	0.4±0.15	0.2-0.6	-	-	-	
23	Mn (µg/l)	61.9±43.75	61.9±26.95	35.0-88.8	700	No relaxation	700	No relaxation
24	Ni (µg/l)	2.3±1.28	2.3±0.79	1.5-3.1	-	-	-	
25	Co (µg/l)	0.1±0.00	0.1±0.00	0.1-0.1	50	No relaxation	50	No relaxation
26	Cu (µg/l)	1.1±0.62	1.1±0.38	0.7-1.5	100	300	400	No relaxation
27	Zn (µg/l)	2.5±1.81	2.5±1.11	1.4-3.6	-	-	-	
28	Ga (µg/l)	2.2±0.88	2.2±0.54	1.7-2.7	20	No relaxation	70	No relaxation
29	As (µg/l)	2.3±3.32	2.3±2.04	0.3-4.3	50	1500	2000	No relaxation
30	Se (µg/l)	3.2±0.61	3.2±0.38	2.8-3.6	500	15000	-	-
31	Rb (µg/l)	5.7±3.23	5.7±1.99	3.7-7.7	100	No relaxation	-	-
32	Sr (µg/l)	481.1±131.04	481.1±80.71	400.4-561.8	3	No relaxation	-	-
33	Ag (µg/l)	0.6±1.35	0.6±0.83	0-1.4	30	200	100	No relaxation
34	Cd (µg/l)	0.01±0.03	0.01±0.02	0.0-0.03	-	-	-	-
35	In (µg/l)	0.02±0.04	0.02±0.02	0.0-0.04	-	-	-	-
36	Cs (µg/l)	0.01±0.03	0.01±0.02	0.0-0.03	10	No relaxation	10	No relaxation
37	Ba (µg/l)	11.1±4.04	11.1±2.49	8.6-13.6	10	50	10	50
38	Pb (µg/l)	0.2±0.07			-	-	-	-
39	Bi (µg/l)	0.4±0.51			10	No relaxation	40	No relaxation

3.13 Conclusions

Overall water quality parameters of the Andhakaranazhy coast evaluated and reported in this chapter are, pH (7.6±0.25), EC (809.4±618.38) mS/cm, Alkalinity (330.2±117.23) mg/L, TH (290.0±108.93) mg/L, DO (4.1±1.95) mg/L, BOD (5.2±2.40) mg/L, Ca^{2+} (83.2± 26.46) mg/L, Mg^{2+} (18.5±11.39) mg/L, TDS (576.3 ± 398.92) mg/L, Na^{+} (119.2±96.21) mg/L, K^{+} (8.3± 8.98) mg/L, Cl^{-} (161.6±169.9) mg/L, SO_4^{2-} (10.2±14.91) mg/L, NO_3^{-} (1.3± 1.41) mg/L, PO_4^{3-} (0.2± 0.18) mg/L & Total Iron (0.8± 0.84) mg/L. Groundwater chemistry of Andhakaranazhy coast revealed that groundwater is having a slightly alkaline behavior, due to the presence of bicarbonate ions. Presence of high concentrations of iron in the groundwater was caused by the recent alluvial deposits of study area. Based on Vesilind [16] classification of hardness, groundwater comes under *too hard for ordinary domestic purposes*. Irrigation parameters indicate, most of the groundwater is suitable for agricultural uses but some treatment methods required. Water sources comes under the class of *C1S1,C2S1 and C3S1* during the study period revealed by USSL diagrams. However, groundwater maintains *excellent to good* and *good to permissible* category during the year 2012. The abundance of major cations and anions in groundwater are in the order of $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-} > PO_4^{3-}$ and $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$ respectively. The dissolved carbon present in the groundwater sources under study is mainly derived from inorganic material. Trace elements are well within the safe standard limits. Presence of E. Coli was reported in most of the groundwater sources, hence the water which comes under class C and E suggested by CPCB. According to LSI, shallow groundwater possess slightly scale forming & corrosive character and little scale forming behaviour was observed by RSI. However, the groundwater is over saturated with carbonate mineral, mainly limestone and it showed a non-aggressive nature as evidenced by AI. Piper diagram reveals that groundwater sources were fall in Facies I (Ca^{2+}-Mg^{2+}-HCO_3^-) with temporary hardness behaviour, followed by Facies III (Na^+-K^+-Cl^--SO_4^{2-}). The Gibbs diagrams indicate that, the chemical composition of groundwater is mainly contributed by weathering of rock forming minerals. Ion exchange, halite dissolution, dissolution of carbonate mineral, and silicate weathering process are prominent occurring in the study area as shown by ionic ratios. The results of ANOVA indicate that, control well exhibited a significant difference between the parameters ($p < 0.01$). During November and December showed significantly higher values for the parameters and January, June, July, August, September, and October registered significantly lower values for the parameters ($p < 0.001$). In shallow groundwater sources, months showed a significant difference between them ($p < 0.01$) March exhibited significantly higher values for the parameters followed by February and December. Significantly lower values of the parameters are observed during January, June, July , August, September, October and November ($p < 0.01$). There is significant difference in the mean WQI of shallow groundwater (SGW) sources and control well (CW) ($p < 0.05$). WQI in SGW is significantly higher than that of CW ($p < 0.05$). Although the overall WQI indicate that, groundwater is not suitable for direct consumption drinking purpose, unless subjected to conventional treatment (pH adjustment and iron removal by simple aeration) followed by disinfection.

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Chapter 4

EVALUATION OF GROUNDWATER CHEMISTRY AND QUALITY ALONG THE CHERAI COAST, ERNAKULAM, KERALA DURING THE YEAR 2012

4.1 Introduction

Cherai is a coastal village under Paravoor Taluk of Ernakulam District, located 10^{o} 14' 22" N latitude and 76^{o} 17' 82" E longitude. The region lies below the mean sea level (msl) and groundwater aquifers are phreatic in nature. Cherai coastal segments is placed between land and ocean, endowed with an elaborate network of backwaters and tidal canals. This beach is known as a tourist destination in Kerala and is exposed to enormous damage by Indian Ocean tsunami of December 26, 2004 [1]. The tourism based development activities are well flourished over years and the place is regarded as a water scarce area. The municipal water supply fails to meet the ever-increasing demand of this fast growing land. Because of this reason this study is very much relevant in the current scenario [2-6]. The work presented in the following session of the thesis comprises the major results and discussions on the water quality parameters of the groundwater sources of the Cherai coast during the year 2012. The original data obtained from the physico-chemical analyses of groundwater, are evaluated for its drinking, irrigation and industrial suitability, for a period time with 12 sampling events in 2012 and for December 2013, 2014, 2015, 2016 and 2017.

Table 4.1: Water quality sampling stations of Cherai coast (Ernakulam) during the year 2012

Station	Remarks	Depth of Water	Location
1. Francis- house owner	Dug well (DW1)	5ft	10°14’93” N 76°17’65” E
2. Simmon- house owner	Dug well (DW2)	3ft	10°15’64” N 76°17’35” E
3. Babu- house owner	Dug well (DW3)	2ft	10°15’60“ N 76°17’36” E
4. Pappu - house owner (CW)	Dug well (DW4)	2ft	10°14’45” N 76°17’77” E
5. Sundaran- house owner	Dug well (DW5)	3ft	10°14’03“ N 76°17’95” E
6. Anandan- house owner	Dug well (DW6)	3ft	10°13’57” N 76°18’11” E
7. Usha- house owner	Bore well (BW1)	5ft	10°13’56” N 76°18’08” E

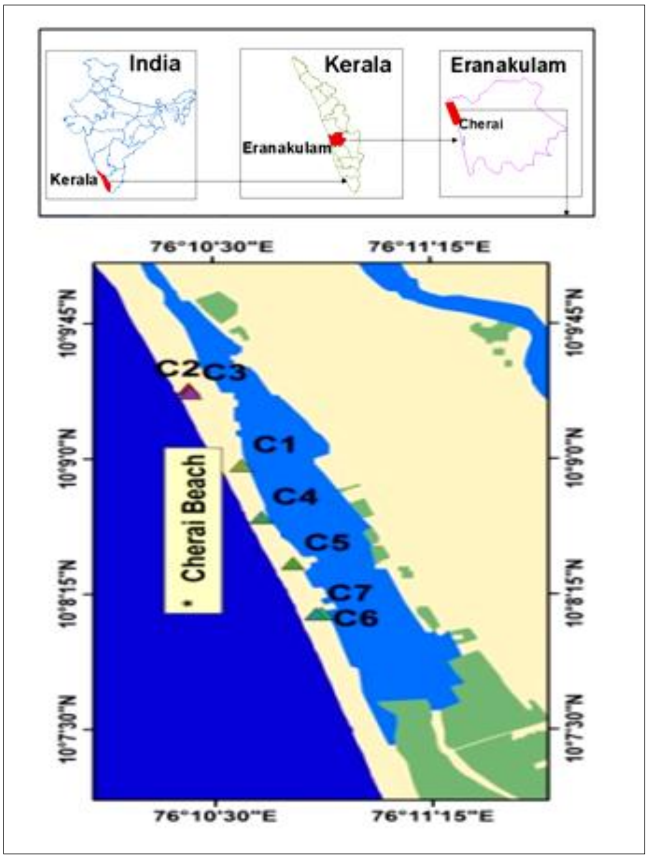


Figure 4.1: Location map of Cherai coast, Ernakulam, Kerala, India, which has been subjected to inundation by 26th December 2004 Indian Ocean Tsunami

The groundwater chemistry and its characteristics of Cherai coast was interpreted using the standard methods [7] and statistical tools based on samples from some stations. Water samples collected from seven (7) shallow groundwater sources, six (6) dug wells and one (1) shallow bore wells (Table 4.1).

4.2 Evaluation of Physico-Chemical Parameters

Overall water quality parameters of the Cherai coast was evaluated and reported in this study during the period 2012, obtained as mean of 12 monthly sampling events starting from January - December 2012, consisting of 7 (seven) sampling points. The major physico-chemical parameters of groundwater analysed includes temperature, pH, Eh, EC, TA, TH, Ca^{2+}, Mg^{2+}, TDS, Na^{+}, K^{+}, Cl^{-} , SO_4^{2-}, NO_3^{-}, PO_4^{3-} & total Iron. The basic data generated during the period 2012 for shallow groundwater was compared with control well.

4.2.1 Temperature

Temperature is an important parameter of groundwater, which is interrelated with pH, conductivity, saturation level of gases etc. Temperature of water for drinking and domestic use should not exceed 30°C.

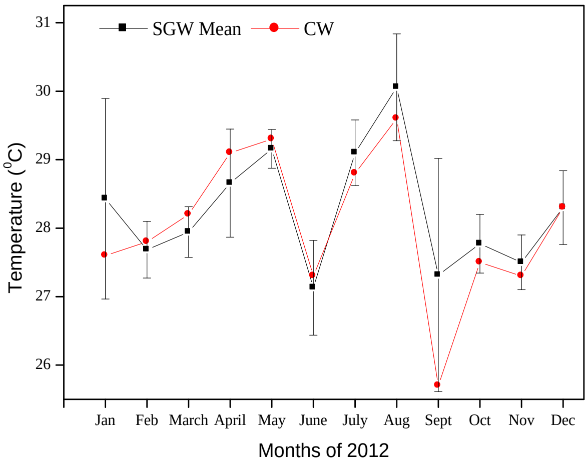


Figure 4.2: Monthly variation of temperature of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

Shallow groundwater sources recorded a fluctuating temperature, with an annual average of temperature 28.3±0.82°C with a CI of 27.8-28.8°C at 95% of confidence limit. In January 2012, temperature was 28.4±1.46°C and it gradually increases upto 29.2±0.28 at the end of May 2012. There is a decrease in water temperature during monsoon season and attains a maximum of 30.1±0.78°C during August 2012. This increase in temperature may be due to the raise in atmospheric temperature [8]. Afterwards, temperature shows a decreasing trend and reaches at 28.3±0.54°C during December 2012. Control well also shows same trend with shallow groundwater sources. It shows an annual average of groundwater temperature 28.0±1.08°C with a CI of 27.3-28.7°C. The lowest temperature was observed during the month September 2012 (25.7°C) and highest in August 2012 (29.6°C).

4.2.2 pH

pH is used to express the intensity of the acid or alkaline condition of a solution. It is a measure of hydrogen ion activity, usually done by electrometric method. pH records an annual average of 7.3±0.38, with a CI of 7-7.5 at 95% of confidence limit in the case of shallow groundwater sources. In January 2012, the pH was 7.7±0.41 and reaches the maximum of 7.9±0.29 during the month August, but within the standard limits [9]. After that the pH showed a decreasing trend and attains 6.6±0.21 in November (Figure 4.3) [8]. During December 2012, pH becomes neutral, 7.0±0.28. However, the control well having high pH values compared to shallow groundwater sources, showed an annual average of pH 7.1±0.38 with a CI of 6.9-7.3 at 95% of confidence limit. The lowest temperature was observed during the month November (6.6) and highest in July (7.9).

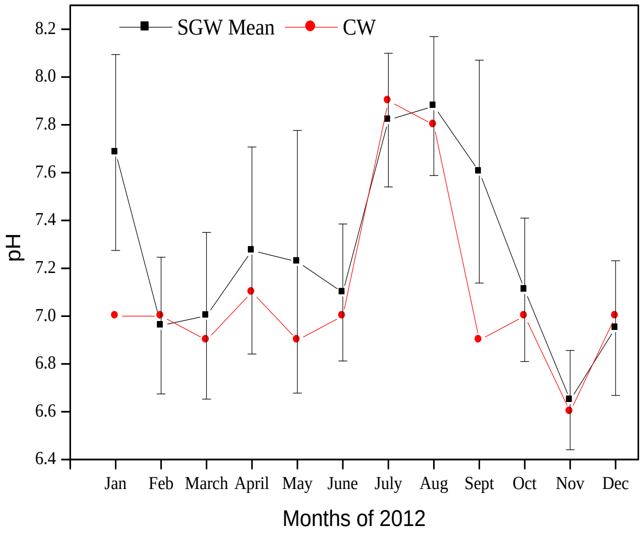


Figure 4.3: Monthly variation of pH of control well (CW) and shallow groundwater (SGW) sourcesalong the Cherai coast, Kerala, India during the year 2012

4.2.3 Redox Potential (Eh)

The oxidation – reduction potential is used to find out the condition of groundwater whether oxidising or reducing in nature. If the value go down to the negative range, indicates the reducing state of water. In oxidising condition value should be positive [10]. In January 2012, groundwater noticed -40.4±22.41 mV of Eh, gradually increases and reached -2.9±18.81 mV in March. Then it gradually decreses and attains a minimum of -55.6±30.90 mV during the month of July 2012. Again the redox potential was enhanced and reaches a maximum value of 16.6±11.90 (Figure 4.4). Control well exhibited an annual mean of redox potential -9.8± 17.90 mV during the year 2012 with a CI of -20.8-1.2 at 95% of confidence limit.

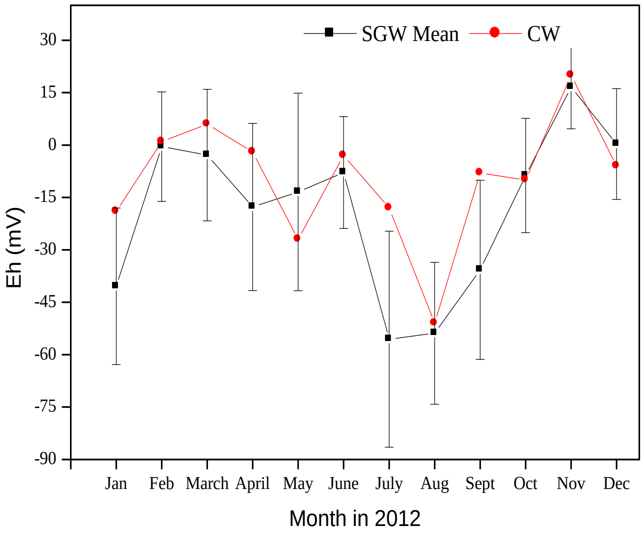


Figure 4.4: Monthly variation of redox potential (Eh) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.4 Electrical Conductivity (EC)

Electrical conductivity is a measure of water capacity to convey electricity, which is directly proportional to its dissolved mineral content. Conductivity was produced in the groundwater due to the factors like, intensive weathering of rocks and leaching of ions from topsoil, anthropogenic sources along with minor influence of climate [11]. EC of shallow groundwater sources showed an annual average of 2357.3±618.38 µS, with a CI of 1976.4-2738.2 µS at 95% of confidence limit. In January, the groundwater sources exhibits an EC of 1324.3±1377.85 µS. It gradually increases and reaches at 5382.9±7247.62 at the end of the March 2012. In May 2012, groundwater having maximum concentration of EC (7178.6±13113.31 µS), because of the high evaporation rate. From June 2012 onwards, the electrical conductivity decreases and attains a minimum of 394.3±264.44 µS during September 2012, as a result of monsoonal dilution. Afterwards EC value showed a gradual increase in groundwater sources of Cherai coast. At the end of December 2012, the EC reached 2688.6±6127.12 µS (Figure 4.5). Control well has an annual EC of 226.7±60.65 µS, with a CI of 189.3-264.1 µS at 95% of confidence limit.

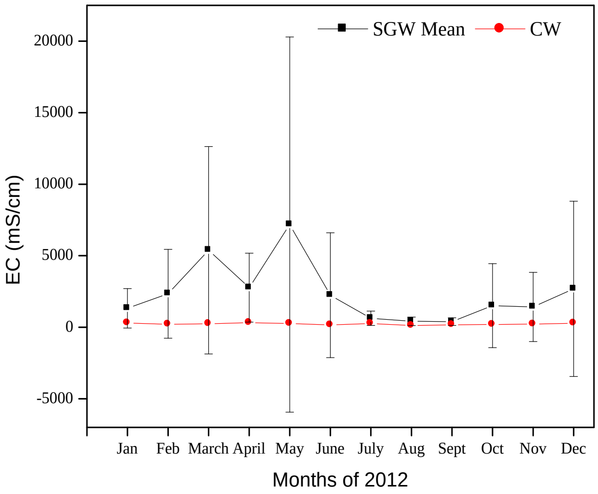


Figure 4.5: Monthly variation of electrical conductivity (EC) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.5 Alkalinity

Alkalinity of water is a measure of its capacity to neutralize acids, expressed in terms of $CaCO_3$. In groundwater, it can be produced due to the presence of decayed organic matter and weathering of rocks and minerals [12]. Cherai coast recorded an annual average of alkalinity 152.3 ± 87.49 mg/L in the case of shallow groundwater sources with a CI of 98.4-206.2 mg/L at 95% of confidence limit. The lowest alkalinity is reported during the month of January 2012 (118.9±38.35 mg/L). Then there is a huge increase observed during February (184.5±139.18 mg/L), due to high evaporation rate. However, the alkalinity was reduced to 156.1±77.94 mg/L in

March 2012 and reached a maximum of 186.0±114.69 mg/L during May 2012. During monsoon season, a gradual decrease was observed and attains an alkalinity of 129.5±87.88 mg/L in August 2012. After that, alkalinity is quite fluctuating and 132.9±53.21 mg/L at the end of December 2012 (Figure 4.6). Control well has an annual average of 106.0±20.99 mg/L with a CI of 93.1-118.9 mg/L at 95% of confidence limit. The maximum value was observed during the months of March and October 2012 equal to 139.5 mg/L.

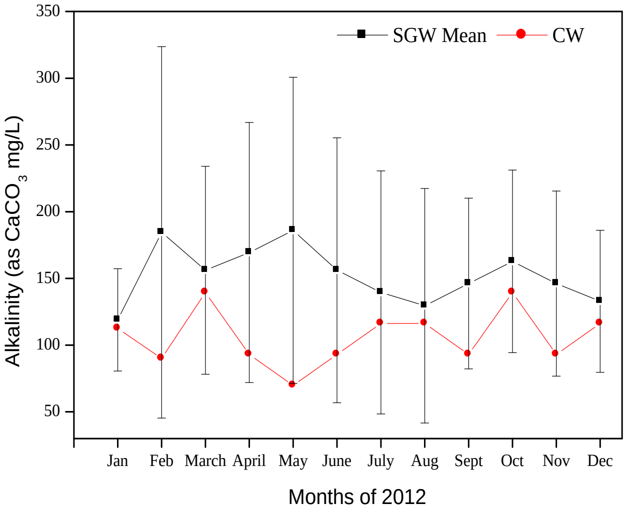


Figure 4.6: Monthly variation of alkalinity of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.6 Total Hardness (TH)

The principle cations, produces the hardness are calcium and magnesium. Groundwater is harder than surface water since it is rich in carbonic acid and dissolved oxygen, which dissolves the rocks containing calcite, gypsum and dolomite. The hardness may be advantageous in certain conditions; it prevents the corrosion in the pipes by forming a thin layer of scale, and reduces the entry of heavy metals from the pipe to the water [13]. The annual average of total hardness (TH) of shallow groundwater sources is 433.1±653.53 mg/L as $CaCO_3$, with a CI of 30.6-835.6 mg/L at 95% of confidence limit. During January 2012, TH was 127.8±102.19 mg/L and gradually increases up to a maximum of 808.5±791.27 mg/L during March 2012. Hardness was observed high during the summer season, may be due to the high evaporation rate. During monsoon season, hardness of groundwater decreases and reaches 133.0±68.23 mg/L in September 2012. Then it gradually increases and attains a value 523.2±1109.11 during December 2012 (Figure 4.7). The control well shows an annual average of 104.3±57.36 mg/L, with a CI of 69.0-139.6 mg/L at 95% of confidence limit.

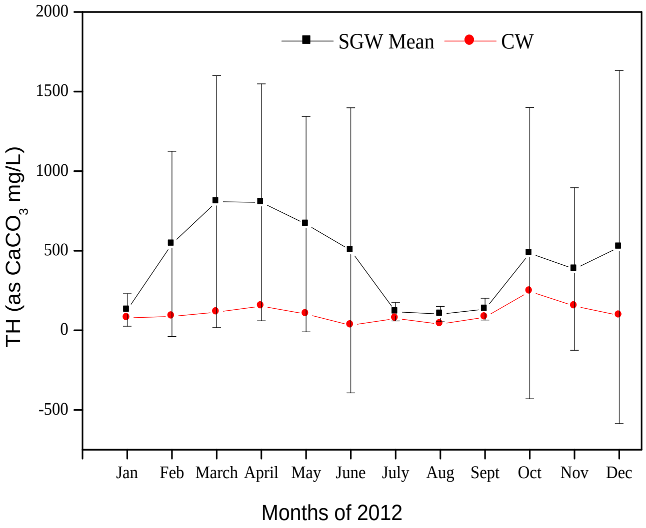


Figure 4.7: Monthly variation of total hardness (TH) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

Table 4.2: Comparison of Alkalinity, TH, TeH in mg/l $CaCO_3$ of shallow groundwater sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

Period	Alk (mg/L)	TH(mg/L)	TeH (mg/L)	PeH (mg/L)	Inference
Jan 2012	118.9±38.35	127.8±102.19	118.9±38.35	8.9	MHH
Feb 2012	184.5±139.18	542.7±581.52	184.5±139.18	358.2	THODU
Mar 2012	156.1±77.94	808.5±791.27	156.1±77.94	652.4	THODU
Apr 2012	169.4±97.46	803.9±744.07	169.4±97.46	634.5	THODU
May2012	186.0±114.69	667.2±676.70	186.0±114.69	481.2	THODU
Jun 2012	156.1±99.29	502.4±895.36	156.1±99.29	346.3	THODU
Jul 2012	139.5±91.04	116.6±57.07	116.6±57.07	0	MHH
Aug 2012	129.5±87.88	102.1±48.75	102.1±48.75	0	MHH
Sep 2012	146.1±63.98	133.0±68.23	133.0±68.23	0	MHH
Oct 2012	162.8±68.45	484.5±914.64	162.8±68.45	321.7	THODU
Nov 2012	146.1±69.38	385.2±510.16	146.1±69.38	239.1	THODU
Dec 2012	132.9±53.21	523.2±1109.11	132.9±53.21	390.3	THODU
$\bar{x} \pm \sigma$	152.3±87.49	433.1±653.53	147.0±26.93		THODU
μ	152.3±53.88	433.1±402.51	147.0±16.59		THODU
CI	98.4-206.2	30.6-835.6	130.4-163.6		ESS-THODU

Based on Vesilind [14] classification, alkalinity was less than total hardness (TH), hence we chose the alkalinity as temporary hardness (TeH). But during June, July and August months of 2012, alkalinity was greater than TH, then the TH is taken as TeH. The difference between TH and TeH will give the permenant hardness (PeH). According to the hardness classification, the overall groundwater comes under *too hard for ordinary domestic use* (THODU) category (Table 4.2).

4.2.7 Dissolved Oxygen (DO)

DO depend on the physical chemical and biochemical activities in the water body. Its concentration decreases with depth. Solubility of oxygen depends on many factors such as temperature, pressure and salinity of the water. However, the increased DO content speeds up the corrosive behaviour of water on iron, steel etc, especially at low pH. High chlorinity would also reduce the DO content of water, which turns harmful for aquatic organisms [15]. Depletion of DO can encourage microbial reduction of nitrate to nitrite, sulphate to sulphide and increase the amount of ferrous iron in groundwater [16]. The shallow groundwater sources of Cherai coast showed an annual average of 3.0±1.25 mg/L of DO, with a CI of 2.1-3.7 mg/L at 95% of confidence limit. DO content of 3.2±1.30 mg/L was reported during January 2012 and it reaches a maximum concentration 3.4±1.76 mg/L during March 2012. Groundwater recorded a very low DO 2.6±1.19 mg/L in November 2012 and finally it attains the value 2.8±0.96 mg/L at the end of December 2012 (Figure 4.8). In the case of control well, DO reported an annual average is 5.7±0.72mg/L, with a CI of 5.3-6.1 mg/L at 95% of confidence limit.

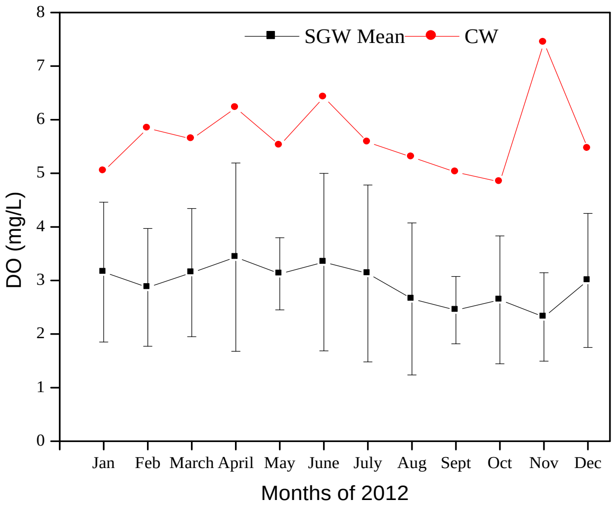


Figure 4.8: Monthly variation of dissolved oxygen (DO) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.8 Biological Oxygen Demand (BOD)

BOD is defined as the amount of oxygen required by bacteria and other microorganisms for the bio chemical degradation and transformation of organic matter [17]. Shallow groundwater recorded an annual average of 6.8±2.04 mg/L during the year 2012 with a CI of 4.9-13.9 mg/L at 95% of confidence limit. BOD value in January is 6.4±1.19 mg/L which increases to 7.4±1.71 mg/L in March 2012. Then it gradually decreases and reaches a maximum concentration of 7.5±2.12 mg/L. Finally the groundwater attains a BOD concentration of 6.9 ±2.76 mg/L (Figure 4.9). An annual average of 3.8±0.69 mg/L of BOD was reported in control well, ranges from 3.4-4.2 mg/L.

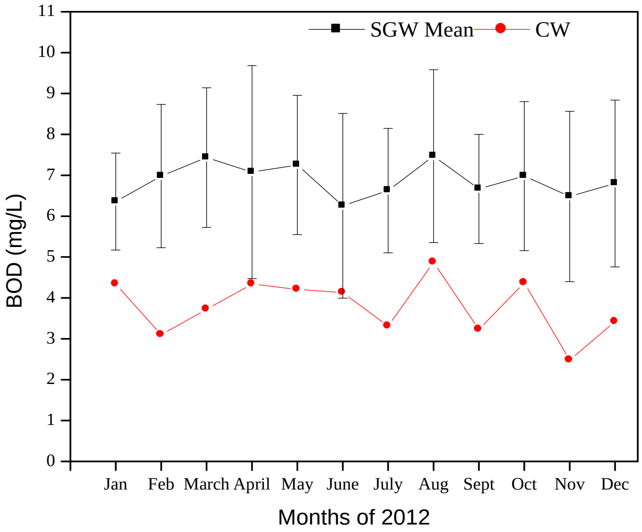


Figure 4.9: Monthly variation of biological oxygen demand (BOD) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.9 Calcium (Ca^{2+})

Calcium is one of the most common ions found in the groundwater aquifer as a result of weathering of minerals such as limestone, gypsum etc. These compounds are stable in water when carbon dioxide is present. But its concentration decreased when calcium carbonate precipitates because of increased water temperature, photosynthetic activity or loss of carbon dioxide due to increases in pressure [18]. Shallow groundwater sources of Cherai coast showed an annual average of 85.6±114.53mg/L of calcium concentration during the year 2012 with a CI of 15.1-156.1 mg/L at 95% of confidence limit. Calcium concentration was reported in January 2012 is 28.9±25.66 which gradually increases and reached a maximum of 243.9±280.18 in March 2012. After that, the concentration decrease slowly and reaches 25.1±14.85 in August 2012. Then it increases and finally attains the calcium content of 71.2±117.41 in December 2012 (Figure 4.10). The control well showed an annual average of 23.0±8.63 mg/L with a CI of 17.7-28.3 mg/L at 95% of confidence limit.

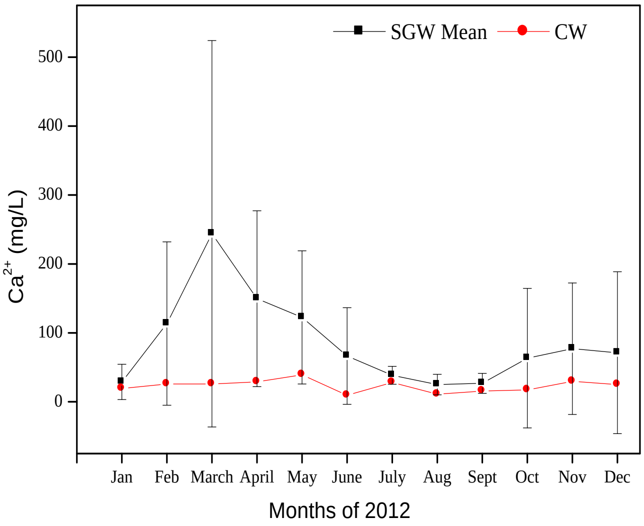


Figure 4.10: Monthly variation of calcium ion (Ca^{2+})of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.10 Magnesium (Mg^{2+})

Magnesium is generally found in lesser concentration in natural waters than calcium, because of the slow dissolution of dolomite. The major source of magnesium (Mg) in the groundwater is due to ion exchange of minerals in rocks and soils by water as observed earlier [19]. Shallow groundwater of Cherai coast reported an annual average of 53±105.03 mg/L of magnesium in groundwater with a CI of 11.7-117.7 mg/L at 95% of confidence limit. In January 2012, groundwater reported magnesium concentration of 13.4±9.85 which slightly increases to a maximum of 104.0±115.18 in March 2012. It gradually decreases and reaches a low concentration of 4.9±6.18 in July 2012. Then it again increases and recorded a value of 83.5±197.47(Figure 4.11). Control well showed an annual average of 11.4±13.32 mg/L magnesium with a CI of 3.2-19.6 mg/L at 95% of confidence limit.

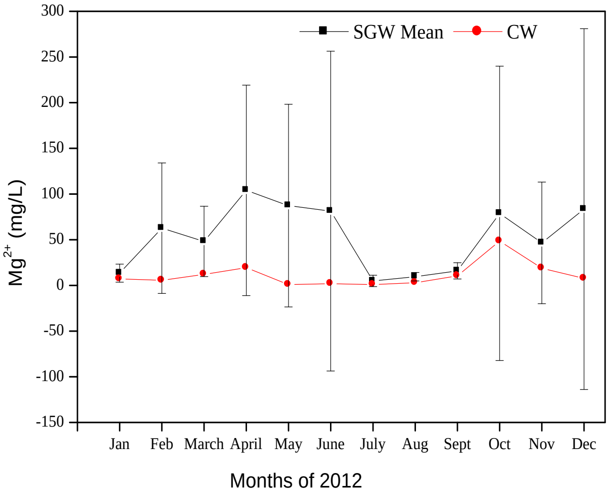


Figure 4.11: Monthly variation of magnesium ion (Mg^{2+}) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.11 Sodium (Na^+)

For shallow groundwater in Cherai coast reported an annual average 229.4±358.59 mg/L of sodium concentration in the dug wells sources with a CI of 8.5-450.2 mg/L at 95% of confidence limit. Sodium was found to be 107.6±115.82 mg/L in January 2012 and it was increased tremendously and attained a maximum of 536.3 ±734.70 mg/L in April 2012. Then the concentration was decreased gradually and reached a value of 89.4±110.95 in November 2012 [20]. However there was a sharp increase observed during the month December 2012 with a concentration of 235.3±436.33 mg/L (Figure 4.12). Control well exhibits an annual mean of 25.6±10.22 mg/L with a CI of 19.3-31.9 mg/L at 95% of confidence limit.

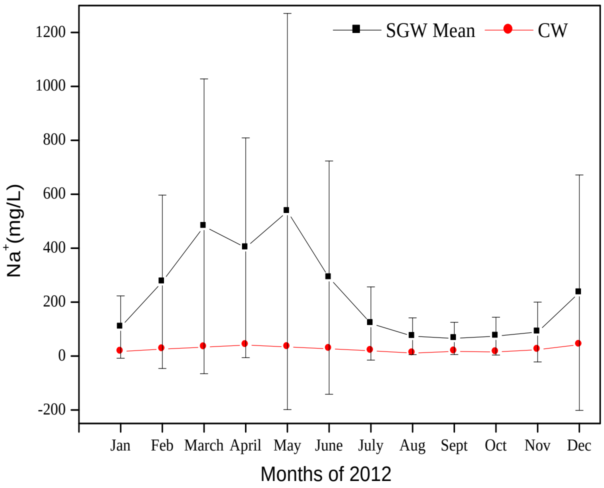


Figure 4.12: Monthly variation of sodium ion (Na^+) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.12 Potassium (K^+)

In groundwater, the concentration of potassium is comparatively very less than one-tenth that of sodium, due to the fact that the potassium minerals are resistant to the weathering process [21]. Shallow groundwater sources exhibits an annual average of 16.5±30.73 mg/L potassium, with a CI of 2.4-35.4 mg/L at 95% of confidence limit. Potassium concentration record 6.7±3.3 mg/L in January 2012 and it gradually increases and reaches a maximum value of 33.9±60.70 mg/L in May 2012. Then the amount was decreased slowly and attains a minimum of 4.9±3.48 mg/L in August 2012. However, there was a sharp increase of potassium observed at the end of year December 2012 (22.8±44.98 mg/L) (Figure 4.13). Control well reported an annual average of 4.3±1.94 mg/L, with a CI of 3.1-5.5 mg/L at 95% of confidence limit.

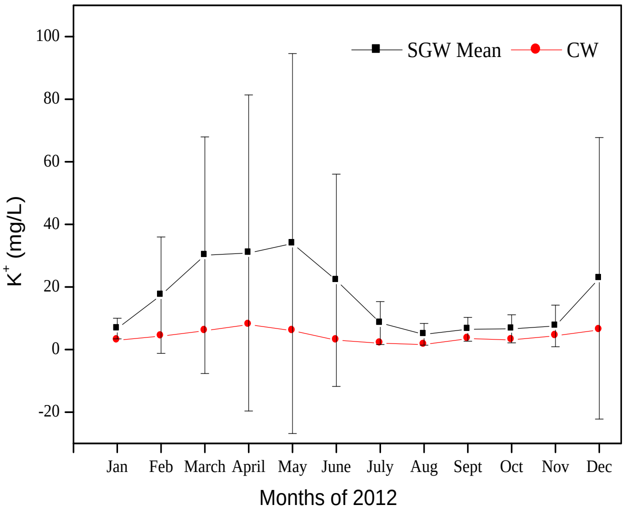


Figure 4.13: Monthly variation of potassium ion (K^+) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.13 Chloride (Cl^-)

The presence of chloride in groundwaters can be attributed to dissolution of salts deposits, discharge of effluents from chemical industries, sea water intrusion in coastal region etc. Higher concentrations of chlorides indicate higher degree of organic pollution [22]. Shallow groundwater showed an annual average of 570.8±1049.69 mg/L of chloride in shallow groundwater sources with a CI of 75.7-1217.3 mg/L at 95% of confidence limit. Chloride concentration was very high in the groundwater of the study area which indicates the presence salt water intrusion. During January 2012, water recorded a chloride of 199.9±218.15 mg/L. Then a sharp increase was noticed and attains a value of 767.9 ±1030.49 mg/L during February 2012 and it gradually increases and reaches a maximum concentration of 1227.0±1821.21 mg/L in the month May 2012. Then it gradually decreases and recorded a minimum of 85.0± 62.24 mg/L. Again the concentration increased and finally attains 731.3±1763.61 mg/L (Figure 4.14). However, the control well has an increased concentration of chloride with an annual average of 36.1±12.06 mg/L, with a CI of 28.7- 43.5 mg/L at 95% of confidence limit

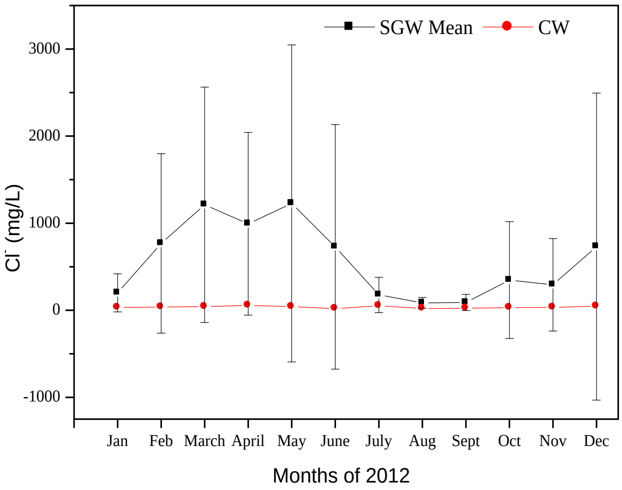


Figure 4.14: Monthly variation of chloride (Cl^-)of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.14 Sulphate (SO_4^{2-})

Sulphate is widely distributed in nature and may be present in natural waters as a result of leaching from gypsum. The reduction in the concentration of sulphate ion may be an indication of microbial reduction [23]. Annual average of sulphate reported for shallow groundwater sources was 25.9±36.88 mg/L with a CI of 3.2-48.6 mg/L at 95% of confidence limit. In January sulphate concentration was 1.6±0.18 mg/L, it gradually increases and reaches a maximum of 76.6±78.05 mg/L in May 2012. But when monsoon comes, sulphate concentration in groundwater gradually reduces and attains 1.3±1.32 mg/L in August 2012. However, September 2012 onwards the sulphate concentration again increases to 29.6±17.13 mg/L in November 2012. But during December 2012, its concentration was slightly decreases to 22.3±34.13 mg/L (Figure 4.15). Control well showed an annual average of 5.3±6.24 mg/L of sulphate, with a CI of 1.5-9.1 mg/L at 95% of confidence limit. It showed a minimum concentration in August (0.5 mg/L) and maximum during May 2012 (18.7 mg/L).

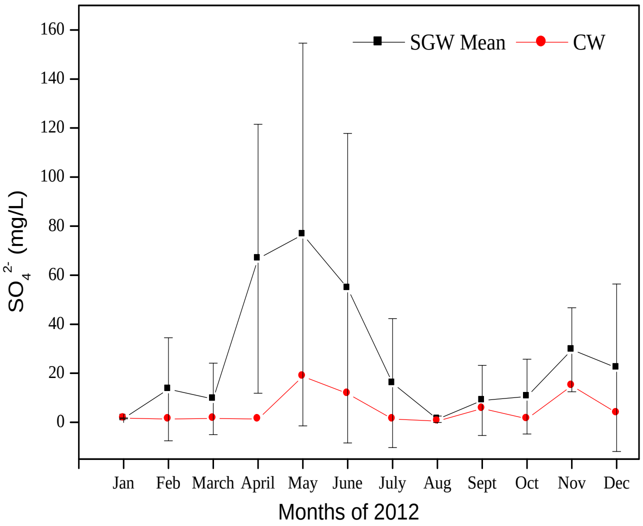


Figure 4.15: Monthly variation of sulphate ion (SO_4^{2-}) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala during the year 2012

4.2.15 Nitrate (NO_3^-)

The presence of nitrate in water indicates organic pollution. Significant contaminant sources of nitrate in groundwater includes human and animal wastes, industrial effluents, application of fertilizers and chemicals, seepage and silage through drainage system etc. As per the BIS Standard for drinking water the maximum desirable limit of nitrate concentration in groundwater is 45 mg/l with no relaxation. Nitrate recorded an annual average of 2.8±2.49 mg/L in dug wells, with a CI of 1.3-4.3 mg/L at 95% of confidence limit (Figure 4.16). Control well showed an annual average of 1.0±0.10 mg/L, with a CI of 0.9-1.1 mg/L at 95% of confidence limit.

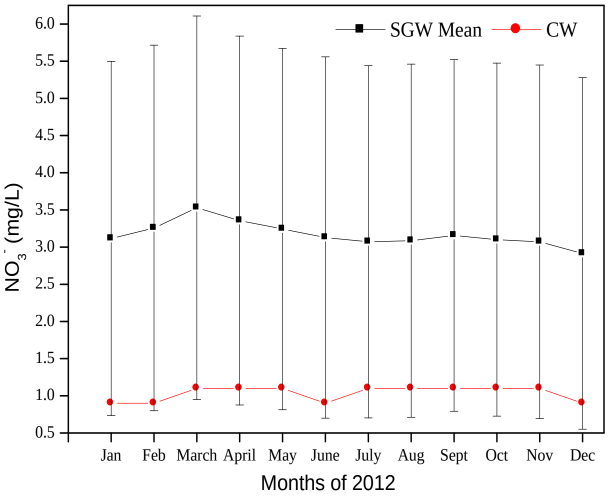


Figure 4.16: Monthly variation of nitrate ion (NO_3^{2-}) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala during the year 2012

4.2.16 Phosphate (PO_4^{3-})

Phosphorus occurs in natural waters and in wastewaters almost solely in the form of various phosphates. But, the concentration is found in large quantities in fresh waters indicates, pollution caused by sewage and industrial wastes, apatite minerals, fertilizers and organic phosphates as applied insecticides [24]. Cherai coast groundwater reported an annual average of 0.4 ± 0.4 mg/L of phosphate in shallow groundwater sources with a CI of 0.2-0.6 mg/L at 95% of confidence limit (Figure 4.17). Control well also reported the iron 0.01±0.03 mg/L contamination during the period 2012, with a CI of 0-0.03 mg/L at 95% of confidence limit.

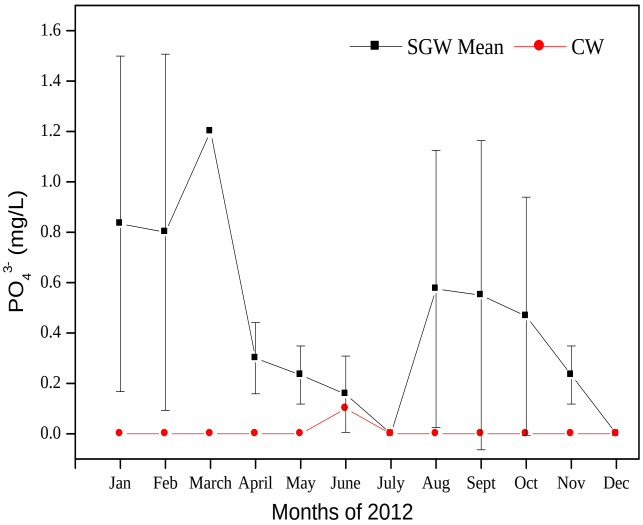


Figure 4.17: Monthly variation of phosphate ion (PO_4^{3-}) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.17 Total Iron

Iron is widely distributed, occurs as pyroxenes, magnetite, biotite, olivine and amphiboles. When exposed to the atmosphere, Fe^{2+} oxidizes to Fe^{3+}, which is insoluble, and precipitate out as $Fe(OH)_2$, causing brown discoloration of the water and the characteristic brown stains in sinks and cloths. The high concentration of iron in groundwater might be due to rusting of casing pipes, non-usage of bore wells for a long time, percolation of iron contaminants through space between bore hole and the casing pipe, disposal of scrap iron in open areas, contamination due to industrial activities etc [25]. Shallow groundwater sources reported an annual average of 1.2±1.22 mg/L of total iron during the year 2012, with a CI of 0.4-1.9 mg/L at 95% of confidence limit. Iron concentration was slightly high in the groundwater of the study area. In January 2012, shallow groundwater recorded iron of 0.4±0.60 mg/L, then it gradually increases and reaches a maximum concentration of 1.8 ±1.0 mg/L in September 2012. Finally the concentration reached to 1.3 ±1.5 mg/L in December 2012 (Figure 4.18). Control well also reported the iron 0.4±0.57 mg/L contamination during the period 2012, with a CI of 0.05-0.75 mg/L at 95% of confidence limit.

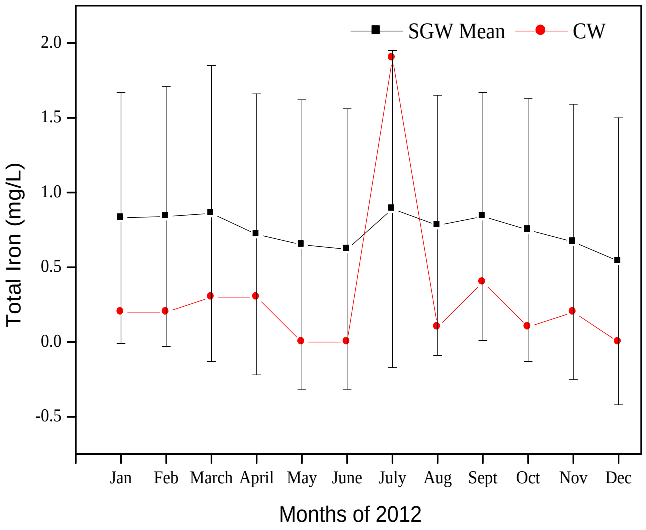


Figure 4.18: Monthly variation of total iron of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

4.2.18 Total Dissolved Solids (TDS)

Total dissolved solids can affect the taste, hardness, corrosivity and encrustation of water, which is a good measure of the concentration of ionic substances in water. The desired level of TDS for public drinking water, is 1,000 mg/l [26]. High concentration of TDS in the groundwater sources is due to the leaching of salts from soil and also domestic sewage, which percolate into the groundwater [28]. TDS reported an annual average of 1603.4±3355.41 mg/L for shallow groundwater sources during the year 2012 with a CI of 463.2-3670 mg/L at 95% of confidence limit.

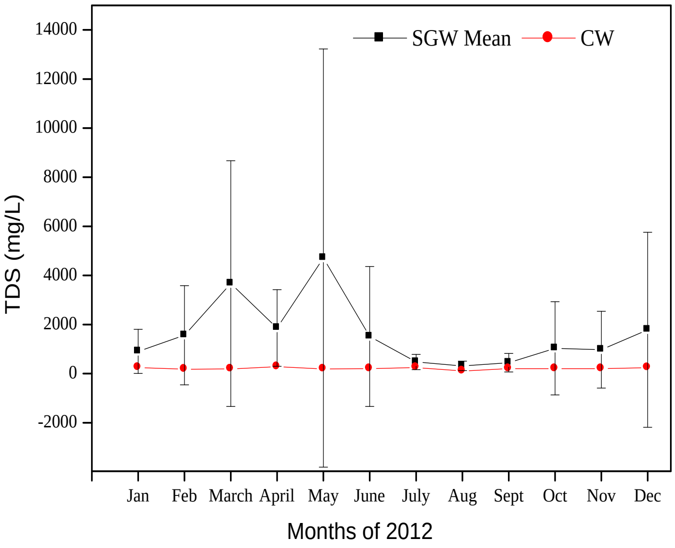


Figure 4.19: Monthly variation of total dissolved solids (TDS) of control well (CW) and shallow groundwater (SGW) sources along the Cherai coast, Kerala, India during the year 2012

In January 2012, TDS reported 906.5±899.02 mg/L, it is gradually increases and attains a value in 3666.4±5004.66 mg/L in March 2012. But during April 2012 TDS was decreased to 1857.5±1561.38 mg/L again it is increased to a maximum of 4708.6±8516.06 mg/L in May 2012. The high concentration of TDS was observed during the summer season, due to the increased evaporation of groundwater. But during monsoon season, the concentration of TDS was decreased. But October 2012 onwards, the concentration again increases and reaches 1785.4±3971.04 mg/L during December 2012 (Figure 4.19). The control well also showed an annual average of 207.5±43.72 mg/L of TDS during the year 2012, with a CI of 180.6-234.4 mg/L at 95% of confidence limit. The maximum concentration was reported during April 2012 (280 mg/L) and a minimum in August 2012 (110 mg/L).

4.3 Irrigation Water Quality

Irrigation suitability of the groundwater sources of Cherai coast can be determined by calculating the sodium percent (Na%), sodium adsorption ratio (SAR) and Kelly's ratio (KR), permeability index (PI), magnesium ratio (MR), USSL and Wilcox diagrams.

4.3.1 Sodium Adsorption Ratio (SAR)

The sodium adsorption ratio is an indicator of the relative proportion of sodium ions in a water sample to those of calcium and magnesium. SAR is used to predict the sodium hazard. It is calculated from the ratio of sodium to calcium and magnesium. The SAR values are grouped into four classes-Low, Medium, High and Very High according to the hazard caused by sodium. High sodium levels can contribute to salinity problems, which can interfere with magnesium and calcium availability. The Pollution Control Board has prescribed 26 as the maximum tolerance limit value of SAR [27]. Table 4.3 shows the monthly variation of SAR of control well (CW) and shallow groundwater (SGW) sources of Cherai coast during the year 2012. Shallow groundwater reported an annual average SAR of 4.3±3.95. During entire period (January-December 2012) SAR maintains an *excellent* (0-10) quality of water for irrigation purposes. Control well showed an annual mean of 1.2 ±0.49 and comes under excellent class.

Table 4.3: Monthly variation of sodium adsorption ratio (SAR) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	SAR	**Water Quality**	**SAR**	**Water Quality**
Jan 2012	0.8	E	4.6 ±6.00	E
Feb 2012	1.2	E	4.3 ±3.19	E
Mar 2012	1.3	E	6.3 ±5.54	E
Apr 2012	1.4	E	5.4 ±3.51	E
May 2012	1.5	E	7.4 ±6.46	E
Jun 2012	2.1	E	5.2 ±3.01	E
Jul 2012	1.0	E	4.5 ±4.52	E
Aug 2012	0.8	E	2.9 ±2.30	E
Sep 2012	0.8	E	2.3 ±1.53	E
Oct 2012	0.4	E	2.6 ±3.04	E
Nov 2012	0.8	E	1.8 ±1.33	E
Dec 2012	1.9	E	3.9 ±2.89	E
$\bar{x} \pm \sigma$	1.2 ±0.49	E	4.3 ±3.95	E
μ	1.2±0.30	E	4.3±2.43	E
CI	0.9-1.5	E	1.9-6.7	E
E-Excellent				

4.3.1.1 USSL diagram

USSL diagrams are used for finding the irrigation water quality. It is plotted by *SAR* against *EC*. Figure 4.20 shows the USSL diagram of shallow groundwater (SGW) sources of Cherai coast during the period

2012. Water is having *good quality* during the months July, August & September 2012 and comes under the class of *C2S1* range. But in January, June, October and November 2012, water comes under the class of *C3S1* with *moderate* water quality due to the increased EC concentration as a result of salt water intrusion [28]. However, February, April and December months of 2012 fall under the class of *C4S1* with *very high salinity hazard* and *low sodium hazard*. Groundwater fall under *C4S2* class with *very high salinity hazard and medium sodium hazard* during the months March and May 2012, but it is beyond the plot limit.

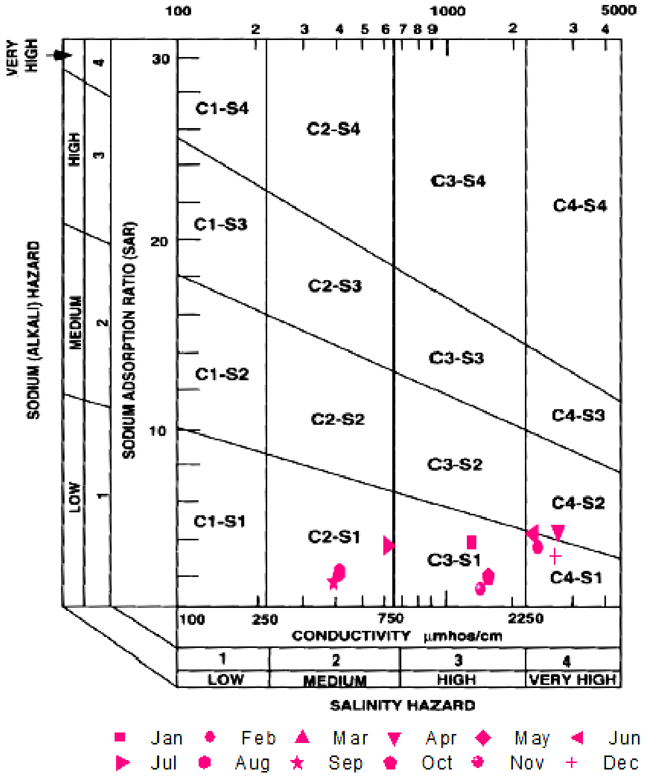


Figure 4.20: USSL diagram of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

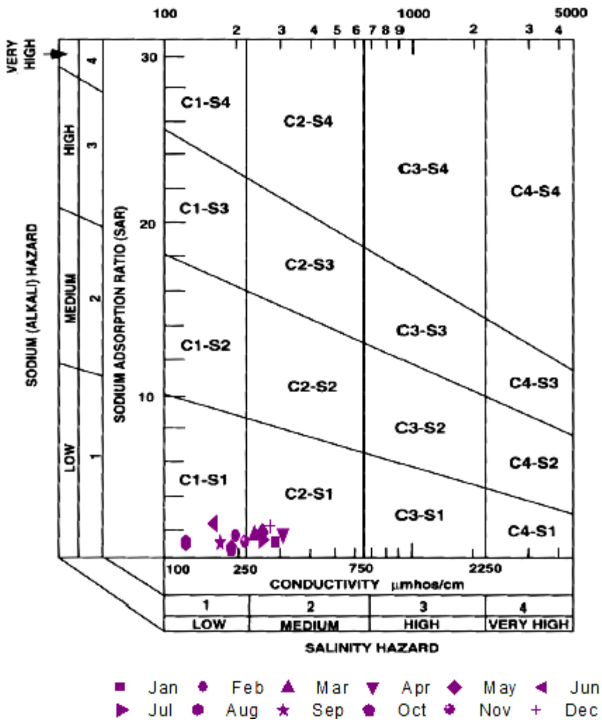


Figure 4.21: USSL diagram of control well (CW) of Cherai coast, Ernakulam, Kerala, India during the year 2012

Control well falls under *C1S1* category during February, March, June, August, Septrember, October & November months of 2012 and having *low salinity hazard and sodium hazard*. However, the groundwater tends to move the class of *C2S1* during the months of January, April, May, July & December 2012, because of the presence of high sodium content (Figure 4.21).

4.3.2 Sodium Percent (Na%)

Percent sodium (% Na) is widely utilized for evaluating the suitability of water quality for irrigation. The % Na is computed with respect to relative proportions of cations present in water, using the following formula:

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

Table 4.4 explains the monthly variation of sodium percent (Na%) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast during the year 2012. Shallow groundwater possess an annual average of 51.7±14.33 of Na% during the year 2012 and water is permissible for irrigation. During November 2012, groundwater has Na% (33.0±12.12) and come under *good* quality for irrigation purposes [29]. Most of the months, Na% is within the permissible class (40-60), *suitable* for agricultural uses. However, in June (61.7±7.42) groundwater falls in *doubtful* category, because of increased sodium content in groundwater.

Table 4.4: Monthly variation of sodium percent (Na%) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	Na%	**Water Quality**	**Na%**	**Water Quality**
Jan 2012	34.4	G	57.1 ±18.07	P
Feb 2012	41.5	P	49.3 ±8.07	P
Mar 2012	41.0	P	51.2 ±12.35	P
Apr 2012	39.5	G	49.9 ±10.28	P
May 2012	44.5	P	57.4 ±10.76	P
Jun 2012	66.6	D	61.7 ±7.42	P
Jul 2012	38.0	G	60.0 ±15.37	P
Aug 2012	39.8	G	54.6 ±14.54	P
Sep 2012	34.1	G	48.2 ±11.27	P
Oct 2012	13.0	E	41.0 ±28.89	P
Nov 2012	27.2	G	33.0 ±12.12	G
Dec 2012	51.5	P	56.6 ±9.44	P
$\bar{x} \pm \sigma$	39.3 ±12.85	G	51.7 ±14.3	P
μ	39.3 ±7.91	G	51.7 ±8.81	P
CI	31.4-47.2	G-P	42.9-60.5	P-D

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

Control well of the coast showed fluctuations in sodium percent, exhibits an annual mean of 39.3 ±12.85. It comes under *doubtful* category during the month June 2012. But overall period, it maintains *good* quality, suitable for irrigation purposes.

4.3.2.1 Wilcox diagram

Wilcox diagram is also used for predicting the irrigation water quality, plotted EC against Na%. During August and September 2012 shallow groundwater (SGW) fall under *excellent* to *good* quality. It becomes *good to permissible* during the month of January, July, October and November 2012. But during February, April, June and December months of 2012 groundwater keeps, *doubtful to unsuitable* quality of water for irrigation as shown in the Figure 4.22. However in March and May 2012 EC values are very high, water falls under *unsuitable* category. In the case of control, entire period groundwater maintains *excellent* quality for irrigation purposes. (Figure 4.23) [3].

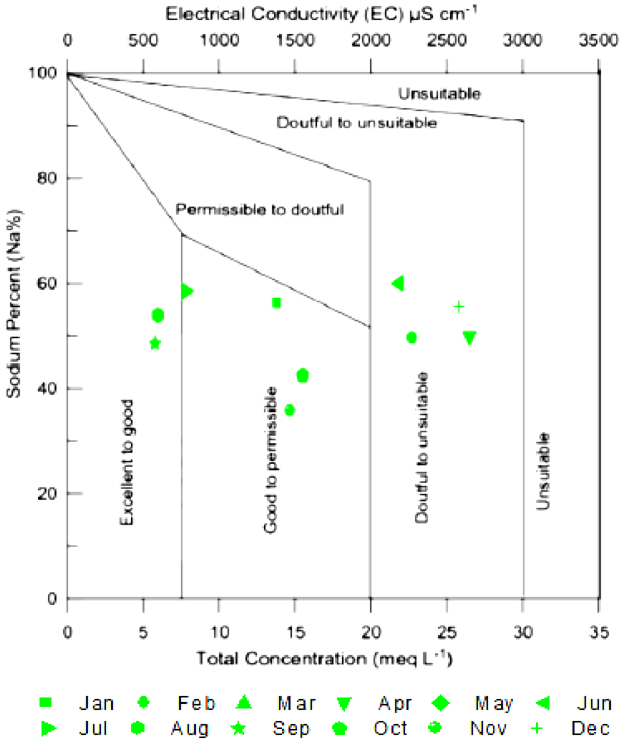


Figure 4.22: Wilcox diagram of shallow groundwater sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

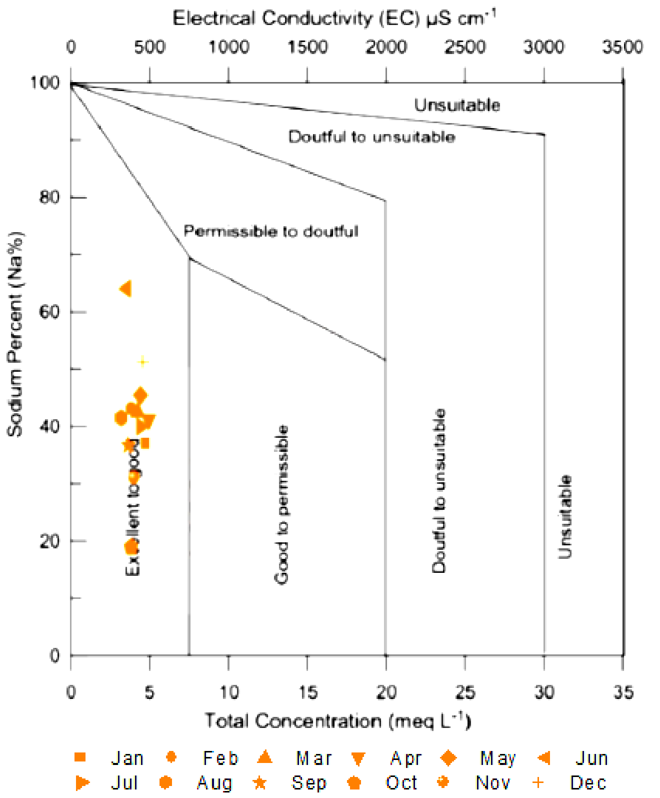


Figure 4.23: Wilcox diagram of control well (CW) of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.3.3 Permeability Index (PI)

The permeability of soil is affected by long-term use of irrigation water and is influenced by sodium, calcium, magnesium and bicarbonate contents in the soil [31]. Doneen (1964) evolved a criterion for evaluating the suitability of water for irrigation based on permeability index. PI is calculated using the following equation:

$$\mathbf{PI=[(Na^{+}+HCO^{3-})/(Ca^{2+}+Mg^{2+}+Na^{+})]\ 100}$$

According to PI, water can be classified as Class I, Class II and Class III. Class I and II are suitable for irrigation purposes with 75% or more of maximum permeability and Class III water is unsuitable for irrigation with 25% of maximum permeability. Shallow groundwater showed an annual average of PI 76.8±16.37 during the year 2012, that reveals groundwater of Cherai coast is *marginally safe (Class II)* for irrigation. Groundwater falls under class II with 75% maximum permeability during the months February, March, April, May, and October and November 2012, and water is good for irrigation purposes. During the remaining months, water occupies under class I with more than 75% maximum permeability. Hence, the water is excellent for agricultural uses. In the case of control well, through out the year permeability comes under class II, marginally safe for irrigation purposes with an annual mean of 44.1 ±14.22 of PI. (Table 4.5).

Table 4.5: Monthly variation of permeability index (PI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	PI	**Water Quality**	**PI**	**Water Quality**
Jan 2012	40.6	Class II	90.5 ±7.46	Class I
Feb 2012	45.2	Class II	71.9 ±6.64	Class II
Mar 2012	44.3	Class II	67.1 ±4.67	Class II
Apr 2012	40.5	Class II	63.0 ±7.77	Class II
May 2012	46.3	Class II	72.6 ±8.73	Class II
Jun 2012	74.9	Class II	81.5 ±4.66	Class I
Jul 2012	44.9	Class II	89.5 ±10.19	Class I
Aug 2012	53.3	Class II	92.0 ±9.40	Class I
Sep 2012	38.9	Class II	84.9 ±7.97	Class I
Oct 2012	15.7	Class II	68.2 ±8.26	Class II
Nov 2012	29.5	Class II	56.9 ±5.90	Class II
Dec 2012	54.7	Class II	83.2 ±8.96	Class I
$\bar{x} \pm \sigma$	44.1 ±14.22	Class II	76.8 ±7.74	Class II
μ	44.1±8.76	Class II	76.8±4.77	Class I
CI	35.3-52.9	Class II	72.0-81.6	Class II-Class I

Class I- Safe for Irrigation (S) Class II-Marginally Safe for Irrigation(MS)

4.3.4 Kelley's Ratio (KR)

Kelly ratio is used for the classification of water for irrigation purposes. Sodium measured against calcium and magnesium was considered by Kelley (1951) [32] for calculating Kelley ratio. All the ions are expressed in meq/L. The values of KI is below one, water is suitable for irrigational practice. KR is calculated by using the formula:

$$\mathbf{KR= Na^{+}/ Ca^{2+} + Mg^{2+}}$$

Kelley's ratio of shallow groundwater recorded an annual average of 1.3±1.35 during the period 2012. Most of the months, groundwater sources are *unsuitable* for irrigation purposes according to KR, except for November 2012. This indicates, the excess sodium concentration in groundwater. Throughout the year control well maintains a *good* quality of water, except during the months of June and December 2012 and considered as suitable for irrigation. It reported an annual mean of KR 0.7 ±0.43 during the year 2012 (Table 4.6) [33].

Table 4.6: Monthly variation of Kelley's ratio (KR) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	Parameters			
	CW		SGW	
	KR	Water Quality	KR	Water Quality
Jan 2012	0.5	S	2.4 ±3.67	US
Feb 2012	0.6	S	1.0 ±0.31	US
Mar 2012	0.6	S	1.1 ±0.62	US
Apr 2012	0.6	S	1.0 ±0.49	US
May 2012	0.7	S	1.4 ±0.69	US
Jun 2012	1.9	US	1.6 ±0.52	US
Jul 2012	0.6	S	2.0 ±1.76	US
Aug 2012	0.6	S	1.4 ±0.94	US
Sep 2012	0.5	S	1.0 ±0.47	US
Oct 2012	0.1	S	1.2 ±1.51	US
Nov 2012	0.3	S	0.5 ±0.34	S
Dec 2012	1.0	US	1.4 ±0.64	US
$\bar{x} \pm \sigma$	0.7 ±0.43	S	1.3 ±1.35	US
μ	0.7±0.26	S	1.3±0.83	US
CI	0.4-1.0	S	0.5-2.1	S-US

S-Suitable US-Unsuitable

4.3.5 Magnesium Adsorption Ratio (MAR)

Generally, calcium and magnesium maintain equilibrium in most waters [34]. In equilibrium Mg^{2+} in waters will adversely affect crop yield [35]. The measure of the effect of magnesium in irrigated water is expressed as magnesium ratio. Paliwal (1972) [36] developed an index for calculating the magnesium adsorption ratio (MAR). MAR is calculated using the formula:

$$\mathbf{MAR = [Mg^{2+}/(Ca^{2+}+Mg^{2+})]x100}$$

If the ratio less than 50 (MAR < 50) means, water is suitable for irrigation. But the value exceeds 50, water is unsuitable for agriculture purposes. MAR exhibits an annual average of 41.8±16.23 in shallow groundwater during the period 2012. Most of the months, the ratio found to be below 50, suitability of agricultural usage except in April 2012. Control well also indicates irrigation suitability during the year 2012, with an annual mean of 37 ±21.75 (Table 4.7).

Table 4.7: Monthly variation of magnesium adsorption ratio (MAR) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**Parameters**			
	CW		**SGW**	
	MAR	**Water Quality**	**MAR**	**Water Quality**
Jan 2012	37.8	S	44.0 ±8.01	S
Feb 2012	26.2	S	45.2 ±10.24	S
Mar 2012	43.4	S	36.4 ±16.89	S
Apr 2012	52.6	US	52.9 ±11.09	US
May 2012	3.9	S	43.9 ±20.24	S
Jun 2012	25.0	S	42.7 ±17.18	S
Jul 2012	5.3	S	13.5 ±10.05	S
Aug 2012	30.1	S	38.9 ±10.87	S
Sep 2012	52.5	US	48.7 ±8.28	S
Oct 2012	82.3	US	48.1 ±32.19	S
Nov 2012	51.1	US	46.1 ±16.47	S
Dec 2012	33.4	S	41.0 ±16.80	S
$\bar{x} \pm \sigma$	37 ±21.75	S	41.8 ±16.23	S
μ	37±13.40	S	41.8±10.0	S
CI	23.6-50.4	S-US	31.8-51.8	S-US

S-Suitable US-Unsuitable

4.4 Measures of Corrosion and Scaling Potential

The indices used to find the corrosion or scale forming potential of groundwater sources are Langelier saturation index, Ryznar stability index and aggressiveness index.

4.4.1 Langelier Saturation Index (LSI)

The Langelier saturation index (LSI), a measure of a solution's ability to dissolve or deposit calcium carbonate, is often used as an indicator of the corrosivity of water. The index is not related directly to corrosion, but is related to the deposition of a calcium carbonate film or scale; this covering can insulate pipes, boilers and other components of a system from contact with water. When no protective scale is formed, water is considered to be aggressive and corrosion can occur [37]. Highly corrosive water can cause system failures or result in health problems because of dissolved lead and other heavy metals. An excess of scale can also damage water systems, necessitating repair or replacement.

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

$$\boldsymbol{pH_s = pK_2 - pK_s + pCa^{2+} + pHCO_3^-} \quad \text{......................} \quad (2)$$

Where pH = actual pH of water

pH_s = pH of saturation for $CaCO_3$

pCa^{2+} = equilibrium calcium content

pK_2 = second protolysis constant for H_2CO_3

pK_s = solubility product constant for $CaCO_{3(s)}$

$pHCO_3^-$ = total alkalinity when pH>9.5

Table 4.8: Monthly variation of Langelier saturation index (LSI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	LSI	**Tendency of water**	**LSI**	**Tendency of water**
Jan 2012	-1.1	SC	-0.4 ±0.48	SCNSF
Feb 2012	-1.1	SC	-0.5 ±0.30	SCNSF
Mar 2012	-1.0	SC	-0.3 ±0.36	SCNSF
Apr 2012	-0.9	SC	-0.1 ±0.30	SCNSF
May 2012	-1.1	SC	-0.1 ±0.48	SCNSF
Jun 2012	-1.5	SC	-0.6 ±0.49	SC
Jul 2012	0.0	BP	0.0 ±0.50	SCNSF
Aug 2012	-0.5	SC	-0.2 ±0.53	SCNSF
Sep 2012	-1.4	SC	-0.4 ±0.44	SCNSF
Oct 2012	-1.1	SC	-0.7 ±0.15	SC
Nov 2012	-1.4	SC	-1.0 ±0.22	SC
Dec 2012	-1.0	SC	-0.9 ±0.18	SC
$\bar{x} \pm \sigma$	-1.0 ±0.41	SC	-0.4 ±0.39	SCNSF
μ	-1.0 ± 0.25	SC	-0.4 ± 0.24	SCNSF
CI	¯1.3-¯0.7	SC	-0.6-¯0.2	SC-SCNSF

Table 4.8 shows the monthly variation of Langelier saturation index (LSI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast. The shallow groundwater sources reported an annual average of -0.44±0.55 during the year 2012. In January-May 2012, LSI is *slightly corrosive* but *non scale forming (SCNSF) behaviour*. But in June groundwater becomes (-0.65±0.64) *serious corrosion* (SC) character. And again the LSI was SCNSF during the months July-September 2012. Afterwards, there was a gradual increase in LSI from October- December 2012 and groundwater is *seriously corrosive*. Control well possess an annual average of 1.0 ±0.41 during the year 2012 and groundwater comes under the category of *serious corrosion*.

4.4.2 Ryznar Stability Index (RSI)

The Ryznar stability index (RSI) is an empirical method used for predicting the scale forming tendencies of water [38]. Groundwater of

Cherai coast reported an annual average RSI of (8.2±0.93) of RSI during the period 2012 and comes under *heavy corrosion* category (Table 4.9). Groundwater recorded an annual mean of 9.2 ±0.52, under the class of *heavy corrosion* during the year 2012 in the case of control well.

$$\boldsymbol{RSI = 2pH_s - pH} \quad \text{...} (3)$$

Table 4.9: Monthly variation of Ryznar stability index (RSI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	RSI	**Tendency of water**	**RSI**	**Tendency of water**
Jan 2012	9.3	HC	8.5 ±0.68	HC
Feb 2012	9.2	HC	8.0 ±0.51	HC
Mar 2012	8.9	HC	7.6 ±0.56	HC
Apr 2012	9.0	HC	7.5 ±0.53	HC
May 2012	9.1	HC	7.5 ±1.05	HC
Jun 2012	10.1	HC	8.4 ±0.91	HC
Jul 2012	8.0	HC	7.8 ±0.82	HC
Aug 2012	8.8	HC	8.3 ±0.94	HC
Sep 2012	9.8	HC	8.4 ±0.64	HC
Oct 2012	9.2	HC	8.5 ±0.29	HC
Nov 2012	9.5	HC	8.7 ±0.48	HC
Dec 2012	9.3	HC	8.7 ±0.26	HC
$\bar{x} \pm \sigma$	9.2 ±0.52	HC	8.2 ±0.68	HC
μ	9.2±0.32	HC	8.2 ±0.42	HC
CI	8.9-9.5	HC	7.8-8.6	HC

HC – Heavy Corrosion

4.4.3 Aggressive Index (AI)

The Aggressive Index (AI), originally developed for monitoring water in asbestos pipe, is sometimes substituted for LSI as an indicator of the corrosivity of water. The AI is derived from the actual pH, calcium hardness and total alkalinity [39]. Where it is applicable, it is simpler and more convenient than the LSI. Because the AI does not include the effects of temperature or dissolved solids, it is less accurate as an analytical tool than the LSI.

$$AI = pH + log\ (AH) \ldots\ldots (4)$$

Where '**A**' is the total alkalinity and '**H**' is calcium hardness in mg/L as $CaCO_3$

Shallow groundwater of Cherai coast indicates, *slightly aggressive* character throughout the year. It is reported with an annual average of AI 11.5±0.57 during the year 2012. The *slightly corrosive* behaviour may be due to the presence of reactive hydrogen ion species. Control well also showed same trend of shallow groundwater, possess *moderately aggressive* nature as shown in the Table 4.10.

Table 4.10: Monthly variation of aggressiveness index (AI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	AI	**Tendency of water**	**AI**	**Tendency of water**
Jan 2012	10.7	MA	11.5 ±0.52	MA
Feb 2012	10.8	MA	11.4 ±0.52	MA
Mar 2012	10.9	MA	11.6 ±0.61	MA
Apr 2012	10.9	MA	11.8 ±0.79	MA
May 2012	10.7	MA	11.8 ±0.62	MA
Jun 2012	10.3	MA	11.3 ±0.66	MA
Jul 2012	11.8	MA	11.9 ±0.56	MA
Aug 2012	11.3	MA	11.6 ±0.42	MA
Sep 2012	10.5	MA	11.5 ±0.60	MA
Oct 2012	10.8	MA	11.2 ±0.43	MA
Nov 2012	10.4	MA	10.9 ±0.56	MA
Dec 2012	10.9	MA	11.0 ±0.44	MA
$\bar{x} \pm \sigma$	10.8 ±0.40	MA	11.5 ±0.57	MA
μ	10.8±0.25		11.5±0.35	
CI	10.6-11.0		11.1-11.9	

MA – Moderately Aggressive

4.5 Piper Plots & Hydrochemical Facies

The Hill-Piper-trilinear diagram [40] (Piper, 1944) consists of three distinct fields-two triangular portions and one diamond shaped area. Water is classified into mainly four different facies based on the data positions in diamond portion of Piper diagram [21].

(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)*

The Piper trilinear diagram of groundwater souces of Cherai coast are presented in the Figure. 4.24 & 4.25, which clearly explains the hydrochemical facies of the study area. In shallow groundwater, most of the months groundwater falls in the *saline type* with sodium dominating cationic triangle and chloride is the anion type. Hence, the hydrochemical facies is characterised by $Na^+ – K^+ – Cl^- – SO_4^{2-}$ type. This indicates the presence of high amount of sodium and chloride in the shallow aquifers as a result of saline intrusion [24]. During October 2012, the water type is shifted towards *permanent hardness* type (Ca^{2+}-Mg^{2+}-Cl^--SO_4^{2-}) with no dominant cation and anion is chloride. The excess of calcium and magnesium may be derived from the reverse ion exchange process [41]. However, during November 2012, piper diagram indicates mixed Ca^{2+}-Mg^{2+}-Cl^- type water, indicating the predominance of *reverse ion exchange* [42].

Control well exhibits a *reverse ion exchange* character in most of the months. During January- April 2012 water is having *temporary hardness* behaviour. It changes to mixed Ca^{2+}-Mg^{2+}-Cl^- type as a result of saltwater intrusion. However, the water get diluted with rain by monsoon and the water type move towards Ca^{2+}-Na^+-HCO_3^- type during June 2012. Again the *reverse ion exchange process* was continued, which enhances the calcium and magnesium ions in the groundwater and the water type shifted to Ca^{2+}-Mg^{2+}-HCO_3^- type (Figure 4.25).

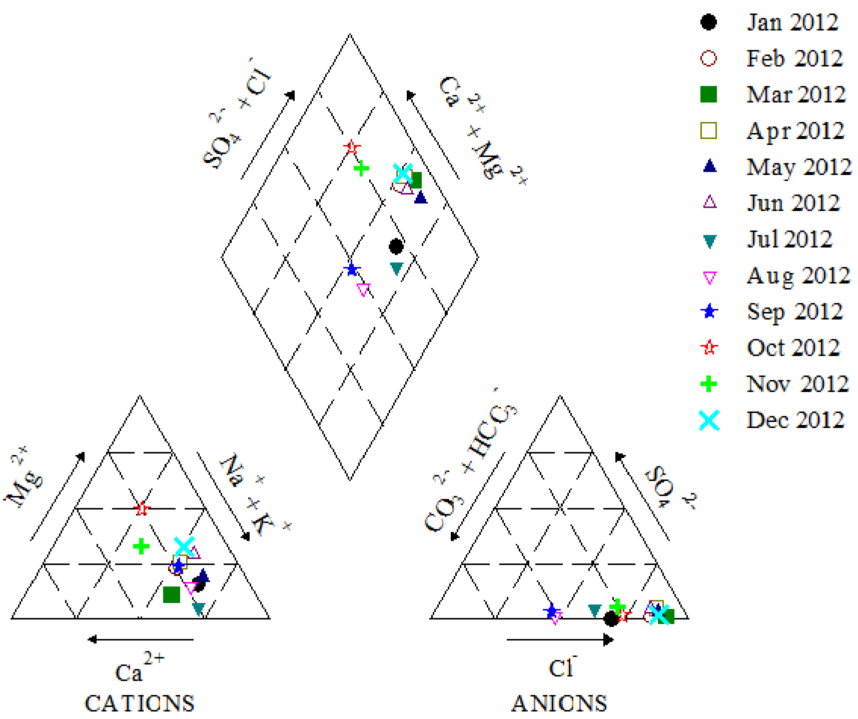


Figure 4.24: Piper diagram of groundwater sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

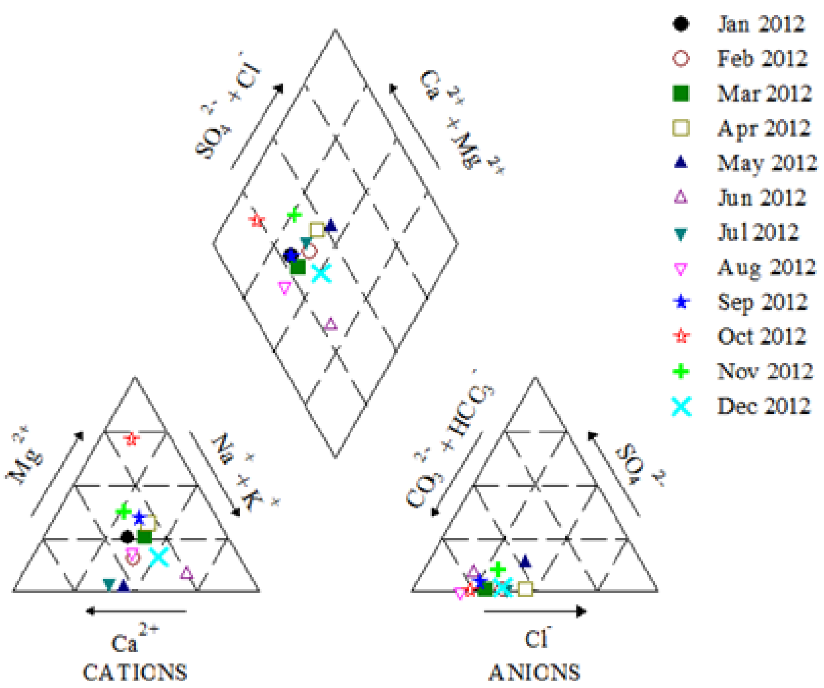


Figure 4.25: Piper diagram of control well (CW) of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.6 Gibb's Diagrams

The composition and source of dissolved constituents in groundwater can be explained by Gibb's diagrams [43]. It is plotted with $Na^+/Na^+ + Ca^{2+}$ / TDS and $Cl^-/Cl^- + HCO_3^-$ / TDS. The groundwater chemistry of Cherai coast was mainly controlled by weathering of rock forming minerals and also the evaporation process, as shown from the Figure 4.26. Most of the month, water chemistry of shallow groundwater sources is controlled by the weathering of rock forming minerals. However, during March and May the TDS exceeds 10000 mg/L, indicates the evaporation process, which increase the concentrations of all species in water. Hence, the chemical composition of shallow groundwater sources are affected by rock- water interaction as well as evaporation processes.

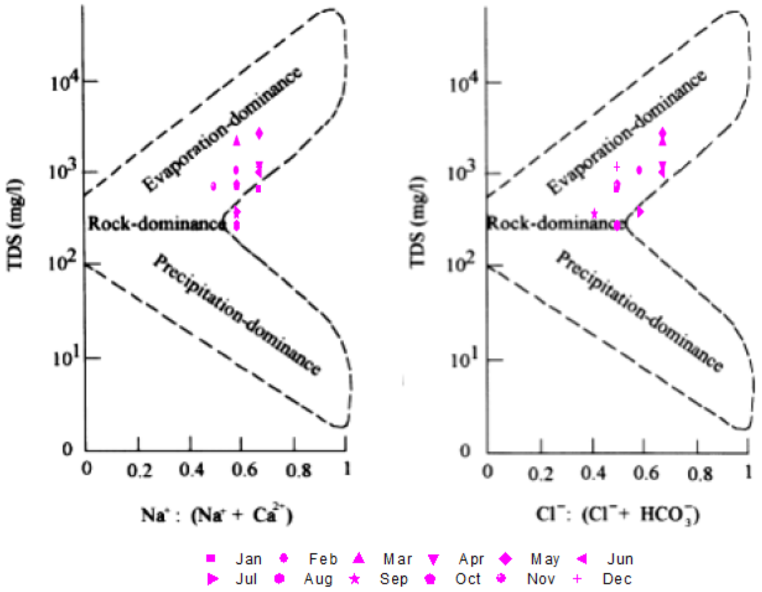


Figure 4.26: Gibb’s Diagram of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

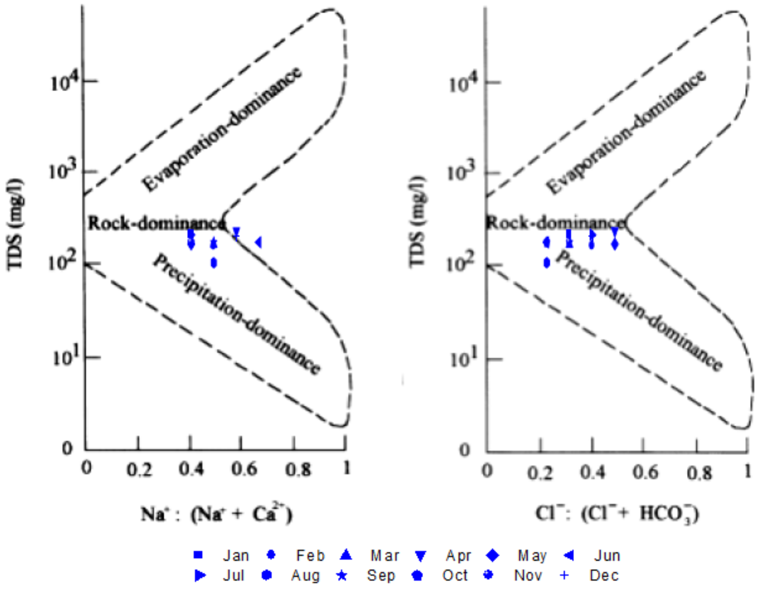


Figure 4.27: Gibb’s Diagram of control well (CW) of Cherai coast, Ernakulam, Kerala, India during the year 2012

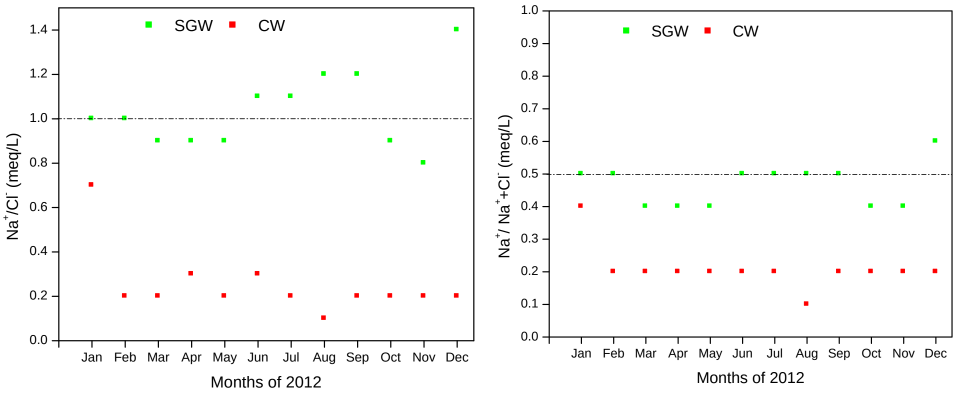
During the entire period of study Jan- Dec.2012 chemical composition of control well is controlled by weathering of rocks, clearly shown in the Figure 4.27.

4.7 Study of Ionic Ratios

4.7.1 Sodium-Chloride Ratio

The ratios of sodium and chloride are used for determination of *ion exchange or reverse ion exchange processes.* If $Na^+/Na^++Cl^- > 0.5$ and if $Na^+/Cl^- > 1.0$, the process taking place is ion exchange and it reverse to that ($Na^+/Na^++Cl^- < 0.5$ and if $Na^+/Cl^- < 1.0$) reverse ion exchange may occurs. Table 4.11 shows the monthly variation of Na^+/Na^++Cl^- and Na^+/Cl^- of control well (CW) and shallow groundwater (SGW) sources of Cherai coast during the year 2012. The shallow groundwater sources showed an annual average of 1.0 ±0.17of Na^+/Cl^- ratio, which indicates that the *ion exchange process* was prevalent in the region. Na^+/Na^++Cl^- ratio also noted that ion exchange process was occurring in the groundwater with an annual mean of 0.5 ±0.04. It means, calcium ion replaces the sodium present in the aquifer system and the water get softened. As a result of this process, sodium concentration in groundwater increased. However, groundwater character shifted from ion exchange to reverse ion exchange during the months February, March, April, May, October and November 2012. This indicates, the enhanced concentration of sodium and chloride in groundwater. In the case of control well, throughout the study period groundwater experiences a reverse ion exchange character. The concentrations of Na^+/Cl^- & $Na^+/ Na^++ Cl^-$ are 0.2 ±0.08 and 0.3 ±0.15

respectively. Scatter diagrams in the Figure 4.28 (a) & (b) also explain the process of ion exchange and reverse ion exchange.



(a) (b)

Figure 4.28: (a) Na^+/Cl^- ratio (b) $Na^+/ Na^+ + Cl^-$ ratio of shallow groundwater sources (SGW) of Cherai coast, Ernakulam, Kerala, India during the year 2012

Table 4.11: Monthly variation of Na^+/Cl and $Na^+/ Na^+ + Cl^-$ of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**CW**			**SGW**		
	$Na^+/ Na^+ + Cl^-$	**Na^+/Cl**	**Inference**	**$Na^+/ Na^+ + Cl^-$**	**Na^+/Cl**	**Inference**
Jan 2012	0.4	0.7	RIE	0.5 ±0.09	1.0±0.37	IE
Feb 2012	0.2	0.2	RIE	0.5±0.14	1.0 ±0.61	IE
Mar 2012	0.2	0.2	RIE	0.4 ±0.12	0.9 ±0.43	RIE
Apr 2012	0.2	0.3	RIE	0.4 ±0.11	0.9±0.42	RIE
May 2012	0.2	0.2	RIE	0.4 ±0.09	0.9±0.37	RIE
Jun 2012	0.2	0.3	RIE	0.5 ±0.12	1.1 ±0.58	IE
Jul 2012	0.2	0.2	RIE	0.5 ±0.10	1.1 ±0.49	IE
Aug 2012	0.1	0.1	RIE	0.5 ±0.07	1.2 ±0.38	IE
Sep 2012	0.2	0.2	RIE	0.5 ±0.03	1.2±0.16	IE
Oct 2012	0.2	0.2	RIE	0.4 ±0.19	0.9±0.52	RIE
Nov 2012	0.2	0.2	RIE	0.4 ±0.13	0.8 ±0.40	RIE
Dec 2012	0.2	0.2	RIE	0.6 ±0.13	1.4 ±0.61	IE
$\overline{x} \pm \sigma$	0.3 ±0.15	0.2 ±0.08	RIE	0.5 ±0.04	1.0 ±0.17	IE
μ	0.3±0.09	0.2±0.05		0.5 ±0.02	1.0 ±0.10	
CI	0.2-0.4	0.15-0.25		0.48-0.52	0.9-1.1	

IE- Ion Exchange RIE-Reverse Ion Exchange

4.7.2 $(Ca^{2+}+Mg^{2+}) / (HCO_3^-+SO_4^{2-})$ Scatter Diagram

The points fall above the 1:1 line indicates carbonate weathering process. In most of the months, shallow groundwater sources falls in the left of the diagram, indicates the occurrence of carbonate dissolution [44]. However, it also possess silicate weathering character during March, April and December 2012. During the months of January and September 2012, water possess both silicate and carbonate weathering processes. In the case of control well, most of the months groundwater possesses weathering of carbonate and silicate bearing rocks. During April, October and November 2012 showed carbonate dissolution. The remaining months reveal that groundwater originated from silicate weathering.

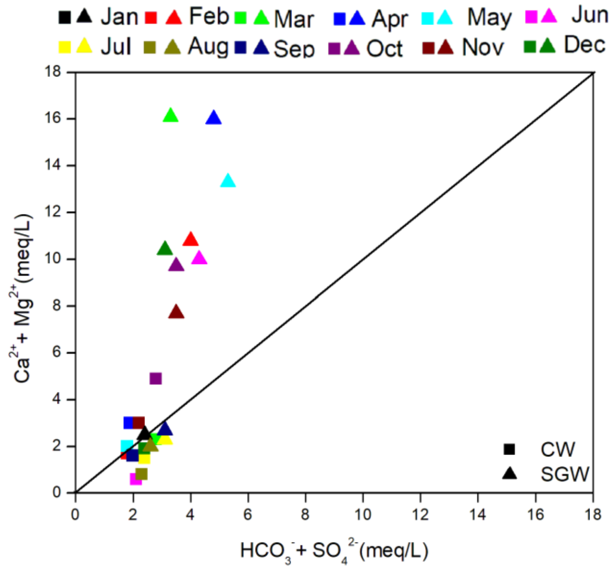


Figure 4.29: (Ca+Mg) / (HCO_3+SO_4) scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.7.3 Na / Ca scatter diagram

In Na/Ca scatter diagram, the concentrations fall below the 1:1 line indicate the occurrence of *ion exchange* phenomena [47]. Here shallow groundwater showed both carbonate dissolution and ion exchange during the months October and November 2012. The reaming months, groundwater is having *ion exchange* character. The point falls above the equiline indicates the carbonate dissolution process. In control well, the ionic concentrations fall along the equiline in most of the months, indicate the occurrence of both carbonate weathering and ion exchange process. However during the month June 2012, water is having an *ion exchange* character.

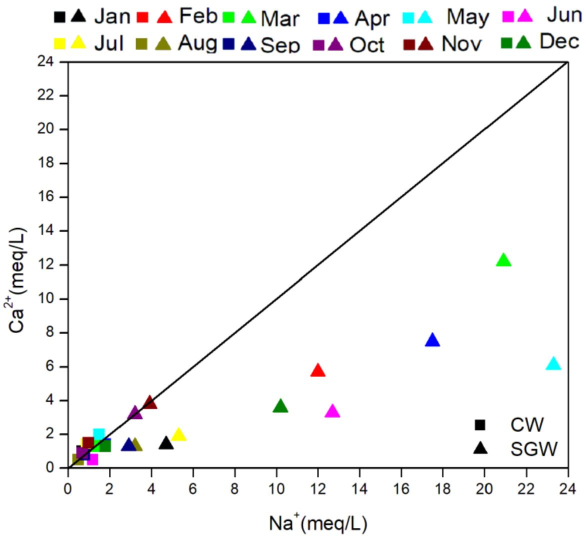


Figure 4.30: Na / Ca scatter diagram scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.7.4 Na / Cl scatter diagram

In NaCl scatter, points falls below the 1:1 line, indicates ion exchange process. If points are move towards the left of 1:1 line, indicates halite dissolution process [46]. From the Figure 31 is clear that, most of the months shallow groundwater sources occupies along 1:1 line, reveal the occurrence of sea water intrusion and ion exchange process. During August, groundwater showed ion exchange character. Sea water intrusion was prominent during the months of February, June, October, November and December 2012. The control well exhibited both ion exchange behaviour and saline water intrusion in most of the months. But during June 2012 water showed prominent ion exchange character.

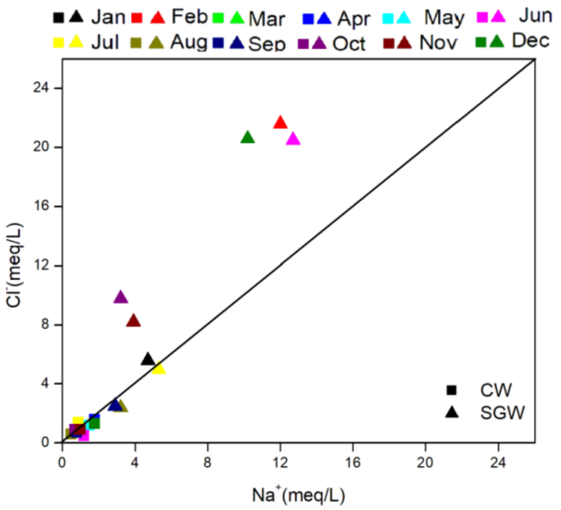


Figure 4.31: Na / Cl scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.7.5 $(TZ^+) / (Na^+ + K^+)$ scatter diagram

In $TZ^+ / Na^+ + K^+$ Scatter points falls below the equiline indicates the occurrence of silicate weathering [47].The shallow groundwater falls below the 1:1 line throughout the period, indicates silicate weathering. In control well, June and August 2012, points fall along the equiline reveal that source of sodium was originated from other sources. The remaining months shows that source of sodium coming from silicate weathering process.

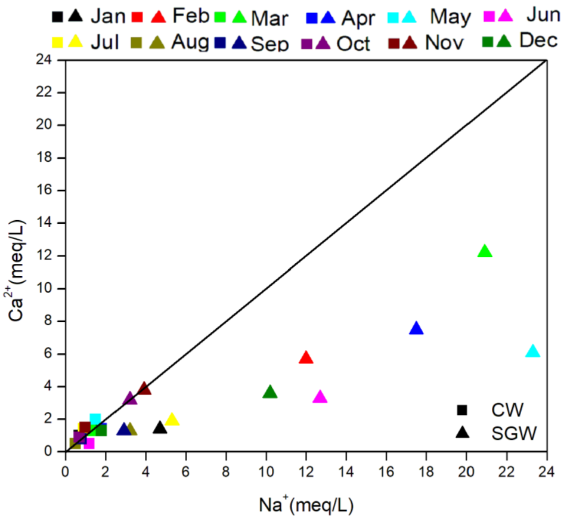


Figure 4.32: (TZ^+) / (Na^++K^+) scatter diagram of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

4.8 Water Quality Index (WQI)

WQI is an important parameter for demarcating groundwater quality and its suitability for drinking purposes. Weighted arithmetic index method has been used for the calculation of WQI [48]. Cherai coast groundwater quality depends on number of physico - chemical parameters such as pH, EC, TA, TDS, DO, BOD, TH, Ca^{2+}, Mg^{2+}, Na^+, $K^{+,}$ Cl^-, SO_4^{2-} and Total Iron Fe(t). Hence, we chose these important parameters and the BIS & WHO standards for the further calculation. Table 4.12 showed the monthly variation of water quality index (WQI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast during year 2012. Shallow groundwater sources reported an annual mean of 324.5±309.51, groundwater is *unfit for drinking purpose* (UDP) throughout the study period (2012).This means, we cannot use this groundwater for human consumption before the treatment methods. In control well, WQI exhibits an annual mean of 89.9± 138.72, comes under *very poor* quality of water.

Table 4.12: Monthly variation of water quality index (WQI) of control well (CW) and shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Period (Month/Year)	**CW**		**SGW**	
	WQI	**Water Quality**	**WQI**	**Water Quality**
Jan 2012	61.4	P	141.0±148.09	UDP
Feb 2012	58.7	P	329.3±407.68	UDP
Mar 2012	87.4	VP	429.4±468.21	UDP
Apr 2012	90.3	VP	341.8±462.76	UDP
May 2012	7.9	E	263.2±273.86	UDP
Jun 2012	7.7	E	289.3±259.34	UDP
Jul 2012	516.7	UDP	260.9±235.02	UDP
Aug 2012	37.2	G	216.2±162.24	UDP
Sep 2012	112.1	UDP	501.7±246.88	UDP
Oct 2012	35.7	G	354.2±215.30	UDP
Nov 2012	57.5	P	282.3±202.25	UDP
Dec 2012	6.1	E	261.3±352.77	UDP
$\bar{x} \pm \sigma$	89.9± 138.72	VP	305.9±305.23	UDP
μ	89.9±85.44	VP	305.9±187.99	UDP
CI	4.5-175.3	E-UDP	117.9-493.9	UDP

E-Excellent G-Good P-Poor VP-Very Poor UDP-Unfit for Drinking Purposes

4.9 Trace Metal Study

The trace metals analyzed in the groundwater, consist of 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). From the Table 4.13, we can see that trace metals present in the groundwater of Cherai coast are well within the safe standard limits [49].

Table 4.13: Trace element analysis in groundwater sources of Cherai coast, Ernakulam, Kerala, India during the month of December 2012

Trace Metals	DW1	DW2	DW3	DW4	DW5	DW6	BW	$\bar{x} \pm \sigma$	BIS
Li (µg/l)	4.5	5.3	3.1	8.4	5.1	7.1	0.2	4.8±2.67	
Al (µg/l)	55.9	28.8	13.0	29.4	34.0	26.4	68.0	36.5±18.88	200
V (µg/l)	0.8	3.4	1.2	5.1	0.6	5.7	0.8	2.5±2.19	
Cr (µg/l)	0.7	1.0	0.4	0.7	0.6	0.5	0.3	0.6±0.23	50
Mn (µg/l)	733.0	69.4	16.3	38.2	145.3	48.2	13.0	151.9±260.09	300
Ni (µg/l)	41.4	3.5	0.9	2.1	3.5	1.3	1.1	7.7±14.91	20
Co (µg/l)	0.2	0.4	0.1	0.3	0.1	0.1	0.1	0.2±0.12	
Cu (µg/l)	0.8	1.9	1.1	3.3	0.8	1.0	2.3	1.6±0.95	1500
Zn (µg/l)	3.4	200.7	1.4	23.0	8.3	3.5	4.7	35.0±73.43	15000
Ga (µg/l)	3.1	3.3	1.5	3.4	3.5	4.8	6.8	3.8±1.65	
As (µg/l)	7.2	4.6	1.9	2.5	0.4	0.4	0.1	2.4±2.63	50
Se (µg/l)	3.9	3.6	2.5	4.2	3.8	3.5	4.6	3.7±0.66	10
Rb (µg/l)	5.4	3.7	9.6	4.0	7.5	7.1	3.4	5.8±2.33	
Sr (µg/l)	71.4	97.6	252.2	146.3	135.7	226.1	36.2	137.9±78.85	
Ag (µg/l)	0.2	ND	ND	0.1	0.1	0.2	0.1	0.1±0.05	100
Cd (µg/l)	0.1	0.1	ND	0.1	0.1	0.1	0.1	0.1±0.00	3
In (µg/l)	ND	ND	ND	ND	ND	0.1	0.1	0.1±0.00	
Cs (µg/l)	ND	ND	ND	ND	ND	ND	ND	0	
Ba (µg/l)	16.6	17.6	8.4	18.6	19.1	25.2	31.3	19.5±7.16	700
Pb (µg/l)	0.3	0.6	0.2	0.2	0.2	0.2	0.3	0.3±0.15	10
Bi (µg/l)	ND	ND	0.8	0.1	ND	0.1	0.2	0.3±0.34	

4.10 Total Organic Carbon Analysis

Total carbon content was determined by using the TOC analyser, which determines total carbon (TC), total inorganic carbon (TIC) and total organic carbon (TOC). The results showed that TIC was greater than TOC, indicates groundwater containing carbons mostly in inorganic form (Table 4.14).

Table 4.14: Total organic carbon (TOC) analysis in shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during the month of February 2012

Station	TC (mg/l)	TIC (mg/l)	TOC (mg/l)
DW1	7.157	4.839	2.318
DW2	14.094	7.666	6.428
DW3	10.52	9.066	1.454
DW4	5.572	4.163	1.409
DW5	0.995	0.694	0.301
DW6	10.675	10.357	0.318
BW	7.037	3.765	3.272
$(\bar{x})\pm SD(\sigma)$	8.0±4.23	5.80 ±3.38	2.21±2.14

4.11 Classification of water based on Designated Best Use (DBU)

Central Pollution Control Board (CPCB), Ministry of Environment and Forest, Government of India were classified the groundwater into five classes according to their designated best use (DBU) [50]. The classes are set by considering some important water quality parameters such as Total Coliforms, pH, dissolved oxygen (DO), biological oxygen demand (BOD), free ammonia, sodium adsorption ratio (SAR) and Boron. Water classes are arranged in the order of deterioration in quality of water. Class A water can be used for drinking purpose without conventional treatment but after disinfection. Class B water is preferred for outdoor bathing. Drinking water source after conventional treatment and disinfection occupies in class C. For the propagation of wildlife and fisheries, we can use Class D water.

Table 4.15: Classification of shallow groundwater sources of Cherai coast, Ernakulam, Kerala, India based on designated best use by CPCB during the period December 2012

Station	Total coliforms MPN/100ml	E. Coli	pH	EC (mS/cm)	DO (mg/L)	BOD (mg/L)	SAR	Boron	Class
DW1	22	Present	7.1	280	3.4	5.46	1.9	0.1	E
DW2	110	Present	7.0	420	3.5	7.88	3.7	0.2	E
DW3	245	Present	6.7	260	3.4	4.14	1.7	0.1	E
DW4	7	Present	7.1	340	4.2	2.64	2.5	0.1	C
DW5	280	Present	7.1	280	2.9	9.02	2.2	0.3	E
DW6	310	Present	7.3	660	1.7	11.72	5.8	0.1	E
BW	2	Absent	6.4	16580	4.7	2.98	9.6	0.3	C

Class E water is being suggested for irrigation and industrial purposes. Table 4.17 shows the classification of shallow groundwater sources of Cherai coast based on designated best use by CPCB during the period

December 2012, indicate that DW1, DW2, DW3 and DW5 comes under the category of class C.

The remaining groundwater DW4 and BW water showing irrigation suitability according to CPCB guidelines.

4.12 Statistical Analysis

4.12.1 Pearson Correlation Matrix

Shallow groundwater of Cherai coast reported very strong correlation between the water quality parameters EC & TDS, EC & Na^+, EC & Cl^-, TDS & Na^+ and TDS & Cl^-, reveals the conductance and dissolved content of the water is mainly produced by the dissolved ions such as Na^+ & Cl^-. Total hardness was strongly correlated with and Ca^{2+} and Mg^{2+}, indicates hardness is mainly constituted by the ions such as calcium and magnesium. Na^+ & Cl^- very strongly correlated with each other, which reveals that they were originated from same source. Strong correlation has existed between Mg^{2+} & TDS, EC & Mg^{2+}, TH & K^+, TDS & SO_4^{2-} and K^+ & SO_4^{2-}, EC & SO_4^{2}, Mg^{2+} & K^+ and Mg^{2+} & Cl^-, shows that saltwater intrusion contributing these ions into the groundwater.

Control wells of Cherai coast showed very strong positive correlations between TH & Mg^{2+} and Na^+ & K^+. Strong correlations are reported in the cases of EC & TDS, EC & Cl^-, and Ca^{2+} & Cl^-. Positive correlations are reported between EC & $Ca^{2+,}$ TDS & Cl^-, Na^+ & Cl^-, K^+ & Cl^-. A strong negative correlations was found between alkalinity and sulphate, indicates the occurrence of sulphate reduction mechanism [51].

Table 4.16: Pearson's correlation matrix of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India during year 2012

Variables	**pH**	**EC**	**Alk**	**DO**	**BOD**	**TH**	**Ca**	**Mg**	**TDS**	**Na**	**K**	**Cl**	**SO_4**	**NO_3**	**PO_4**	**Fe(t)**
pH	**1**															
EC	0.175	**1**														
Alk	0.079	0.349	**1**													
DO	0.625	-0.093	0.034	**1**												
BOD	-0.126	0.151	-0.283	-0.607	**1**											
TH	-0.074	0.423	0.400	-0.157	0.092	**1**										
Ca	-0.001	0.035	0.448	0.009	-0.111	**0.850**	**1**									
Mg	-0.131	**0.716**	0.182	-0.293	0.298	**0.776**	0.326	**1**								
TDS	0.212	**0.994**	0.382	-0.089	0.154	0.424	0.041	**0.711**	**1**							
Na	0.250	**0.881**	0.545	-0.058	0.223	0.498	0.231	0.616	**0.903**	**1**						
K	-0.260	0.496	0.259	-0.094	-0.092	**0.794**	0.635	**0.663**	0.490	0.441	**1**					
Cl	0.234	**0.920**	0.345	-0.123	0.335	0.530	0.223	**0.684**	**0.907**	**0.917**	0.452	**1**				
SO_4	-0.071	**0.697**	0.056	-0.035	0.088	0.338	0.008	0.596	**0.711**	0.598	**0.703**	0.533	**1**			
NO_3	-0.491	-0.246	0.152	-0.550	0.550	0.132	0.241	-0.051	-0.253	-0.046	-0.066	-0.050	-0.337	**1**		
PO_4	-0.197	-0.126	-0.276	-0.334	0.096	-0.172	-0.308	0.059	-0.132	-0.364	-0.166	-0.217	-0.186	-0.170	**1**	
Fe(t)	0.121	0.278	0.073	0.114	-0.322	-0.039	-0.082	0.029	0.286	0.364	0.029	0.252	0.221	-0.490	-0.150	**1**

Values in bold are different from 0 with a significance level alpha=0.05

Table 4.17: Pearson's correlation matrix of control well of Cherai coast, Ernakulam , Kerala, India during year 2012

Variables	**pH**	**EC**	**Alk**	**DO**	**BOD**	**TH**	**Ca**	**Mg**	**TDS**	**Na**	**K**	**Cl**	**SO_4**	**NO_3**	**PO_4**	**Fe(t)**
pH	**1**															
EC	-0.169	**1**														
Alk	0.264	-0.058	**1**													
DO	-0.326	0.054	-0.411	**1**												
BOD	0.360	-0.068	0.197	-0.487	**1**											
TH	-0.388	0.238	0.309	-0.005	-0.057	**1**										
Ca	-0.229	**0.666**	-0.349	0.268	-0.352	0.294	**1**									
Mg	-0.314	-0.013	0.459	-0.110	0.079	**0.927**	-0.086	**1**								
TDS	-0.140	**0.843**	-0.036	0.084	-0.164	0.244	0.354	0.116	**1**							
Na	-0.364	0.616	-0.254	0.325	-0.145	0.072	0.564	-0.146	0.474	**1**						
K	-0.514	0.635	-0.237	0.263	-0.098	0.325	0.621	0.095	0.437	**0.909**	**1**					
Cl	0.082	**0.826**	0.021	0.115	-0.207	0.286	**0.764**	-0.001	**0.669**	**0.674**	**0.650**	**1**				
SO_4	-0.493	-0.048	**-0.670**	0.500	-0.233	-0.053	0.366	-0.199	-0.116	0.214	0.170	-0.173	**1**			
NO_3	0.180	-0.101	0.108	0.003	0.049	0.407	0.260	0.322	-0.169	-0.180	0.044	0.128	0.082	**1**		
PO_4	-0.077	-0.346	-0.195	0.317	0.153	-0.400	-0.494	-0.223	-0.054	0.043	-0.205	-0.449	0.322	-0.426	**1**	
Fe(t)	0.623	0.192	0.170	-0.053	-0.286	-0.121	0.186	-0.200	0.342	-0.206	-0.323	0.413	-0.291	0.297	-0.188	**1**

Values in bold are different from 0 with a significance level alpha=0.05

4.12.2 Analysis of Co-Variance (ANOVA)

The results of two –way ANOVA conducted for the study are follows,

a) Whether there is any significant difference between mean values of various parameters in CW stratum at different months of 2012

Table 4.18: ANOVA table for the comparison of water quality parameters between different months of control well of Andhakaranazhy coast during the year 2012

Source	**SS**	**df**	**ms**	**F**	**p- value**
Total	685459.6271	215			
Parameter	613856.3868	17	36109.1992	102.689	$p < 0.001$
Months	5847.2683	11	531.5698	1.512	$p > 0.05$
Residual	65755.9720	187	351.6362		

<u>Inferences</u>

1) Very high significant differences were noted in the parameter values ($p < 0.001$). TDS is significantly the most high followed by Alkalinity and TH ($p < 0.001$).

   Eh is significantly the least compared to all other parameters.

2) There is no significant difference between months ($p > 0.05$)

b) Whether there is any significant difference between mean values of various parameters in shallow groundwater sources of Cherai coast during the each month of year 2012

Table 4.19: ANOVA table for the comparison of water quality parameters between different months of shallow groundwater sources of Andhakaranazhy coast during the year 2012

Source	**ss**	**df**	**ms**	**F**	**p- Value**
Total	104417297.0460	215			
Parameters	31200038.0257	17	1835296.3545	4.893	$p < 0.001$
Months	3069358.6483	11	279032.6044	0.743	$p > 0.05$
Residual	70147900.9953	187	375122.4652		

Inferences

1) Between parameters, showed a very high significant difference ($p < 0.001$) TDS is Significatnly very high among all the parameters, followed by Cl^-, TH and Na^+.

   Eh is having significantly very low value followed by PO_4^{3-}, Total Iron, DO and NO_3^-.

2) There is no significant difference between months ($p > 0.05$).

c) Whether there is any significant difference between water quality index of control well (CW) and shallow groundwater sources of Cherai coast during the year 2012.

Table 4.20: ANOVA table for the comparison of water quality parameters between different months of shallow groundwater sources of Andhakaranazhy coast during the year 2012

	SGW	**CW**
n	12	12
Mean	305.8833	89.8917
S^2		13823.6555
T		4.500
Df		22
p - value		$p< 0.001$

Inferences

1) WQI of Cherai coast is significantly very high in SGW compared to that in CW ($p < 0.001$).

Table 4.21: Physico- chemical characteristics of shallow ground water sources of the Cherai Coastal area during each month of year 2012

2012		Temp $(^{0}\mathrm{C})$	pH	Eh	EC (µS/cm)	TA (mg/L)	TH (mg/L)	Ca (mg/L)	Mg (mg/L)	HCO$_3$ (mg/L)	Na (mg/L)	K (mg/L)	Cl (mg/L)	TDS (mg/L)	Fe (mg/L)	SO$_4$ (mg/L)	PO$_4$ (mg/L)	NO$_3$ (mg/L)	DO (mg/L)	BOD (mg/L)
Jan	$\bar{x}\pm\sigma$	28.4±1.5	7.7±0.4	-40.4±22.4	1.3±1.4	118.9±38.3	127.8±102.2	28.9±25.7	13.4±9.9	145.1±46.8	107.6±115.8	6.7±3.3	199.9±218.1	906.5±899.0	0.5±0.6	1.6±0.2	0.4±0.6	3.1±2.4	3.2±1.3	6.4±1.2
	CI	27.1 -29.8	7.3-8.1	-61.2 19.7	0.0 -2.6	83.5 -154.4	33.3 -222.3	5.2 -52.6	4.3 -22.5	101.8 -188.4	0.5 -214.8	3.7 -9.8	-1.9 -401.7	75.0 -1738.0	-0.08-1	1.5 -1.8	-0.2 -0.9	0.9-5.3	1.9 -4.4	5.26-7.5
Feb	$\bar{x}\pm\sigma$	27.7±0.4	7.0±0.3	-0.4±15.7	2.3±3.1	184.5±139.2	542.7±581.5	113.6±118.4	62.6±71.4	225.1±169.8	275.6±321.6	17.4±18.6	767.9±1030.5	1564.3±2017.7	1.4±1.7	13.5±21.0	0.2±0.5	3.3±2.5	2.9±1.1	7.0±1.8
	CI	27.3 -28.1	6.7-7.2	-14.9 -14.1	-0.5- 5.2	55.8 -313.2	4.9 -1080.6	4.0 -223.1	-3.4 -128.7	68.0 -382.1	-21.8 -573.0	0.2 -34.6	-185.2 -1721.0	-301.8 -3430.4	-0.2-2.9	-6.0 -32.9	-0.2 -0.7	1.0-5.5	1.9-3.9	5.36-8.6
Mar	$\bar{x}\pm\sigma$	27.9±0.4	7.0±0.3	-2.9±18.8	5.4±7.2	156.1±77.9	808.5±791.3	243.9±280.2	48.1±38.5	190.5±95.1	481.3±546.7	30.1±37.8	1211.5±1351.9	3666.4±5004.7	1.5±1.9	9.5±14.6	0.2±0.5	3.5±2.6	3.1±1.2	7.4±1.7
	CI	27.6 -28.3	6.7-7.3	-20.3 -14.5	-1.3 -12.1	84.0 -228.2	76.7 -1540.3	-15.3 -503.0	12.5 -83.8	102.5 -278.4	-24.3 -986.9	-4.8 -65.1	-38.9 -2461.9	-962.3 -8295.1	-0.2-3.2	-4.0 -23.0	-0.2-0.6	1.1- 5.9	2.0 -4.3	5.85 -9
Apr	$\bar{x}\pm\sigma$	28.7±0.8	7.3±0.4	-17.7±23.9	2.8±2.4	169.4±97.5	803.9±744.1	149.6±127.5	104.0±115.2	206.7±118.9	401.9±407.7	30.9±50.5	993.0±1048.7	1857.5±1561.4	1.2±1.8	66.7±54.8	0.1±0.2	3.4±2.5	3.4±1.8	7.1±2.6
	CI	27.9 -29.4	6.9-7.7	-39.9 -4.4	0.5 -5.0	79.3 -259.5	115.8 -1492.1	31.7 -267.6	-2.5 -210.6	96.7 -316.6	24.8 -778.9	-15.9 -77.6	23.0 -1962.9	413.4 -3301.6	-0..5-2.9	16.0 -117.4	-0.1 -0.2	1.1 -5.7	1.8 -5.1	4.67-9.5
May	$\bar{x}\pm\sigma$	29.2±0.3	7.2±0.5	-13.428.3	7.2±13.1	186.0±114.7	667.2±676.7	122.5±96.6	87.3±110.9	226.9±139.9	536.3±734.7	33.9±60.7	1227.0±1821.2	4708.6±8516.1	1.1±1.1	76.6±78.0	0.1±0.1	3.2±2.4	3.1±0.7	7.3±1.7
	CI	28.9 -29.4	6.7-7.7	-39.6 -12.7	-4.9 -19.3	79.9 -292.1	41.3 -1293.0	33.2 -211.9	-15.3 -189.9	97.5 -356.3	-143.2 -1215.8	-22.3 -90.0	-457.4 -2911.4	-3167.8-12584.9	0.06 -2	4.4 -148.8	0.0 -0.2	1.0- 5.5	2.5 -3.7	5.7 - 8.9
Jun	$\bar{x}\pm\sigma$	27.1±0.7	7.1±0.3	-7.9±16.0	2.2±4.4	156.1±99.3	502.4±895.4	66.5±70.1	81.3±175.0	190.5±121.1	291.0±432.5	22.1±33.9	728.9±1404.7	1512.9±2850.3	1.2±1.0	54.7±63.1	0.2±0.2	3.1±2.4	3.3±1.7	6.3±2.3
	CI	26.5 -27.8	6.8-7.4	-22.6 -6.9	-1.8 -6.3	64.3 -247.9	-325.7 -1330.5	1.7 -131.3	-80.5 -243.2	78.4 -302.5	-109.0 -691.0	-9.2 -53.5	-570.3 -2028.1	-1123.4 -4149.1	0.26 -2.07	-3.7 -113	0.0 -0.3	0.9 -5.4	1.8 -4.9	4.17 -8.34
Jul	$\bar{x}\pm\sigma$	29.1±0.5	7.8±0.3	-55.6±30.9	0.6±0.5	139.5±91.0	116.6±57.1	38.5±13.1	4.9±6.2	170.2±111.1	121.0±135.8	8.5±6.8	176.4±202.8	473.1±307.0	1.1±0.9	16.0±26.3	0.0±0.0	3.1±2.4	3.1±1.6	6.6±1.5
	CI	28.7 -29.5	7.6-8.1	-84.2- -27.0	0.2 -1.1	55.3 - 223.7	63.8 -169.3	26.5 -50.6	-0.8 -10.6	67.5 -272.9	-4.6 -246.6	2.1 -14.8	-11.2 -363.9	189.2 -757.1	0.2 -1.9	-8.4 -40.3	0.0 -0.0	0.9 -5.3	1.6 -4.7	5.22 -8
Aug	$\bar{x}\pm\sigma$	30.1±0.8	7.9±0.3	-53.9±20.3	0.4±0.3	129.5±87.9	102.1±48.7	25.1±14.8	9.5±4.6	158.0±107.2	73.4±68.4	4.9±3.5	85.0±62.2	315.7±192.2	0.7±0.6	1.3±1.3	0.3±0.5	3.1±2.4	2.7±1.4	7.5±2
	CI	29.3 -30.8	7.6-8.1	-72.6- -35.1	0.1 -0.7	48.3 -210.8	57.0 -147.2	11.4 -38.8	5.3 -13.7	58.9 -257.2	10.2 -136.6	1.7 -8.1	27.5 -142.6	138.0 -493.4	0.15-1.3	0.0 -2.5	-0.1 -0.8	0.9 -5.3	1.3-4.0	5.51 -9.4
Sep	$\bar{x}\pm\sigma$	27.3±1.7	7.6±0.5	-35.7±25.6	0.4±0.3	146.1±64.0	133.0±68.2	26.9±14.5	15.9±8.9	178.3±78.1	65.7±60.0	6.5±3.8	89.6±93.0	444.3±375.4	1.8±1	8.9±14.3	0.3±0.5	3.2±2.4	2.4±0.6	6.7±1.3
	CI	25.7 -28.9	7.2-8.0	-59.4- -12.0	0.1 -0.6	87.0 -205.3	69.9 -196.1	13.5 -40.3	7.7 -24.1	106.1 -250.5	10.2 -121.1	3.0 -10.0	3.6 -175.7	97.0-791.5	0.9 -2.7	-4.3 -22.1	-0.2 -0.8	1.0 -5.3	1.9 -3.0	5.43-7.9
Oct	$\bar{x}\pm\sigma$	27.8±0.4	7.1±0.3	-8.7±16.4	1.5±2.9	162.8±68.4	`484.5±914.6	63.4±101.1	78.9±161.0	198.6±83.5	74.0±70.3	6.6±4.5	346.5±670.4	1031.4±1899.4	1.3±0.8	10.5±15.2	0.2±0.4	3.1±2.4	2.6±1.2	7.0±1.8
	CI	27.4 -28.2	6.8-7.4	-23.9-6.4	-1.2 -4.2	99.4 -226.1	-361.4 -1330.4	-30.1 -156.9	-70.0 -227.8	121.3 -275.8	9.1 -139.0	2.5 -10.8	-273.6 -966.5	-725.3 -2788.1	0.47-2	-3.6-24.6	-0.1 -0.5	0.9 -5.3	1.5 -3.7	5.29 -8.7
Nov	$\bar{x}\pm\sigma$	27.5±0.4	6.6±0.2	16.6±11.9	1.4±2.4	146.1±69.4	385.2±510.2	77.1±95.3	46.6±66.6	178.3±84.6	89.4±111.0	7.5±6.6	292.2±530.6	974.5±1563.7	1.0±0.8	29.6±17.1	0.1±0.1	3.1±2.4	2.3±0.8	6.5±2
	CI	27.1 -27.9	6.5-6.8	5.6-27.6	-0.8 -3.7	82.0 -210.3	-86.6 -857.1	-11.1 -165.3	-15.0 -108.1	100.0 -256.6	-13.2 -192.0	1.4 -13.7	-198.6 -782.9-	-471.7 -2420.7	0.25-1.7	13.7 -45.4	0.0 -0.2	0.9 -5.3	1.6 -3.1	4.56 -8.4
Dec	$\bar{x}\pm\sigma$	28.3±0.5	7.0±0.3	0.3±15.9	0.6±0.5	132.9±53.2	523.2±1109.1	71.2±117.4	83.5±197.5	162.1±64.9	235.3±436.3	22.8±45.0	731.3±1763.6	1785.4±3971.0	1.3±1.5	22.3±34.1	0.0±0.1	2.9±2.4	3.4±1.0	6.3±3.4
	CI	27.8 -28.8	6.7-7.2	-14.4-15.0	0.1-1.0	83.6 - 182.1	-502.6 -1549.0	-37.4 -179.8	-99.1 -266.2	102.0 -222.1	-168.3 - 638.8	-18.8 -64.4	-899.9 - 362.4	-1887.3 -5458	-0.1-2.6	-9.3 -53.8	0.0 -0.0	0.7 -5.1	2.5 -4.3	3.13-9.4

Table 4.22: Physico-chemical characteristics of shallow groundwater sources of Cherai coast, Ernakulam, Kerala, India during the year 2012

Sl No.	Parameter	Mean ($\bar{x}$)± SD (σ)	True Value (μ)	Confidence Interval (CI)	Drinking water standards as per IS 10500: 2012		WHO 2011	
					Acceptable	Permissible	Most desirable	Max. allowable
1	Temperature °C	28.3±0.82	28.3±0.51	27.8-28.8	-	-	-	
2	pH	7.3 ± 0.38	7.3±0.23	7.1-7.5	6.5-8.5	No relaxation	6.5-8.5	No relaxation
3	Eh mV	-18.3±21.25	-18.3±13.09	-31.4--5.2	-	-	1.5	-
4	EC (mS/cm)	2.2 ± 4.80	2.2±2.96	-0.8-5.2	-	-	-	-
5	Alk (mg/L)as$CaCO_3$	152.3 ± 87.49	152.3±53.88	98.4-206.2	200	600	-	-
6	TH(mg/L)as $CaCO_3$	433.1 ± 653.53	433.1±402.51	30.6-835.6	300	600	100	500
7	DO (mg/L)	3.0±1.25	3.0±0.77	2.23-3.77				
8	BOD (mg/L)	6.8±2.04	6.8±1.26	5.54-8.06				
9	Ca (mg/L)	85.6 ± 114.53	85.6±70.54	15.1-156.1	75	200	75	200
10	Mg (mg/L)	53 ± 105.03	53±64.69	-11.7-117.7	30	100	50	150
11	Na (mg/L)	229.4 ± 358.59	229.4±220.85	8.5-450.3	-	-	-	200
12	K (mg/L)	16.5 ± 30.73	16.5±18.93	-2.4-35.4	-	-	-	12
13	Cl^- (mg/L)	570.8 ± 1049.69	570.8±646.50	-75.7-1217.3	250	1000	250	600
14	SO_4^{2-} (mg/L)	25.9 ± 36.88	25.9±22.71	3.2-48.6	200	400	250	400
15	NO_3^- (mg/L)	3.2±2.41	3.2±1.48	1.7-4.7	45	No relaxation	50	-
16	PO_4^{3-} (mg/L)	0.4 ± 0.4	0.4±0.25	0.2-0.6				
17	Total Iron (mg/L)	1.2 ± 1.22	1.2±0.75	0.4-2.0	0.3	No relaxation	0.1	-
18	TDS(mg/L)	1603 ± 3355.41	1603±2066.58	-463.58-3669.58	500	2000	500	1500
				Trace Elements				
19	Li (μg/L)	4.8±2.67	4.8±1.64	3.2-6.4				
20	Al (μg/L)	36.5±18.88	36.5±11.63	24.9-48.1	-	-	-	
21	V (μg/L)	2.5±2.19	2.5±1.35	1.2-3.8	-	-	-	
22	Cr (μg/L)	0.6±0.23	0.6±0.14	0.5-0.7	-	-	-	
23	Mn (μg/L)	151.9±260.09	151.9±160.19	-8.3-312.1	700	No relaxation	700	No relaxation
24	Ni (μg/L)	7.7±14.91	7.7±9.18	-1.5-16.9	-	-	-	
25	Co (μg/L)	0.2±0.12	0.2±0.07	0.1-0.3	50	No relaxation	50	No relaxation
26	Cu (μg/L)	1.6±0.95	1.6±0.59	1.0-2.2	100	300	400	No relaxation
27	Zn (μg/L)	35.0±73.43	35±45.23	-10.2-80.2	-	-	-	
28	Ga (μg/L)	3.8±1.65	3.8±1.02	2.8-4.8	20	No relaxation	70	No relaxation
29	As (μg/L)	2.4±2.63	2.4±1.62	0.8-4.0	50	1500	2000	No relaxation
30	Se (μg/L)	3.7±0.66	3.7±0.41	3.3-4.1	500	15000	-	-
31	Rb (μg/L)	5.8±2.33	5.8±1.44	4.4-7.2	100	No relaxation	-	-
32	Sr (μg/L)	137.9±78.85	137.9±48.56	89.3-186.5	3	No relaxation	-	-
33	Ag (μg/L)	0.1±0.05	0.1±0.03	0.1-0.1	30	200	100	No relaxation
34	Cd (μg/L)	0.1±0.00	0.1±0.00	0.10-0.10	-	-	-	-
35	In (μg/L)	0.1±0.00	0.1±0.00	0.10-0.10	-	-	-	-
36	Cs (μg/L)	0	0	0	10	No relaxation	10	No relaxation
37	Ba (μg/L)	19.5±7.16	19.5±4.41	15.1-23.9	10	50	10	50
38	Pb (μg/L)	0.3±0.15	0.3±0.09	0.2-0.4	-	-	-	-
39	Bi (μg/L)	0.3±0.34	0.3±0.21	0.1-0.5	10	No relaxation	40	No relaxation

4.10 Conclusions

The groundwater chemistry of Cherai coast is mainly depended on the parameters such as pH, temperature, total dissolved solids, alkalinity and hardness. The soil type of this coastal stretch is composed of coastal alluvium. This is the main reason for iron contamination in groundwater sources of the study area. Salt water intrusion is a crucial problem when considering the drinking water sources. Most of the groundwater aquifers lie between 2-8 m depth, affected by incursion of saline water very severely. Irrigation water quality parameters showed that most of the groundwater is suitable for agricultural uses but some treatment methods are required. Water comes under the class of *C1S1, C2S1, C3S1, C4S1 and C4S2* indicates the dominance of sea water intrusion. Wilcox diagrams showed groundwater becomes *excellent to good*, *good to permissible* and permissible to doubtful category during the year 2012. The abundance of major cations and anions in the groundwater are in the order of $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$ and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ respectively. The carbon present in the groundwater sources under study is mainly originated from inorganic source. Trace elements are within the permissible standard limits of BIS. However, the presence of E. Coli was reported in all dug wells, which needs serious attention to protect from contamination. Based on CPCB classification, DW1, DW2, DW3 & DW5 comes under the *class C* and DW4 & BW falls in *Class E*. According to LSI, shallow groundwater possess *slightly corrosive but non-scale forming* (SCNSF) character and *heavy corrosion* (HC) behaviour was observed by RSI. However, the groundwater exhibits moderately aggressive nature as evidenced by AI. Corrosion and scaling indices showed groundwater having strong corrosive behaviour than scale forming. Hence, the water possess moderatly aggressive character in most of the study period. According to Vesilind (2004) classification of hardness, groundwater becomes *too hard for ordinary domestic purposes*. Hydrochemical facies of groundwater constitutes mainly Na^{+}- K^{+} - Cl^{-} - SO_4^{2-} type followed by Ca^{2+}- Mg^{2+} - Cl^{-}- SO_4^{2-}, mixed Ca^{2+}-Mg^{2+}-Cl^{-}, Ca^{2+}-Na^{+}-HCO_3^{-} and Ca^{2+}-Mg^{2+}-HCO_3^{-} type. Study areas chemical composition was controlled by both weathering and evaporation processes evidenced by Gibb's diagrams. Ion exchange, reverse ion exchange, evaporation, weathering of carbonate and silicate mineral are the major processes occurring in the study areas. ANOVA results showed that there is no significant difference between months ($p > 0.05$) of control well. Shallow groundwater showed a very high significant difference ($p < 0.001$). TDS is significantly very high among all the parameters, followed by Cl^{-}, TH and Na^{+}. Eh is having significantly very low value followed by PO_4^{3-}, total iron, DO and NO_3^{-}. WQI of Cherai coast is significantly very high in SGW compared to that in CW ($p < 0.001$). WQI explains that, groundwater is not suitable for direct consumption drinking purpose, unless subjected to conventional treatment.

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Chapter 5

TEMPORAL AND SPATIAL VARIATION OF GROUNDWATER QUALITY ALONG THE ANDHAKARANAZHY COAST, ALAPPUZHA DURING THE PERIOD 2001-2017

5.1 Introduction

This chapter discusses the temporal and spatial variation of groundwater quality of shallow groundwater sources of the tsunami affected region of Andhakaranazhy coast for a period from 2001-2017. The variation of water quality parameters discussed in the Chapter 3 gives us an insight into the groundwater chemistry of the phreatic groundwater of the region. The study was continued during December months of subsequent years 2013, 2014, 2015, 2016 & 2017, after the one year complete sampling in the year 2012. The data generated for the study period 2012-2017 were compared with the available secondary data of April 2001 [1] year 2005 and December 2008 [2]. The major findings of the study were discussed in this chapter with respect to temporal and spatial variation of groundwater quality along the Andhakaranazhy coast, Alappuzha during the period 2001-2017. Here, results of year 2001 are presented for comparison as it is treated as the available data obtained from the literature to have a reference to the water quality preexisted. Results of year 2005 and 2008 are presented to obtain an orientation of the post tsunamic situation with respect to groundwater of the region [2]. The objective of the study is to evaluate variability of the groundwater quality of the region on a time scale for future references.

5.2 Physico-Chemical Parameters

Physico-chemical parameters analysed includes pH, EC, alkalinity, total hardness, DO, BOD, calcium, magnesium , sodium, potassium, chloride, sulphate, nitrate, phosphate, TDS and total iron.

5.2.1 pH

In 2001, pH of shallow groundwater sources (SGW) was 7.8±0.76. But it shows an annual mean of 7.4±0.2 during the year 2005 (Figure 5.1). A gradual decrease was observed from 2005 to December 2008 and attains a value of 7.2±0.2 (December 2008). The 2012 study reveals that pH maintains an annual mean pH of 7.6±0.25. In December 2013, the pH showed 7.9±0.26. It slightly decreases during December 2014 (7.4±0.24). But December 2015 (7.6±0.29) onwards, pH shows a gradual increase and attains a maximum value in December 2016 (8.1±0.17). A drastic decrease was observed from December 2016 to December 2017 and maintains a value of 7.3±0.30. pH showed a slightly alkaline behaviour throughout the study period from 2001-2017,with exception in post tsunamic period 2005 and 2008 within the standard limits of BIS (6.5 -8.5) [3]. The presence of bicarbonate ion is responsible for the alkaline behaviour of the groundwater in the study area.

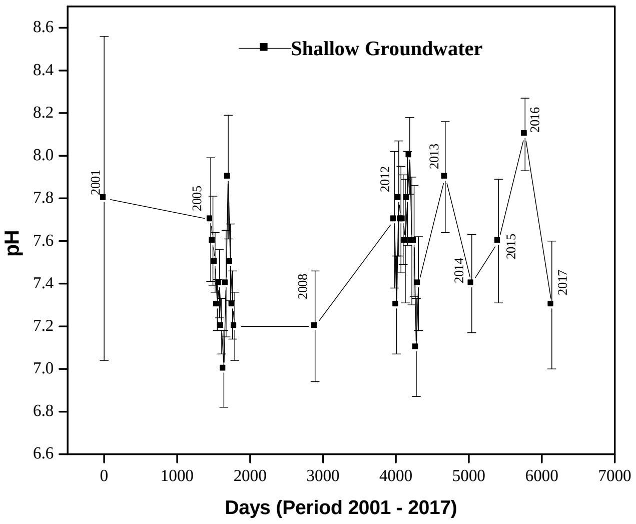

Figure 5.1: Temporal and spatial variation of pH of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.2 Electrical Conductivity (EC)

Electrical conductivity measures the salinity of groundwater. In 2001, electrical conductivity (EC) of shallow groundwater was 0.4±0.07mS/cm. But after the tsunami event, a sharp increase can be seen during the year 2005 and maintains an annual average of EC 2.7±1.5 mS/cm (Figure 5.2). But in December 2008, EC shows a sharp decrease and attains 0.9±0.6 mS/cm. In 2012 annual mean reveals that electrical conductivity is slightly decreased to 0.8±0.62 during the year. But huge increase was again happend and EC increased to 2.2±1.91 mS/cm in December 2013. December 2014 (1.5±1.59) onwards, EC showed a gradual decrease and reaches 1.2±0.93 mS/cm in December 2015. But in December of 2016, a drastic increase was again observed with an EC of 3.1±3.18 mS/cm. During December 2017, the EC was decreased to

1.4±1.27 mS/cm. The concentration of EC exceeds the standard limits in some of the study periods [4]. This high value of EC indicates, the presence of increased concentration of mineral ions, as a result of salt water intrusion.

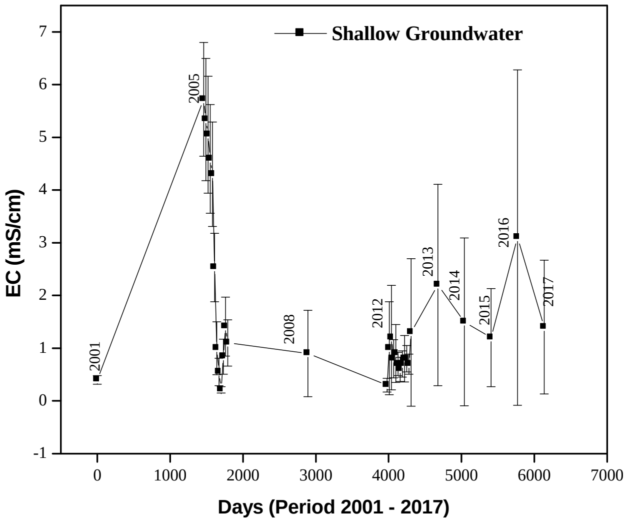

Figure 5.2: Temporal and spatial variation of electrical conductivity (EC) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.3 Alkalinity

Alkalinity of shallow groundwater reported 35.5±47.01 mg/L during April 2001 [1]. As a result of tsunami incident, the alkalinity was increased and maintains an annual mean of 324±63 mg/L during the year 2005 [2] (Figure 5.3). But in December 2008, a sharp decrease was observed in the alkalinity and reaches a concentration of 34±8 mg/L. A gradual increase was observed from 2012 onwards. During 2012, reported an annual mean of 330.2±117.23 mg/L. December 2013 observed an alkalinity of

467±226.24 mg/L, a maximum alkalinity during the study period. But the concentration was within the standard limits of BIS (600 mg/l) [3]. But in 2014 decreases to 363±184.54 mg/L. The results of subsequent years analysis reveals, almost a steady state of alkalinity, that is, a gradual increase of alkalinity can be observed from 2015 to 2017; 255.7±40.74 mg/L in December 2015, 290.7±77.01 mg/L (December 2016) and 417.8±209.46 (December 2017). Alkalinity showed a permissible limit of concentrations during the study period. Enhanced concentrations indicate the weathering of limestone rocks, which liberates HCO_3 into groundwater.

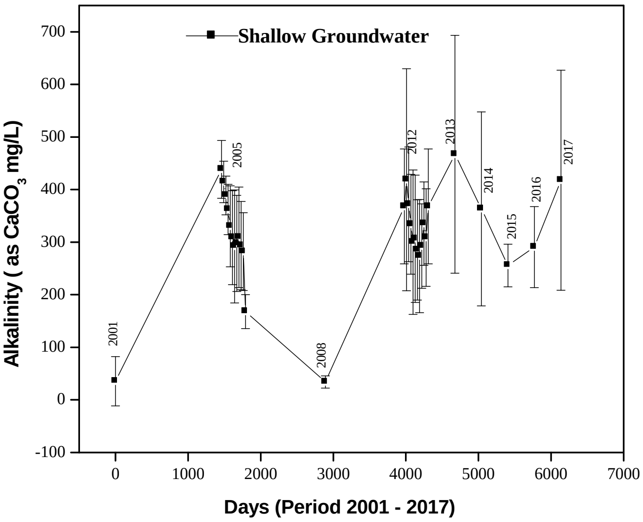

Figure 5.3: Temporal and spatial variation of alkalinity of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.4 Total Hardness (TH)

The 2001 data reveals that total hardness of shallow groundwater sources having very low concentration (7.1±57 mg/L). But after the tsunami, the hardness of water was enhanced and attains an annual mean of

382±207 mg/L during the year 2005. In December 2008, total hardness show a slight decrease of 203 ± 59 mg/L. A gradual increase of total hardness observed from 2012 onwards with an annual mean of 290±108.93 mg/L. It attains a value of 331.1 ± 158.17 mg/L in December 2013 then to 374.2 ± 253.04 mg/L in December 2014. A sharp decrease was observed from December 2014 to December 2015 and reported a total hardness of 224.5 ± 107.13 mg/L (Figure 5.4). Gradual increase of total hardness was again observed from 2016 onwards and the concentration was jumped from 251 ± 111.72 mg/L (December 2016) to 340.1 ± 137.49 mg/L (December 2017). The study period reveals that hardness was within the standard limits [3]. Weathering of carbonate minerals such as limestone act as a source of total hardness in the study area.

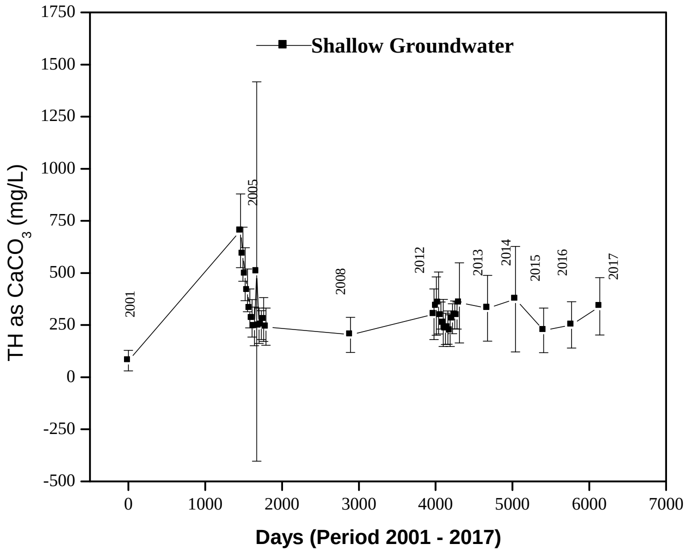

Figure 5.4: Temporal and spatial variation of total hardness (TH) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.5 Disssolved Oxygen (DO)

DO content was decreased over the years, which indicates the degradation of water quality. During the year 2005, DO exhibits an annual mean of 2.0±0.5 in shallow groundwater sources. It was decreased to 1.03± 0.7 in December 2008. However, during the year 2012, the DO was increased to 4.1± 1.95 mg/L which reveals the improvement of water quality over the time during the post tsunamic period. The December month of years 2013, 2014, 2015 and 2016 showed DO value of 3.8±0.9, 3.7± 2.8, 3.2 ± 2.0 and 3.3 ± 1.0 mg/L respectively. Finally, the shallow groundwater reaches at 2.4±1.78 mg/L of DO during December 2017 (Figure 5.5). The results of DO are reveals prominence of slight anoxic condition prevalent in groundwater sources.

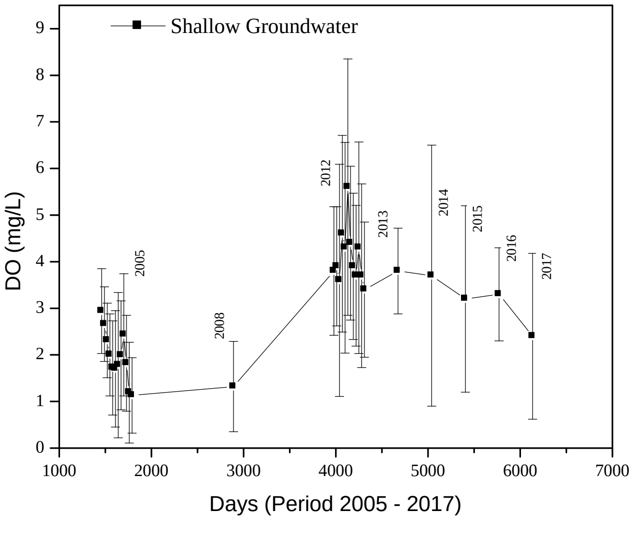

Figure 5.5: Temporal and spatial variation of dissolved oxygen (DO) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.6 Biological Oxygen Demand (BOD)

The shallow groundwater reported a BOD of 5.6 ±1.8 mg/L during the year 2005. In December 2008, it was again increased as revealed by the low DO in groundwater. During the year 2012, groundwater recorded an annual mean of 5.2 ± 2.40 mg/L of BOD. During December 2013 to December 2017, we can see a slight increase in BOD. In December 2013, BOD was 6.1 ± 4.50 mg/L, increased to 7.7±7.58 mg/L in December 2014 and reaches 9.5 ± 5.18 mg/L during December 2015. December 2016 shows a maximum BOD (9.9±8.7 mg/l) during the study period from 2005-2017. Finally, the shallow groundwater attains a BOD value of 8.8 ± 7.79 mg/L during the year 2017 (Figure 5.6). The results showed the presence of oxygen demanding waste and subsequent contamination of the groundwater sources.

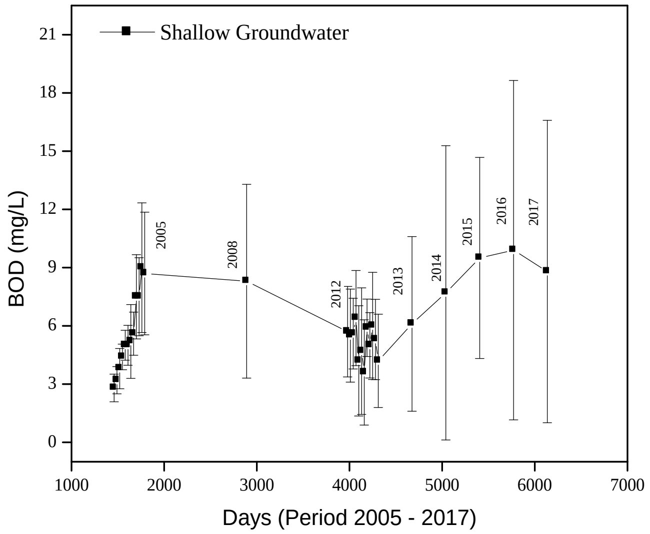

Figure 5.6: Temporal and spatial variation of biological oxygen demand (BOD) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.7 Calcium (Ca^{2+})

Shallow groundwater sources of 2001 data reported a calcium concentration of 23 ± 19.34 mg/L. But after the tsunami event, calcium content was increased to an annual mean of 101 ± 37 mg/L during the year 2005. A decrease was observed during December 2008 with a concentration of 41 ± 9 mg/L of calcium. Gradually, the concentration was again increased and attains an annual average of 83.2 ± 26.46 mg/L during the year 2012. In December 2013 the calcium content was maximum (104.3±26.47 mg/L). Then a gradual decrease was observed from 2014 onwards with a value of 93.1 ± 37.5 mg/L. It reaches 58.2±30.1 mg/L in December 2015 (Figure 5.7). Again, a sharp increase was found with the calcium content of 96.5 ± 57.8 mg/L in December 2016 and finally attains 103.1 ± 36.72 mg/L of calcium in December 2017.

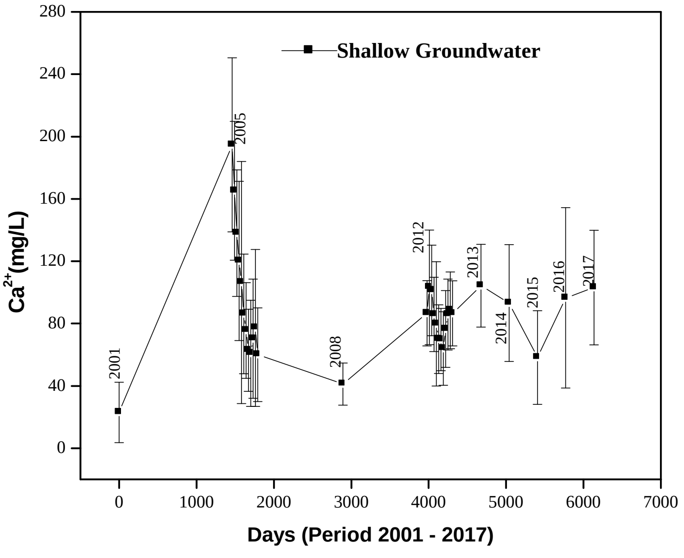

Figure 5.7: Temporal and spatial variation of calcium (Ca^{2+}) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

This high amount of calcium ions in groundwater indicates the presence of calcium carbonate bearing rocks/minerals in the study area and their probable leaching mechanism [5]. But the concentrations are within the permissible limit of BIS standards during the study period [3].

5.2.8 Magnesium (Mg^{2+})

The shallow groundwater exhibits a magnesium content of 5.4 ± 2.23 mg/L during April 2001. It was increased to 34 ±14 mg/L during the year 2005. However, we can see a gradual decrease in magnesium concentration from December 2008 (24 ±10 mg/L) to December 2013 (17±24.1 mg/L). Magnesium reported an annual mean of 18.5 ± 11.39 mg/L during the year 2012. It slightly decreases to 17 ±24.08 mg/L during December 2013. But a drastic increase was noticed in December 2014 (34.2 ±48.02 mg/L). Then we can observe that, a sharp increase of Mg^{2+} ions of 19.1 ±11.09 mg/L in December 2015 (Figure 5.8).

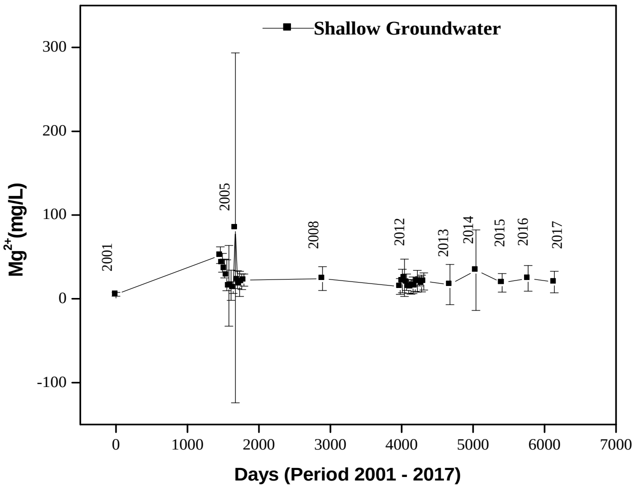

Figure 5.8: Temporal and spatial variation of magnesium (Mg^{2+}) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

But in December 2016 the concentration was again increased to 24.5 ± 15.26 mg/L. Finally the value reaches 20±12.92 mg/L in December 2017. Source of magnesium in the study area is the weathering of limestone, which releases Mg^{2+} ions into groundwater [5]. But the concentrations are well within the permissible limit of BIS standard (100 mg/L) [3].

5.2.9 Sodium (Na^+)

Pre tsunami data of the year 2001reveals that, shallow groundwater sources had a sodium ion of 30.3±14.55 mg/L during the period. But the huge increase of sodium concentration in the groundwater can be seen during the year 2005 with an annual average of 286±150 mg/L. However, a sharp decrease was observed in December 2008, with a concentration of 79±49 mg/L. Again, the concentration was increased to annual mean of 119.2±96.21mg/L in 2012 and reaches 131.6± 129.44 mg/L in December 2013. But December 2014 onwards, sodium concentration was gradually decreased (127.8±130.42 mg/L) and attains a concentration of 104.8±53.7mg/L in December 2015, after that sodium reached a low value of 81.9±60.63 mg/L in December 2016 (Figure 5.9). But a drastic increase was observed in December 2017 (138.9±111.75 mg/L). Salt water intrusion and silicate weathering are the sources of sodium in groundwater of the study area. The NaCl scatter diagram also supports this process [6].

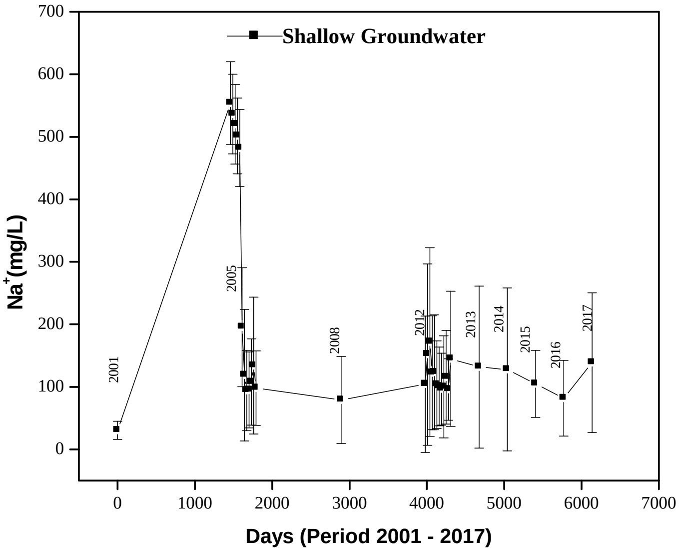

Figure 5.9: Temporal and spatial variation of sodium (Na^+) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.10 Potassium (K^+)

In 2001, shallow groundwater (SGW) sources exhibits a potassium concentration of 11.9±10.30 mg/L. It was increased to 13±6mg/L during 2005, indicates the prominence of salt water intrusion by 26th December 2004 Indian Ocean tsunami. Afterwards, the concentration was decreased to 9±7 mg/L (December 2008). Gradually a slight decrease was observed from the annual mean 8.3±8.98 mg/L (Year 2012) to 6.7±6.31mg/L (December 2013). But during December 2014, the concentration was again increased to 9.3±9.31mg/L. It reaches concentrations of 8.9 ±7.22 mg/L in December 2015 and 5.2±6.16 mg/L in December 2016 (Figure 5.10). A slight increase was again observed from December 2016 to December 2017 and attains a potassium content of 9.5± 9.83 mg/L. In natural water the concentration of potassium is usually reported to be less than (< 12). Comparably a high amount during 2005 indicates, the instance of salt water intrusion occurred in the study area during tsunami inundation [2].

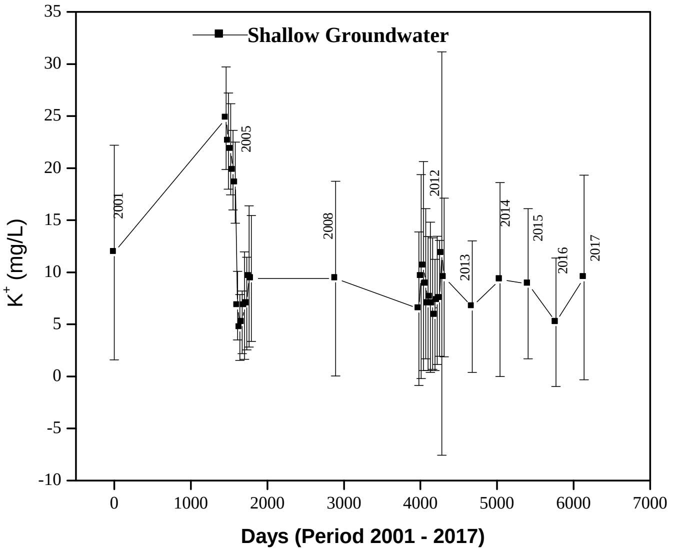

Figure 5.10: Temporal and spatial variation of potassium (K^+) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.11 Chloride (Cl^-)

In 2001 data, observed a concentration of chloride of 53.3±15.04 mg/L in shallow groundwater sources. But it reaches a very high amount in 2005 with an annual average of 361±158 mg/L, which clearly indicates the salt water intrusion due to tsunami event. But the concentration was dropped down in December 2008 to 76 ± 30 mg/L (Figure 5.11). From 2012 onwards the concentration was again increased and attains an annual average of 161.6±169.9 mg/L. In December 2013, the concentration was slightly decreased to 155.3 ± 153.46 mg/L. Again, we can see a drastic increase in chloride during December 2014 (213.4±242.98 mg/L). Then a sharp decrease was observed in December 2015 (160.8±113.81 mg/L) and December 2016 (169±144.61 mg/L). Finally the concentration was increased to 207.1±178.61 mg/L in 2017 December. The increased amount of chloride indicates presence of salt water intrusion in the study area [2]. Throughout the study period chloride maintains a concentration within standard permissible limits of BIS (1000 mg/L) [3].

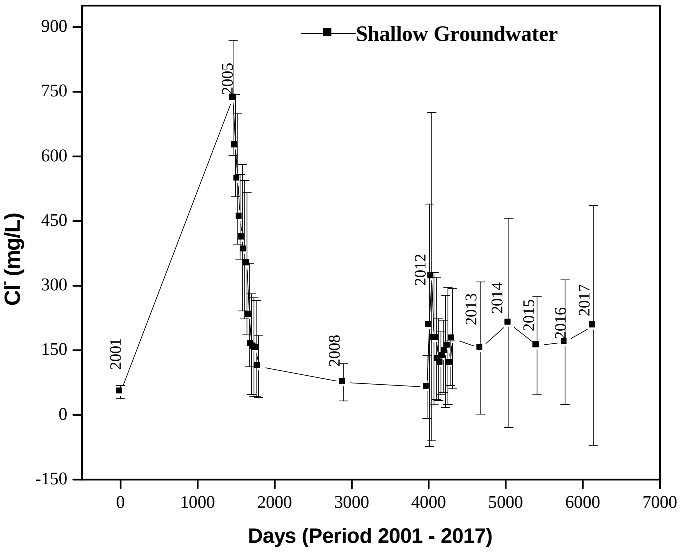

Figure 5.11: Temporal and spatial variation of chloride (Cl^-) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.12 Sulphate (SO_4^{2-})

In 2001, shallow groundwater (SGW) sources reported sulphate of 25.4 ±19.83 mg/L. During 2012, the concentration was decreased to 16±3mg/L. Again, the concentration was dropped down in December 2008 to 5±6 mg/L. However, groundwater showed a drastic increase of sulphate and attains an annual mean of 10.2±14.91 mg/L during the year 2012 (Figure 5.12). The result of subsequent years analysis reveals, that concentration of sulphate was reduced and stabilised. That is 2.3±3.85 mg/L (December 2013), 4.7±4.39 (December 2014), 4.4±6.33 mg/L (December 2015), 3.3±4.6 mg/L (December 2016) and finally reaches 4.2±3.48 mg/L in December 2017.

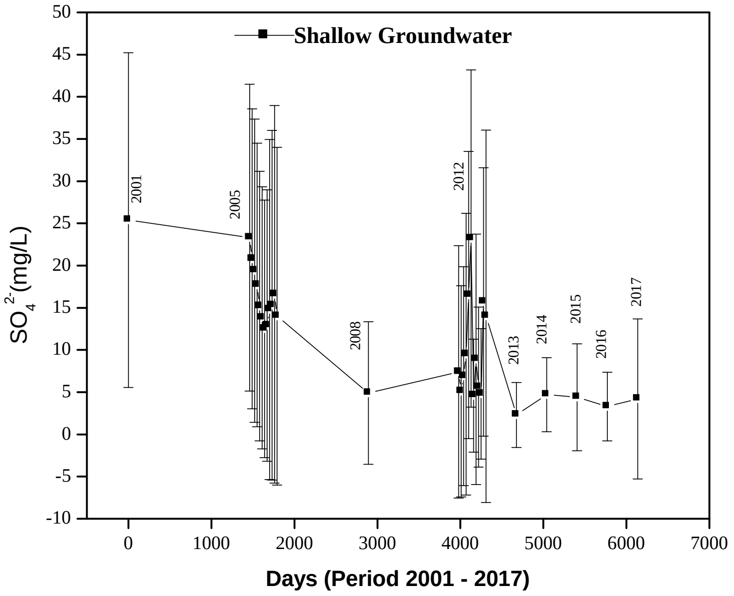

Figure 5.12: Temporal and spatial variation of sulphate (SO_4^{2-}) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.13 Nitrate (NO_3^-)

The concentration of nitrate of shallow groundwater recorded an annual mean of 0.40±0.09 mg/L during the year 2005 and then the concentration was slightly increased to 1.42±0.12 mg/L on December

2008. The concentration was stabilised in December 2008 onwards and maintains a minimum concentration of nitrate throughout the study period from 2005 -2017. In 2012, groundwater exhibits an annual mean of 1.3±1.41mg/L of nitrate and the concentration remains the same during December 2013 (1.3±1.43 mg/L). Although it was slightly increased to 1.4±1.38 mg/L in December 2014 (Figure 5.13). During December 2015, nitrate reaches at 1.3±1.42 mg/L and the concentration becomes constant during December 2016 (1.5±1.43). Finally, the nitrate attains a concentration of 1.3±1.43 mg/L during December 2017. The data clearly noticed that, nitrate content was very low in the study area [2].

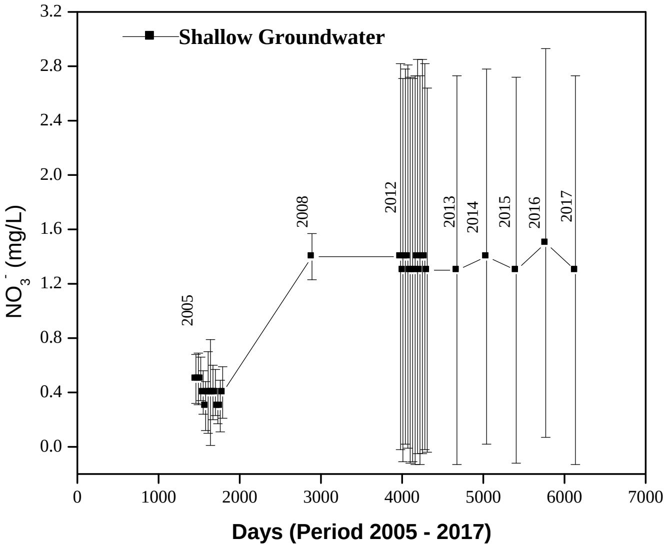

Figure 5.13: Temporal and spatial variation of nitrate (NO_3^-) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.14 Phosphate (PO_4^{3-})

Pre-tsunami data (2001) is not available with respect to the concentration of phosphate ion. It was observed a very low concentration throughout the study period till December 2017. During the year 2005, exhibited an annual mean of 0.3±0.08 mg/L of phosphate in shallow groundwater sources (Figure 5.14). But it is slightly increased during December 2008 (0.4±0.3 mg/L). In 2012, phosphate reported an annual average of 0.2± 0.18 mg/L and the concentration remains constant during December 2013 (0.2±0.12 mg/L). Phosphate concentrations of subsequent years are 0.1 mg/L in December 2014, 0.2±0.11mg/L in December 2015, 0.2±0.07 mg/L in December 2016 and finally attains 0.2±0.15 mg/L in December 2017.

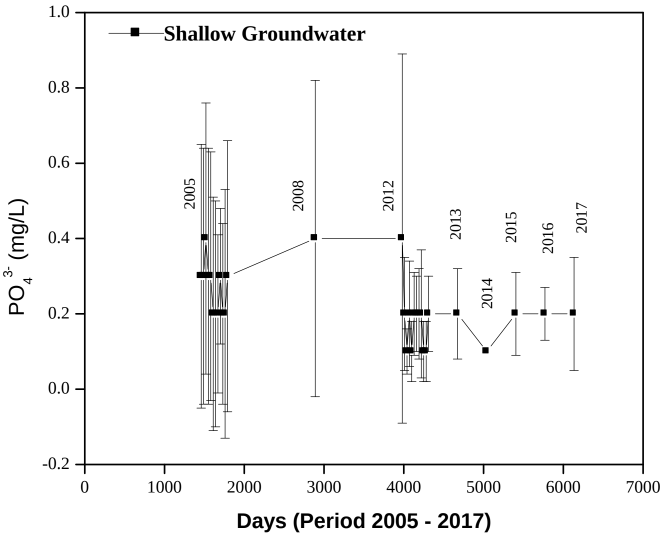

Figure 5.14: Temporal and spatial variation of phosphate (PO_4^{3-}) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.15 Total Iron

Total iron concentration of the study area exceeds the standard limits of BIS &WHO throughout the study periods. It is mainly due to the presence of soil structures containing coastal alluvium [7]. Groundwater reported an annual mean of 0.11±0.07 mg/L of iron during the year 2005. There is a gradual increase of iron content during the period December 2008 (0.16±0.18 mg/L). In 2012, shallow groundwater show an annual mean of 0.8±0.84 mg/L and then the concentration was slightly decreases to 0.6±0.47 mg/L during the period December 2013 (Figure 5.15). Subsequent years analysis of groundwater showed an iron content of 0.6±0.18 mg/L (December 2014), 1.3±2.93 mg/L (December 2015), 0.8±0.81 mg/L (December 2016) and 1.2±1.33 mg/L (December 2017) reveal the contamination of water by soluble (Fe^{2+}) iron in the study area.

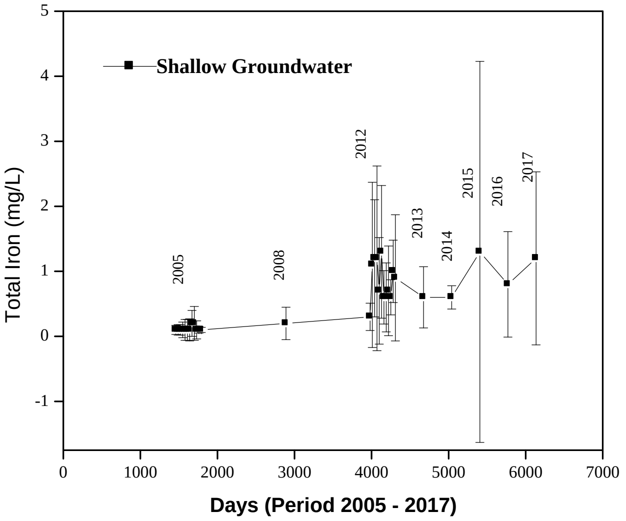

Figure 5.15: Temporal and spatial variation of total iron of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.2.16 Total Dissolved Solids (TDS)

Shallow groundwater of Andhakaranazhy coast showed a TDS concentration of 1747.24±140.5 mg/L during the year 2005. This increased TDS content was happening as a result of Tsunami event. Then a sharp decrease of TDS found in December 2008 (666.9±293.5 mg/L). In 2012, again the TDS decreased to 576.3±398.9 mg/L. A huge increase of TDS (1469±1242.6 mg/L) was noticed in December 2013. In December 2014, a drop in TDS was noticed (985.6 ± 1032.95) and then the amount slightly decreased to 801±611.92 mg/L in December 2015 (Figure 5.16). But in December 2016, a tremendous increase in TDS was observed (2033.7±2074.3 mg/L). During December 2017, a sharp decline in TDS was occurred to 653.6±477.4 mg/L. This high concentration of TDS was produced by the weathering process as well as the saltwater intrusion [5].

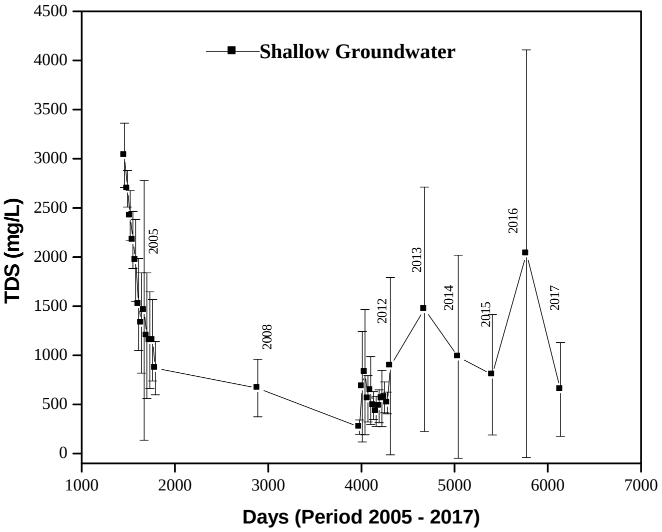

Figure 5.16: Temporal and spatial variation of total dissolved solids (TDS) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3 Irrigation water quality parameters

Irrigation parameters include sodium adsorption ratio, sodium percent, permeability index, Kelley's ratio, magnesium adsorption ratio, USSL and Wilcox diagrams

5.3.1 Sodium Adsorption Raito (SAR)

SAR can be useful to find the potential of groundwater to indulge in cation exchange reactions within the soil. Under conditions if groundwater is rich in sodium have a tendency to replace the adsorbed Ca or Mg present in the soil or aquifer material. According to SAR, irrigation water is classified into four categories - excellent (0-10), good (10-18), fair (18-26) & poor (>26). In most of the condition studied groundwater comes under *excellent class* (SAR between 0-10) indicates the occurrence of ion exchange processes within the soil. But during March, April and May months of 2005, groundwater becomes slightly sodium rich than Ca and Mg and comes under good quality can be used for agricultural purposes. This may be due to the fact that sea water intrusion very prevalent during these months. During the first decade of April 2001, reported SAR of 2.5 and comes under *excellent* class of water for irrigation. But in January 2005, SAR is 9.3 and it gradually increases as a result of tsunami event. During March, April, May of 2005, groundwater becomes good quality having SAR of 10.5, 11.0 and 11.9 respectively (Table 5.1). It may be due to the salt water intrusion, which leads to high concentration of Na ions in groundwater. However, January 2005 (5.2) onwards the SAR becomes stabilized and exsists within the *excellent* category, as shown in the Figure 5.17.

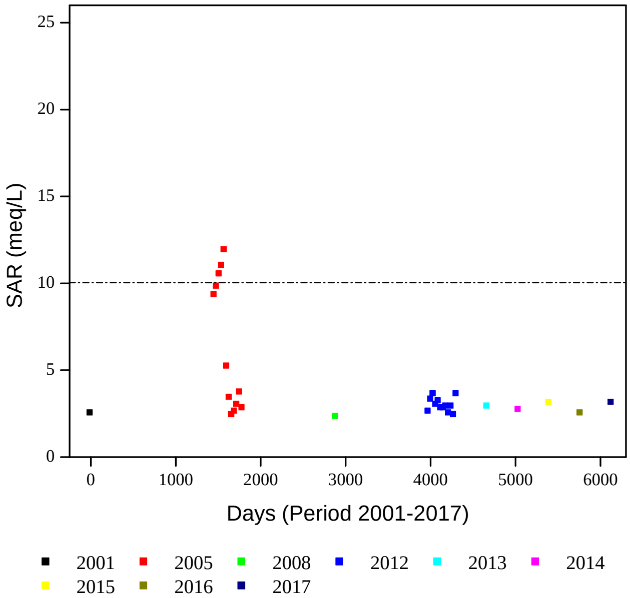

Figure 5.17: Temporal and spatial variation of sodium adsorption ratio (SAR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3.1.1 USSL Diagram

Groundwater comes under C1S1 indicates, water having *low sodium and salinity hazard*, good for irrigation purposes. C2S1 type means that water with *low sodium hazard and medium salinity hazard*. Water with *low sodium hazard and high salinity hazard* falls in C3S1. The C4S1 type water having *low sodium hazard and very high salinity hazard*. If the concentrations fall in the C4S3, indicates groundwater possess high sodium hazard and very high salinity hazard (Figure 5.18). Here most of the points are fall in the C2S1 and C3S1 region. Other water types includes C1S1, C4S1 & C4S3 proved that very high salinity and sodium were attributed by the tsunami event [2,8].

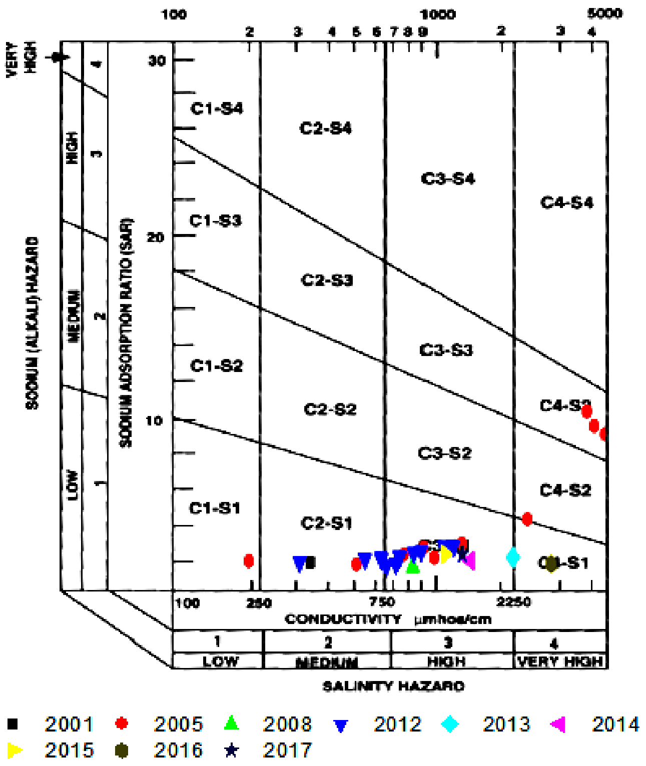

Figure 5.18: USSL diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean Tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3.2 Sodium Percent (Na%)

The sodium ion in the groundwater is measured as its percentage and this value has been used for the evaluation of irrigation water quality. Irrigation water classified based on Na% are excellent **(<20)**, good **(20-40)**, permissible **(40-60)**, doubtful **(60-80)** & unsuitable **(>80)**. Shallow groundwater sources recorded a sodium percent of 56 during the period April 2001, indicates that water comes under *permissible* class. However, 2005 onwards, water quality was degraded by the tsunami and the sodium percent becomes increased [2]. From January-May 2005, groundwater is having *doubtful* character, not suitable for irrigation. As a result of monsoonal dilution, the water get diluted and sodium concentration was decreased. Hence, groundwater again comes in the class of *permissible* during June & July months of 2005 and reaches in the *good* class of water during August 2012. September 2005 onwards, groundwater becomes *permissible* category with values ranges between 40-60 (Table 5.1).

Table 5.1: Temporal and spatial variation of sodium adsorption ratio (SAR) and sodium percent (Na%) of shallow groundwater (SGW) sources of Alappuzha, Kerala, India for the period 2001-2017

Year/Month	SAR	Inference	% Na	Inference
Apr 2001	2.5	E	56	P
Jan 2005	9.3	E	64.1	D
Feb 2005	9.8	E	67.0	D
Mar 2005	10.5	G	70.2	D
Apr 2005	11.0	G	72.9	D
May 2005	11.9	G	76.6	D
Jun 2005	5.2	E	59.1	P
Jul 2005	3.4	E	44.2	P
Aug 2005	2.4	E	39.2	G
Sep 2005	2.6	E	43.9	P
Oct 2005	3.0	E	45.4	P
Nov 2005	3.7	E	45.4	P
Dec 2005	2.8	E	45.4	P
Dec 2008	2.3	E	43.2	P
Jan 2012	2.6	E	37.8	G
Feb 2012	3.3	E	42.9	P
Mar 2012	3.6	E	45.5	P
Apr 2012	3.0	E	43.8	P
May 2012	3.2	E	46.0	P
Jun 2012	2.8	E	45.8	P
Jul 2012	2.8	E	45.9	P
Aug 2012	2.9	E	47.7	P
Sep 2012	2.5	E	39.7	P
Oct 2012	2.9	E	42.7	P
Nov 2012	2.4	E	40.8	P
Dec 2012	3.6	E	47.4	P
Dec 2013	2.9	E	41.4	P
Dec 2014	2.7	E	37.9	G
Dec 2015	3.1	E	50.5	P
Dec 2016	2.5	E	39.1	G
Dec 2017	3.1	E	42.7	P

E – Excellent G- Good P- Poor D – Doubtful

In 2012 January, the groundwater posseess *good* quality of water for irrigation. During the period February –Decemeber 2012, irrigation water quality of groundwater becomes permissible. In December 2013, groundwater occurs in the class of permissible and then the value is reached at 37.9 during the peiod December 2014. In December 2015, sodium percent was 50.5, indicating water is permissible for irrigation use. A sharp decrease of Na% occurred in December 2016 (39.1) and the irrigation quality becomes *good*. Finally, the value was jumped to the class of *permissible* with *a* sodium percent of 42.7 as shown in the (Figure 5.19).

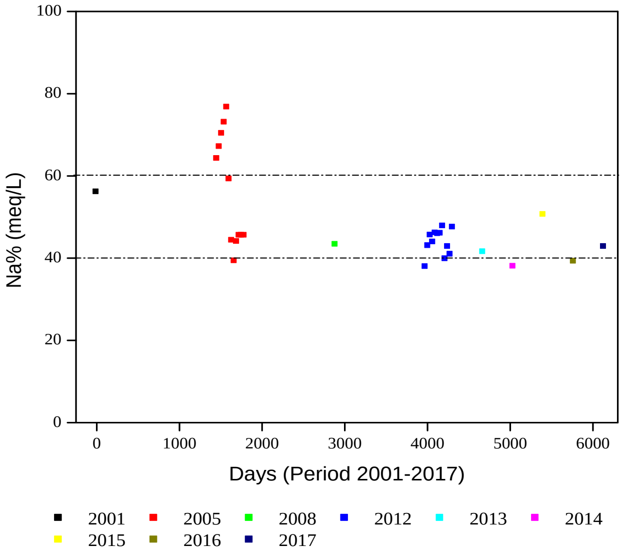

Figure 5.19: Temporal and spatial variation of sodium percent (Na%) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3.2.1 Wilcox Diagram

To evaluate the suitability of groundwater to irrigation, we plotted the EC against the sodium percent values of the groundwater. The salts present in the groundwater will affect soil structure, permeability and aeration, which indirectly affect plant growth [9]. Wilcox diagram indicate that, water comes under *excellent to good* range during the period April 2001. But after the Tsunami incident, water quality become changed and it moved to the *unsuitable* category during the period from January-June 2005. However, water quality was improved after the monsoonal dilution and reached the *good to permissible* category. During August and September 2005 months showed *excellent to good quality* of water. In December 2008, groundwater possesses *good quality*. Most of the months in 2012 showed good quality for irrigation purposes, except the month of January 2012. During January 2012, quality of water has been enhanced to the *excellent* class (Figure 5.20).

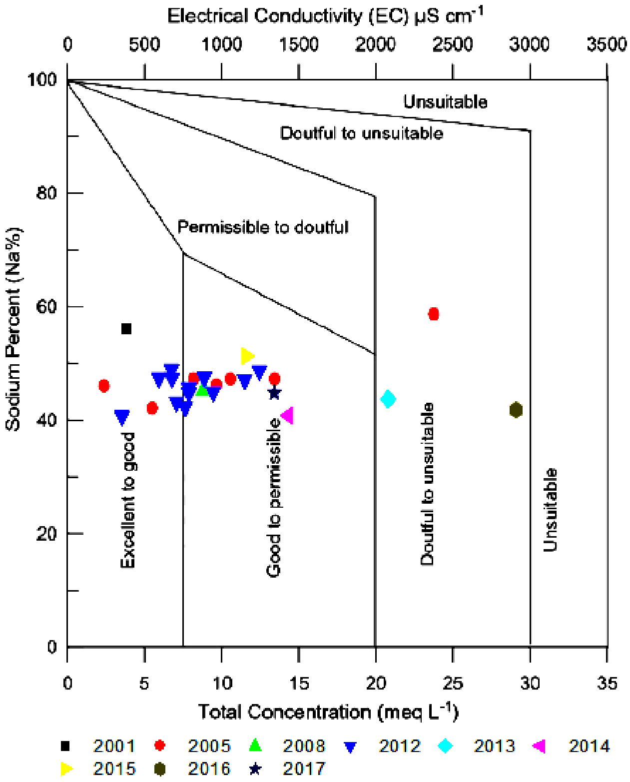

Figure 5.20: Wilcox diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

Groundwater noticed deterioration in the quality in December 2013. But it reaches *good to permissible* class in Dcember 2014. Again the quality become changed to unsuitable category during December 2016. Though, the quality become improved to the class of *good to permissible* at the end of 2017.

5.3.3 Permeability Index (PI)

The permeability index classified the groundwater (Doneen, 1964) into three categories for the determination of irrigation suitability. The long term use of irrigation water having very high amount of ions such as sodium, calcium, magnesium, and bicarbonate affect the soil permeability. Greater PI reveals that, groundwater having no permeability and infiltration problems. Accordingly, C*lass I* and *Class II* are suitable for irrigation purposes with 75% or more of maximum permeability and *Class III* water is unsuitable for irrigation with 25% of maximum permeability [10]. Table 5.2 indicate that, in most of the time groundwater comes under class II. This means the permeability index of groundwater exists between 25-75 %, marginally safe for irrigation purposes. In some of the period, groundwater is having PI greater than 75% and water becomes safe for agricultural uses. It happened in February-June 2005, August 2012 and December 2015. And finally in December 2017, groundwater was marginally safe for irrigation activities as (PI=68.7) shown in the (Figure 5.21).

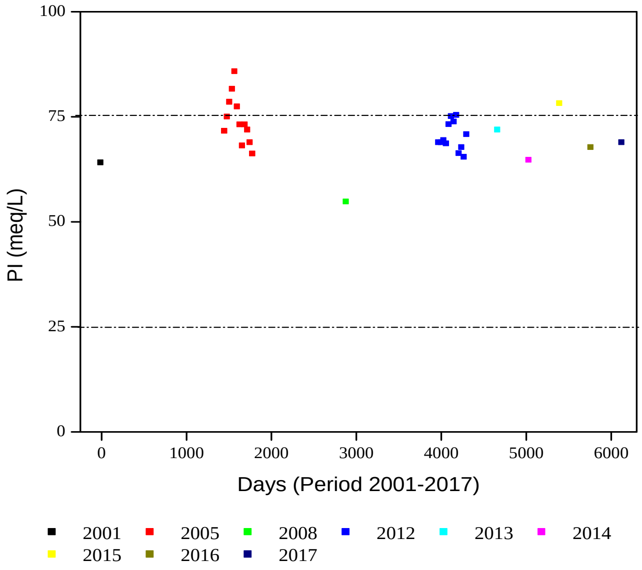

Figure 5.21: Temporal and spatial variation of permeability index (PI) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3.4 Kelly's ratio (KR)

Kelly's ratio is a measure of sodium concentration against Ca and Mg ions in groundwater, used to find the irrigation suitability. If the ratio is less than one, indicate the suitability of groundwater for agricultural purposes and KR>1, water is unsuitable for irrigation. From the Table 5.2, it is clear that, groundwater having high sodium content than Ca and Mg ions. This high sodium content of groundwater may be attributed by natural softening processes and also by sea water intrusion. During year April 2001, groundwater is suitable for irrigation as shown by KR. However, in January - June 2005 groundwater showed unsuitability for irrigation, may be because of the tsunami impact. But in august and September 2005 groundwater becomes *suitable* as a result of reverse ion exchange process. Again the groundwater becomes rich in sodium in

October and November 2005 by ion exchange process, which causes unsuitability [2]. Again the KR becomes less than one during the period December 2005. In December 2008 also observed suitability of water. And January – April 2012, indicates the dissolution process of limestone. The high sodium content of groundwater can be observed during the months of May, August, December 2012 and also in the December months of 2015 and 2016. During December 2017grounwater becomes suitable for irrigation purposes as evidenced by Kelly's Ratio (KR) as shown in the (Figure 5.22)

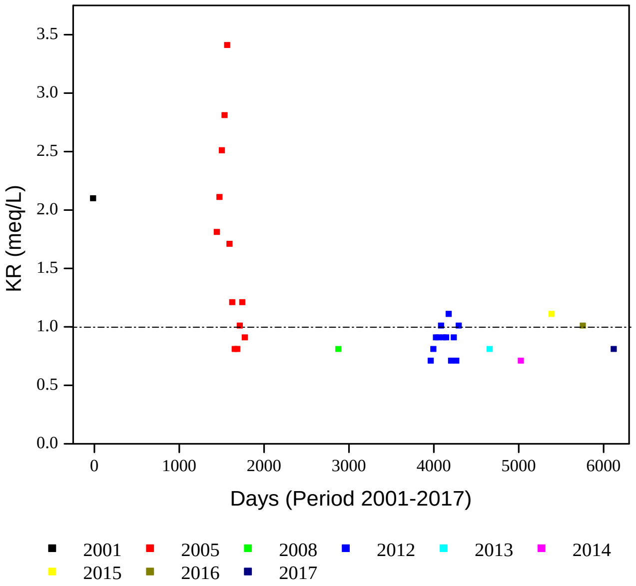

Figure 5.22 Temporal and spatial variation of Kelley's ratio (KR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.3.5 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 [11]. During April 2001, water reported magnesium adsorption ratio of 34, suitable for agricultural purposes. The year 2005, also shows suitability for irrigation evidenced by the MAR. It reaches at 46.9 during the period December 2008. Magnesium adsorption ratio noticed below 50 in all months of 2012, indicate suitability for irrigation (Table 5.2). In December 2013, MAR of groundwater becomes 17.2 and it reduces to 3.6 in December 2014. Groundwater recorded MAR of 3.0, 3.2 & 22.9 in December months of 2015, 2016 and 2017 respectively. This indicates that magnesium concentration was not much more than the calcium ion, attributed by the weathering of calcium carbonate minerals. Figure 5.23 also explained by the temporal and spatial variation of magnesium adsorption ratio, indicates groundwater suitability for irrigation purposes.

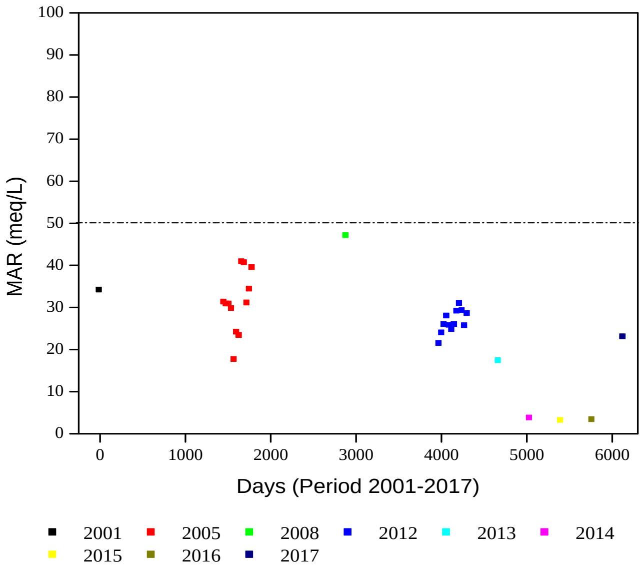

Figure 5.23: Temporal and spatial variation of magnesium adsorption ratio (MAR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

Table 5.2: Temporal and spacial variation of Kelley's ratio (KR), magnesium adsorption ratio (MAR) and permeability index (PI) of shallow groundwater (SGW) sources of Alappuzha, Kerala, India for the period 2001-2017

Year/Month	KR	Inference	MAR	Inference	PI	Inference
Apr 2001	2.09	U	34	S	63.9	Class II
Jan 2005	1.8	U	31.1	S	71.4	Class II
Feb 2005	2.1	U	30.7	S	74.8	Class II
Mar 2005	2.5	U	30.7	S	78.3	Class I
Apr 2005	2.8	U	29.6	S	81.4	Class I
May 2005	3.4	U	17.5	S	85.6	Class I
Jun 2005	1.7	U	24.0	S	77.2	Class I
Jul 2005	1.2	U	23.2	S	72.9	Class II
Aug 2005	0.8	S	40.7	S	67.9	Class II
Sep 2005	0.8	S	40.5	S	72.9	Class II
Oct 2005	1.0	U	30.9	S	71.7	Class II
Nov 2005	1.2	U	34.2	S	68.7	Class II
Dec 2005	0.9	S	39.3	S	66.0	Class II
Dec 2008	0.8	S	46.9	S	54.6	Class II
Jan 2012	0.7	S	21.3	S	68.7	Class II
Feb 2012	0.8	S	23.8	S	68.7	Class II
Mar 2012	0.9	S	25.8	S	69.2	Class II
Apr 2012	0.9	S	27.8	S	68.4	Class II
May 2012	1.0	U	25.6	S	73.0	Class II
Jun 2012	0.9	S	24.6	S	74.9	Class II
Jul 2012	0.9	S	25.8	S	73.6	Class II
Aug 2012	1.1	U	29.0	S	75.2	Class I
Sep 2012	0.7	S	30.8	S	66.1	Class II
Oct 2012	0.9	S	29.1	S	67.5	Class II
Nov 2012	0.7	S	25.5	S	65.2	Class II
Dec 2012	1.0	U	28.4	S	70.6	Class II
Dec 2013	0.8	S	17.2	S	71.7	Class II
Dec 2014	0.7	S	3.6	S	64.5	Class II
Dec 2015	1.1	U	3.0	S	78.0	Class I
Dec 2016	1.0	U	3.2	S	67.5	Class II
Dec 2017	0.8	S	22.9	S	68.7	Class II

Table 5.3: Temporal and spatial variation of Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI) of shallow groundwater (SGW) sources of Alappuzha, Kerala, India for the period 2001-2017

Year/Month	LSI	Inference	RSI	Inference	AI	Inference
Jan 2005	1.0			LS	13.0	NA
Feb 2005	0.8	SFNC	6.0	LSC	12.8	NA
Mar 2005	0.6	SFNC	6.2	LSC	12.6	NA
Apr 2005	0.4	SSFC	6.6	LSC	12.3	NA
May 2005	0.3	SSFC	6.8	LSC	12.2	NA
Jun 2005	0.0	SSFC	7.2	CS	11.9	MA
Jul 2005	-0.3	SCNSF	7.6	HC	11.7	MA
Aug 2005	0.1	SSFC	7.2	CS	12.0	NA
Sep 2005	0.6	SFNC	6.8	LSC	12.5	NA
Oct 2005	0.3	SSFC	7.0	CS	12.2	NA
Nov 2005	0.0	SSFC	7.3	CS	11.9	MA
Dec 2005	-0.3	SCNSF	7.9	HC	11.6	MA
Dec 2008	-1.2	SC	9.6	HC	10.7	MA
Jan 2012	0.6	SFNC	6.4	LSC	12.5	NA
Feb 2012	0.4	SSFC	6.6	LSC	12.3	NA
Mar 2012	0.9	SFNC	6.1	LSC	12.8	NA
Apr 2012	0.6	SFNC	6.5	LSC	12.5	NA
May 2012	0.5	SFNC	6.8	LSC	12.3	NA
Jun 2012	0.3	SSFC	6.9	LSC	12.2	NA
Jul 2012	0.5	SFNC	6.7	LSC	12.4	NA
Aug 2012	0.7	SFNC	6.6	LSC	12.6	NA
Sep 2012	0.4	SSFC	6.7	LSC	12.3	NA
Oct 2012	0.5	SFNC	6.5	LSC	12.4	NA
Nov 2012	0.0	SSFC	7.1	CS	11.9	MA
Dec 2012	0.3	SSFC	6.7	LSC	12.2	NA
Dec 2013	0.9	SFNC	6.0	LSC	12.9	NA
Dec 2014	0.3	SSFC	6.7	LSC	12.3	NA
Dec 2015	0.2	SSFC	7.2	CS	12.1	NA
Dec 2016	0.9	SFNC	6.4	LSC	12.8	NA
Dec 2017	0.3	SSFC	6.6	LSC	12.3	NA

5.4 Measures of corrosion and scaling potential

Various indices are used for the study of scaling potential and corrosion of groundwater sources. They are Langelier saturation index (LSI), Ryznar stability index (RSI) and Aggressiveness index (AI)

5.4.1 Langelier saturation index (LSI)

The shallow groundwater sources of Andhakaranazhy coast come under scale forming and non corrosive (SFNC) character in January – March 2005 as the water has an ideal ionic balance. But April – June 2005, LSI of groundwater becomes *slightly scale forming and corrosive* (SSFC) character. This may be due to the enhanced concentration of ions such as sodium, chloride, potassium etc. by salt water intrusion as it affect pH, alkalinity and hardness. Groundwater falls in SSFC and SFNC class in the alternate months. However, in July and December months of 2005 groundwater having *slightly corrosive but non scale forming* (SCNSF) character. The negative values of LSI indicate highly corrosive property of groundwater of the coast. Very *serious corrosion* (SC) of groundwater has been noticed in December 2008 (Table 5.3). However, during the year 2012 reported scale forming and non corrossive behaviour of water. The tendency of water has been same during the year December 2013. In December 2014 & 2015, groundwater becomes *slightly scale forming and corrosive.* The LSI move towards *scale forming and non corrosive* type in December 2016 and finally the groundwater reaches in **SSFC category**.

5.4.2 Ryznar stability index (RSI)

Groundwater possesses a *little scale or corrosive* property during the year 2005. However, the water becomes corrosion significant (CS) character during June, August, October and November months of 2005. Water noticed with *heavy corrosion* during the months July and December 2005. In December 2008 also observed heavy *corrosion* nature of water. During the year 2012, little scale forming or corrosive character was observed with significant corrosion character in November. Water maintains LSC behaviour in December 2013 and 2014 (Table 5.3). However, in December 2015, behaviour of water changed to CS, indicating the carbonate weathering process. Again the water comes under the category of LSC in the December months of 2016 & 2017 [12].

5.4.3 Aggressiveness index (AI)

Aggressiveness index mainly used to measure corrosion. From the Table 5.3, it is clear that groundwater showed non corrosive character in most of the study period. In 2005, the water become moderately aggressive during the period of June, July, November, December 2005. Period December 2008 also showed slightly corrosive character. The year 2012 reported, non aggressive character of water except the month November 2012. The December months of subsequent years 2013, 2014, 2015, 2016 and 2017 maintains a non-aggressive behaviour. The slightly corrosive character may occur through the dissolution of carbonate mineral [5].

5.5 Gibb’s Diagrams

Chemical composition of the shallow groundwater sources reveals that, weatherings of rocks are mainly contributing to the ionic concentrations of the study area. However, the process of evaporation also concentrates the ionis species in water and it was noticed during the period January-November 2005. In 2012, groundwater chemistry was mainly controlled by weathering of rocks. Evaporation rate was high during the period December 2013 as shown in the diagram. However, during December 2014 and December 2015 the ionic concentrations contributed from rock-water interaction. In December 2016, the source of ions is coming from the evaporation process. But in December 2017, weathering of rock forming minerals controls the ion chemistry of water in the study area as evidenced from the Figure 5.24 [13].

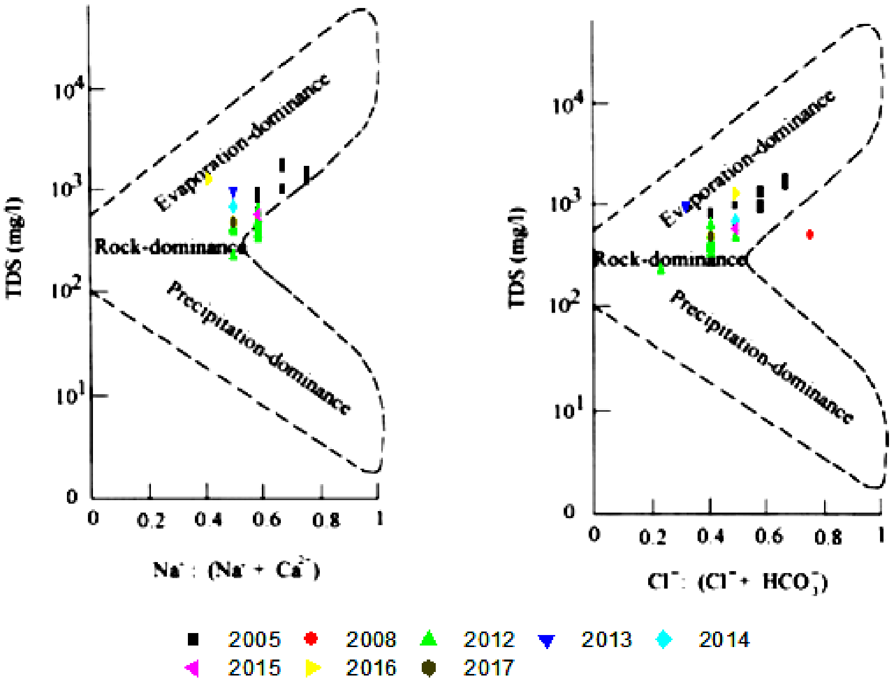

Figure 5.24: Gibb's diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.6 Hill-Piper-Trilinear Diagram

The water type of the shallow groundwater sources was assessed by using the piper diagrams. Kerala coast noticed a slightly saline character during the period April 2001. The groundwater becomes strong saline nature during the year 2005 as a result of saltwater intrusion by 26th December 2004 Indian Ocean tsunami. However, the water type maintains NaCl type during December 2008. But 2012 onwards, water type shifted towards the right corner of the piper diagram with a prominent temporary hardness behaviour. This temporary hardness nature was mainly controlled by the geology of the study area. Means, study area is composed of carbonate bearing minerals such as limestone, which releases calcium, magnesium and bicarbonate ions into the groundwater [8]. Enhanced concentration of bicarbonate ions produced both from carbonate and silicate weathering causes the temporary hardness of water Figure 5.25.

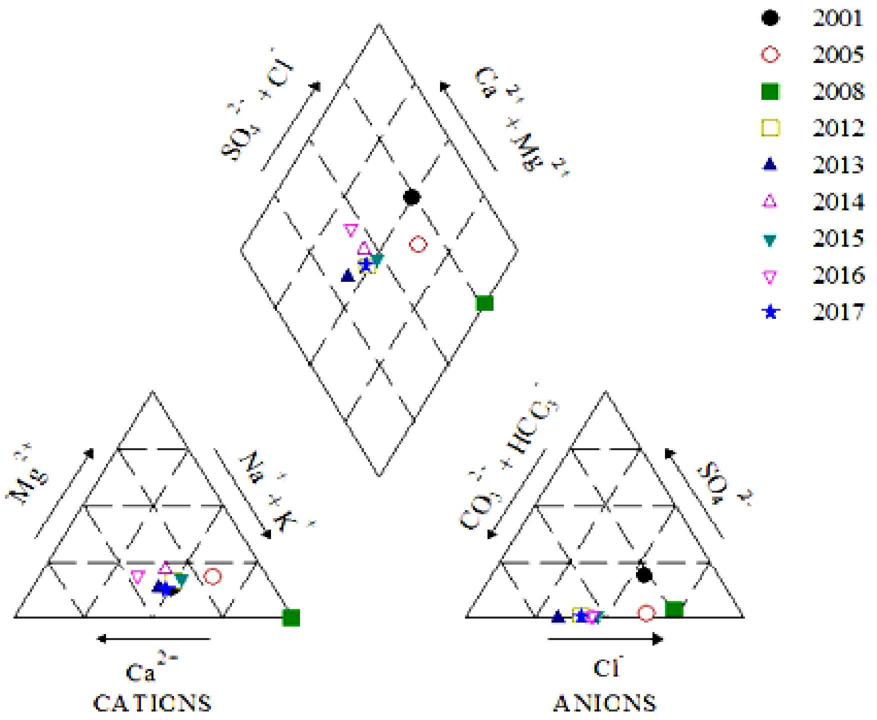

Figure 5.25: Piper diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

5.7 Sodium-Chloride ratios

The ratio of sodium and chloride showed the ion exchange processes in groundwater aquifer system. Normally the groundwater exhibits ion exchange behavior in the study area. But it showed the reverse ion exchange in certain months, indicates the presence of high Na$^+$ content in groundwater. The saltwater intrusion is a major source of Na$^+$ ions in groundwater. During April 2001, water having reverse ion exchange behaviour. It becomes ion exchange, indicate that halite dissolution not much affected the coast by the Indian Ocean Tsunami. The results were revealed that the groundwater possess high sodium content during the months of June, July and August 2005, which may happened by the salt water intrusion (Table 5.4). After that, water reached to the normal condition, become ion exchange behaviour [2]. However, September 2005 onwards groundwater showed prominent ion exchange character. The scatter diagrams alsosupport the process of ion exchange (Figure 5.26).

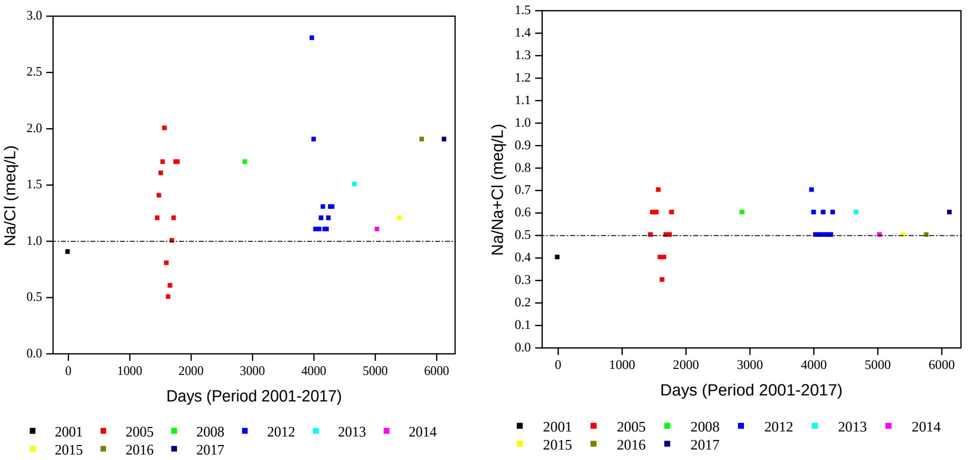

Figure 5.26: Temporal and spatial variation of Na$^+$/Cl$^-$ and Na$^+$/ Na$^+$+ Cl$^-$ of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

Table 5.4: Temporal and spacial variation of Na^+/Cl^- and $Na^+/ Na^+ + Cl^-$ of shallow groundwater (SGW) sources of Alappuzha, Kerala, India for the period 2001-2017

Year/Month	Na^+/Cl^-	$Na^+/ Na^+ + Cl^-$	Inference
Apr 2001	0.9	0.4	RIE
Jan 2005	1.2	0.5	IE
Feb 2005	1.4	0.6	IE
Mar 2005	1.6	0.6	IE
Apr 2005	1.7	0.6	IE
May 2005	2.0	0.7	IE
Jun 2005	0.8	0.4	RIE
Jul 2005	0.5	0.3	RIE
Aug 2005	0.6	0.4	RIE
Sep 2005	1.0	0.5	IE
Oct 2005	1.2	0.5	IE
Nov 2005	1.7	0.5	IE
Dec 2005	1.7	0.6	IE
Dec 2008	1.7	0.6	IE
Jan 2012	2.8	0.7	IE
Feb 2012	1.9	0.6	IE
Mar 2012	1.1	0.5	IE
Apr 2012	1.1	0.5	IE
May 2012	1.1	0.5	IE
Jun 2012	1.2	0.5	IE
Jul 2012	1.3	0.6	IE
Aug 2012	1.1	0.5	IE
Sep 2012	1.1	0.5	IE
Oct 2012	1.2	0.5	IE
Nov 2012	1.3	0.5	IE
Dec 2012	1.3	0.6	IE
Dec 2013	1.5	0.6	IE
Dec 2014	1.1	0.5	IE
Dec 2015	1.2	0.5	IE
Dec 2016	1.9	0.5	IE
Dec 2017	1.9	0.6	IE
IE-Ion Exchange		RIE-Reverse Ion Exchange	

5.8 Water Quality Index (WQI)

The pre tsunami data (April 2001) on shallow groundwater sources of the coastal stretch of Kerala was found to be 57.6, indicates good for drinking purposes. During the year of 2005, the water quality index of shallow wells of Andhakaranazhy coast was slightly good (25-50) and the quality of water becomes deteriorated over the years, finally reaches unfit for drinking purpose category (>100). During January 2005, the water quality index was 50.0 and comes under *good* quality of water. Then gradually, the groundwater quality degrades and reaches very poor category during September 2005. At the end of December 2005, the quality again comes under *poor* category with WQI 60.7. But during December 2008, the groundwater becomes *very poor* quality having WQI of 81.6. From 2012 onwards, WQI showed high value (>100) indicates groundwater is unfit for drinking purposes (Table 5.5). The present status of shallow groundwater sources of the study area is not suitable for drinking purposes as evidenced by WQI [14]. Temporal and spatial variation of water quality index was also shown from the Figure 5.27.

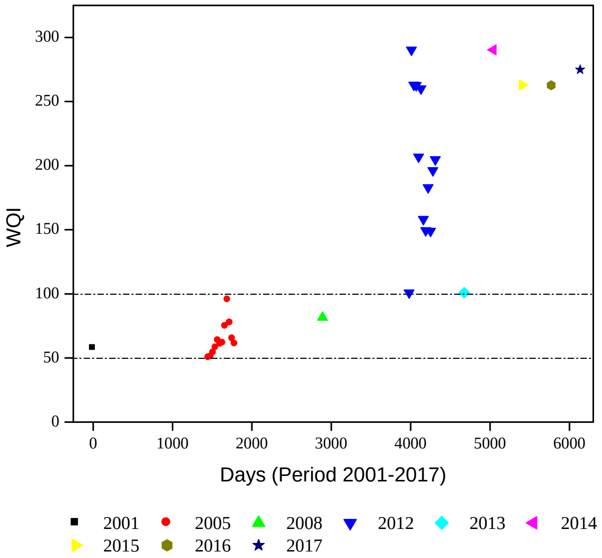

Figure 5.27: Temporal and spatial variation of water quality index (WQI) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Andhakaranazhy, Alappuzha, Kerala, India for the period 2001-2017

Table 5.5: Temporal and spacial variation of water quality index (WQI) of shallow groundwater (SGW) sources of Alappuzha, Kerala, India for the period 2001-2017

Year/Month	WQI	Water Quality	Grading
Apr 2001	57.6	P	C
Jan 2005	50.0	G	B
Feb 2005	50.7	P	C
Mar 2005	53.9	P	C
Apr 2005	57.9	P	C
May 2005	63.4	P	C
Jun 2005	60.6	P	C
Jul 2005	61.5	P	C
Aug 2005	74.6	P	C
Sep 2005	95.2	VP	D
Oct 2005	77.2	VP	D
Nov 2005	64.8	P	C
Dec 2005	60.7	P	C
Dec 2008	81.6	VP	D
Jan 2012	100.9	UDP	E
Feb 2012	290.3	UDP	E
Mar 2012	263.0	UDP	E
Apr 2012	262.7	UDP	E
May 2012	206.9	UDP	E
Jun 2012	260.1	UDP	E
Jul 2012	158.2	UDP	E
Aug 2012	149.5	UDP	E
Sep 2012	183.0	UDP	E
Oct 2012	149.0	UDP	E
Nov 2012	196.3	UDP	E
Dec 2012	204.8	UDP	E
Dec 2013	100.9	UDP	E
Dec 2014	290.3	UDP	E
Dec 2015	263.0	UDP	E
Dec 2016	262.7	UDP	E
Dec 2017	244.8	UDP	E

G-Good P-Poor VP-Very Poor UDP-Unfit for Drinking Purposes

5.9 Statistical Analysis

Results of ANOVA test conducted to check the hypothesis given below

a) Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the months of December for years 2013, 2014, 2015, 2016 and December 2017.

Table 5.6: ANOVA table for the comparison of water quality parameters of shallow groundwater sources of Andhakaranazhy coast between December months of year 2008, 2013, 2014, 2015,2016 and 2017

Source	**ss**	**df**	**ms**	**F**	**p – value**
Total	8607064.8387	95			
Parameters	6925002.7844	15	461666.8523	19.903	$p < 0.001$
Years	142333.4038	5	28466.6808	1.227	$p > 0.05$
Residual	1739728.6505	75	23196.3820		

Inferences

1) Parameter value showed a very high significant difference ($p < 0.001$) TDS is significantly the highest followed by Alkalinity and TH. Significantly low values were found for the parameters Total iron, PO_4^{3-}, DO, EC, pH and BOD.

2) Between years there is no significant difference ($p > 0.05$).

Table 5.7: Physico Chemical characteristics of shallow groundwater sources of Andhakaranazhy coast, Alappuzha, Kerala, India during the year 2001, 2005, 2008, 2012, 2013, 2014, 2015, 2016 & 2017

Water Quality Parameter	Apr-01	Annual Mean 2005	Dec-08	Annual mean 2012	Dec-13	Dec-14	Dec-15	Dec-16	Dec-17	WHO 2011	BIS (2012) Permissible limit
pH	7.8±0.76	7.4±0.2	7.2±0.2	7.6±0.25	7.9±0.26	7.4±0.23	7.6±0.29	8.1±0.17	7.3±0.30	6.5-8.5	6.5-8.5
EC (mS/cm)	0.4±0.08	2.7±1.5	0.9±0.6	0.8±0.62	2.2±1.91	1.5±1.59	1.2±0.93	3.1±3.18	1.4±1.27	1.5	
Alkalinity (mg/L)	35.5±47.01	324±63	34±8	330.2±117.23	467.1±226.24	363.3±184.54	255.7±40.74	290.7±77.01	417.8±209.46		600
DO (mg/L)		2.0±0.5	1.3±0.7	4.1± 1.95	3.8±0.92	3.7±2.8	3.2±2.0	3.3±1.0	2.4±1.78		
BOD (mg/L)		5.6±1.8	8.3±3.5	5.2±2.40	6.1±4.50	7.7±7.58	9.5±5.18	9.9±8.74	8.8±7.79		
TH (mg/L)	79.5±49.16	382±207	203±59	290.0±108.93	331.1±158.17	374.2±253.04	224.5±107.13	251±111.72	340.1±137.49	100	600
Ca^{2+} (mg/L)	23.0±19.34	101±37	41±9	83.2± 26.46	104.3±26.47	93.1±37.5	58.2±30.1	96.5±57.82	103.1±36.72	75	200
Mg^{2+} (mg/L)	5.4±2.23	34 ±44	24±10	18.5±11.39	17±24.08	34.2±48.02	19.1±11.09	24.5±15.26	20.0±12.92	30	100
Na^{+} (mg/L)	30.3±14.55	286±150	79±49	119.2±96.21	131.6±129.44	127.8±130.42	104.8±53.7	81.9±60.63	138.9±111.75		
K^{+} (mg/L)	11.9±10.30	13±6	9±7	8.3± 8.98	6.7±6.31	9.3±9.31	8.9±7.22	5.2±6.16	9.5±9.83		
Cl^{-} (mg/L)	53.3±15.04	361±158	76±30	161.6±169.9	155.3±153.46	213.4±242.98	160.8±113.81	169±144.61	207.1±278.61	250	1000
SO_4^{2-} (mg/L)	25.4±19.83	16±3	5±6	10.2±14.91	2.3±3.85	4.7±4.39	4.4±6.33	3.3±4.06	4.2±9.48	250	400
NO_3^{-} (mg/L)		0.40±0.09	1.42±0.12	1.3± 1.41	1.3±1.43	1.4±1.38	1.3±1.42	1.5±1.43	1.3±1.43	50	45
PO_4^{3-} (mg/L)		0.28±0.08	0.38±0.3	0.2± 0.18	0.2±0.12	0.1±0	0.2±0.11	0.2±0.07	0.2±0.15		
Total Iron (mg/L)		0.11±0.07	0.16±0.18	0.8± 0.84	0.6±0.47	0.6±0.18	1.3±2.93	0.8±0.81	1.2±1.33	0.1	0.3
TDS (mg/L)		1747.24±140.51	666.9±293.47	576.3 ± 398.92	1469.5 ±1242.62	985.6± 1032.95	801 ±611.92	2033.7 ±2074.31	653.6 ±477.39		2000

5.10 Conclusions

The spatio-temporal variation of water quality parameters of shallow groundwater sources of Andhakaranazhy coast are elaborately is discussed in this chapter for a period from 2001 to 2017. The study reveals certain physico-chemical parameters such as alkalinity, total hardness, calcium, sodium, chloride and total iron showed in very high concentration. Most of the period groundwater sources indicate the suitability of water for irrigation purpose. As perthe indices evaluated- LSI, RSI water is having slightly scale forming and corrossive character. Aggressiveness index showed non-aggressive behaviour in most of the study period. Sodium chloride ratio suggests that prominent ion exchange is occurring in the study area. Chemical composition of water is suitably explained by Gibb’s diagram, reveals that evaporation and weathering processes control the groundwater chemistry. The phreatic ground water of Andhakaranazhy coastal region is characterized by prominent temporary hardness water type, evidenced by Piper diagrams. WQI is found to be greater than 100 in most of the period, indicates water is unfit for drinking purpose unless subjected to convenional pretreatment. Parameter evaluated showed a very high significant difference ($p < 0.001$). TDS is significantly the highest observed followed by Alkalinity and TH. Significantly low values were found for the parameters and the following inferences are obtained Fe(t), PO_4^{3-}, DO, EC, pH and BOD. Between the years, there is no significant difference ($p > 0.05$). In the post tsunamic period, there is not much water quality variations observed specifically during 2008-2017. The ANOVA results showed that parameters differ significantly over the years ($p < 0.001$). TDS showed significantly higher value followed by Cl^-, and TH.

Significantly lower values for the parameters are observed for PO_4^{3-}, NO_3^{-}, SO_4^{2-}, EC, pH, DO and BOD. Years also showed a significant difference between them ($p < 0.001$). 2016 and 2017 showed significantly higher values for the parameters ($p < 0.001$). Significantly lower values for the parameters occur during 2008, 2013, 2014 and 2015.

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Chapter 6

TEMPORAL SPATIAL VARIATION OF GROUNDWATER QUALITY ALONG THE CHERAI COAST, ERNAKULAM DURING THE PERIOD 2001-2017

6.1 Introduction

This chapter discusses the temporal and spatial variation of groundwater quality of shallow groundwater sources of the tsunami affected region of Cherai coast, Ernakulam during the period 2001-2017. The variation of water quality parameters discussed in the Chapter 4 gives us an idea about the groundwater chemistry of the Cherai coast during the year 2012. The study carried out for December months of years 2013, 2014, 2015, 2016 & 2017, after the one year sampling in 2012. The data generated for the study period 2012-2017 were compared with the available secondary data of April 2001 [1], year 2005 and December 2008 [2]. The major findings of the study, temporal and spatial variation of groundwater quality along the Cherai coast, Ernakulam during the period 2001-2017, were discussed in this chapter.

Physico-chemical parameters analysed includes pH, EC, alkalinity, total hardness, DO, BOD, calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate, phosphate, TDS and total iron. Irrigation parameters sodium adsorption ratio, sodium percent, permeability index, Kelley's ratio, magnesium adsorption ratio, USSL and Wilcox diagrams were used to assess the suitability of water. Corrosion and scaling potential of the groundwater was carried with the help of Langelier satuturation index, Ryznar stability index & aggressiveness index. Water type of the region was determined by Hill-Piper trilinear diagrams. Gibbs diagrams explains the chemical composition of water. The results are discussed in the following sections.

6.2 Physico-Chemical Parameters

Physico-chemical parameters analysed includes pH, EC, alkalinity, total hardness, DO, BOD, calcium, magnesium, sodium, potassium, chloride, sulphate, nitrate, phosphate, TDS and total iron.

6.2.1 pH

During April 200l, costal stretch of Kerala reported pH of shallow groundwater sources (SGW) as 7.8±0.76. But it showed an annual mean of 7.3±0.37 during the year 2005 and a gradual decrease was observed from 2005 to December 2008 and attains a value of 6.5±0.20 (December 2008). The 2012 study reveals that pH maintains an annual mean of 7.3 ± 0.38. In December 2013, slight enhancement was noticed in pH (7.5±0.38). It slightly decreases during December 2014 (7.1±0.43). But December 2015 (7.5±0.20) onwards, pH showed a gradual decrease and attains a value in December 2016 (7.2±0.24). A drastic decrease was observed from December 2016 to December 2017 and maintains a value of 6.9±0.28. pH showed a slightly alkaline behaviour throughout the study period from 2001 – 2017, within the standard limits of BIS (6.5 -8.5) [3]. The presence of bicarbonate ion is responsible for the alkaline behaviour of the groundwater in the study area.

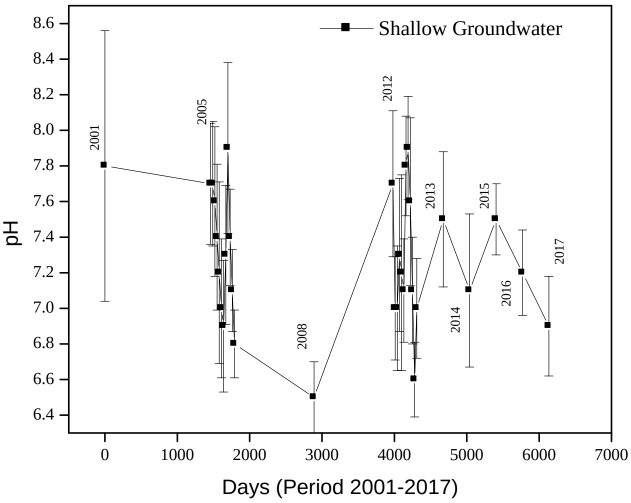

Figure 6.1: Temporal and spatial variation of pH of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.2 Electrical Conductivity (EC)

In 2001, electrical conductivity (EC) of shallow groundwater was 0.4±0.08 mS/cm. But after the tsunami event, an increase in EC can be seen during the year 2005 and maintains an annual average EC of 1.5±0.84 mS/cm. But in December 2008, EC becomes 0.3±0.18mS/cm. But a huge increase was observed during the year 2012 with an annual mean of EC 2.4 ± 5.11 mS/cm. It decreased to 1.4±1.20 mS/cm in December 2013 and 1.5±2.16 in December 2014. The subsequent years results are 1.6±1.75 mS/cm in December 2015, 1.5±1.75 mS/cm in December 2016 and 1.9±2.57 mS/cm in December 2016. The concentration of EC exceeds the standard limits in some of the study periods. This high EC indicates intrusion of salt water into the aquifer [2].

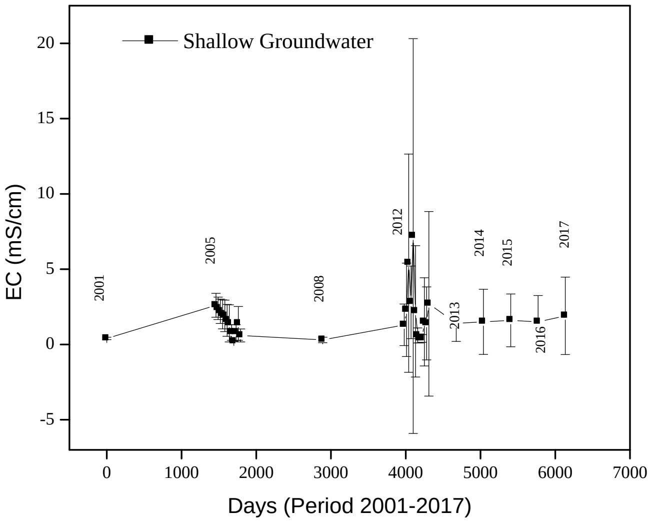

Figure 6.2: Temporal and spatial variation of electrical conductivity (EC) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.3 Alkalinity

Alkalinity of shallow groundwater showed 35.5±47.01 mg/L during April 2001. As a result of tsunami incident, the alkalinity was increased and maintains an annual mean of 203.2±74.91 mg/L. But in December 2008, a sharp decrease was observed in the alkalinity and reaches a concentration of 20.0±6.32 mg/L. In 2012, groundwater reported an annual mean of 152.3 ± 87.49 mg/L, increased to 229.8±146.92 mg/L in December 2013. In December 2014, alkalinity of water decreases to 173.4±130.09 mg/L. Tremendous increase was found during the month of December 2015 (251.6±182.27 mg/L). Then a gradual decrease of alkalinity can be observed in December 2016 (197.5±136.40 mg/L) and (183.1±135.55 mg/L) in December 2017. Weathering of silicate and carbonate minerals are responsible for the alkalinity of water [4].

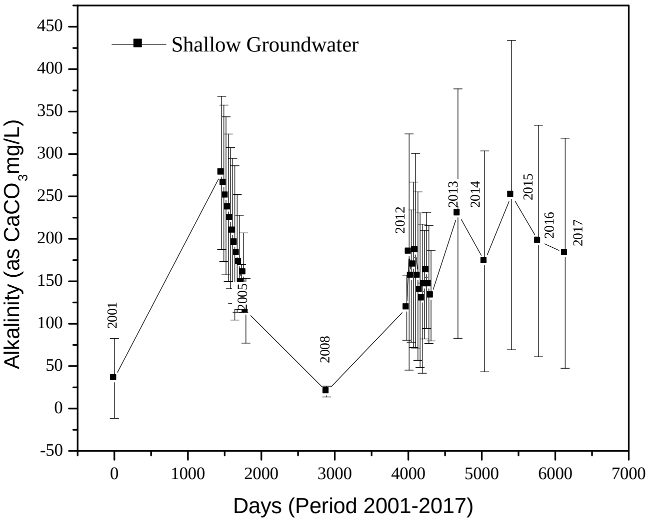

Figure 6.3: Temporal and spatial variation of alkalinity of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.4 Total Hardness (TH)

The 2001 data reveals that total hardness of shallow groundwater sources are having very low concentration (7.1±57mg/L). But after the tsunami, the hardness of water was enhanced and attains an annual mean of 248.8±91.44mg/L during the year 2005. In December 2008, total hardness show a slight decrease to 201.3±318.37mg/L. A gradual increase of total hardness observed from 2012 onwards with an annual mean of 433.1 ± 653.53mg/L. It decreases to 195.4±183.88 mg/L in December 2013 and then shows a gradual increase of 206.6±156.91 mg/L in December 2014 and 231.8±279.01mg/L in December 2015. However, a tremendous increase was found in December 2016 (577.2±443.51mg/L), which then decreases to 528.4±564.24 mg/L in December 2017.

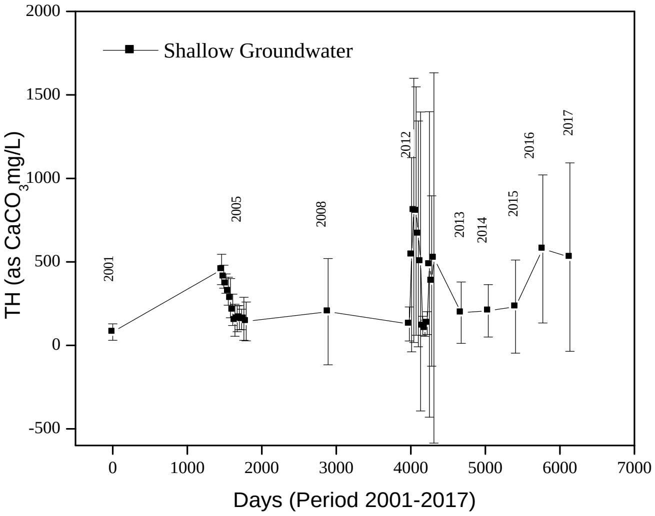

Figure 6.4: Temporal and spatial variation of total hardness (TH) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.5 Disssolved Oxygen (DO)

Dissolved oxygen content was decreased over the years, which indicates the degradation of water quality. During the year 2005, DO exhibits an annual mean of 3.0±1.79 mg/L in shallow groundwater sources. It was decreased to 2.3±1.71 mg/L in December 2008. However, during the year 2012, the DO was increased to 3.0± 1.25 mg/L which revealed the improvement of water quality. DO of groundwater during the December months of respective years 2013, 2014, 2015 & 2016 are 3.4±1.78, 2.0±0.8, 3.5±1.24 and 3.4±1.27 mg/L. Finally the shallow groundwater reached a DO of 2.8±1.38 mg/L during December 2017. The results of DO are characterized by oxygen deficient condition in groundwater sources.

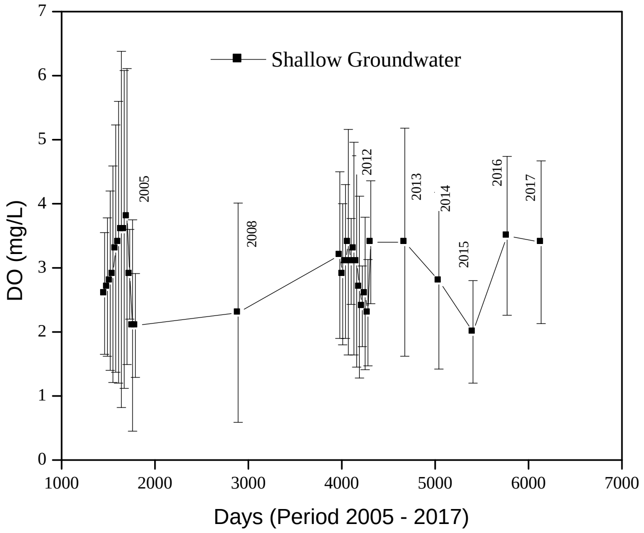

Figure 6.5: Temporal and spatial variation of dissolved oxygen (DO) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.6 Biological Oxygen Demand (BOD)

The shallow groundwater reported a BOD of 9.7±2.72mg/L during the year 2005. In December 2008, it was decreased to 4.5±1.20 mg/L. BOD is gradually increased from 2012 (6.8±2.04mg/L) onwards 7.6±1.88 mg/L in December 2013, 11.3±5.84 mg/L in December 2014, 12.0±3.74 mg/L in December 2015 and reached 6.8±0.37 mg/L during December 2016. Finally the shallow groundwater attained a BOD of 9.6±3.46 mg/L during the year 2017. The results showed the presence of oxygen demanding waste in the groundwater sources.

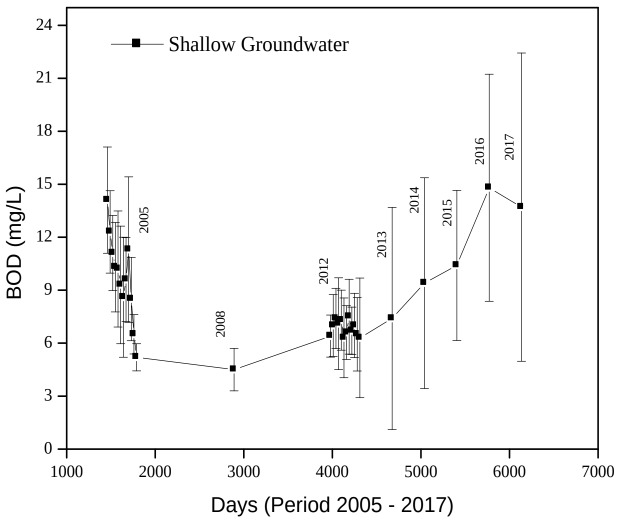

Figure 6.6: Temporal and spatial variation of biological oxygen demand (BOD) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.7 Calcium (Ca^{2+})

Shallow groundwater sources of 2001 data reported a calcium concentration of 23 ± 19.34 mg/L. But after the tsunami event, calcium content was increased to an annual mean of 59.4±28.62 mg/L during the year 2005. A decrease was observed during December 2008 with a concentration of 34.9±30.24mg/L of calcium. A sharp increase of calcium was found in the year 2012 with an annual mean of 85.6 ± 114.53 mg/L. In December 2013 the calcium content was 52.9±50.23 mg/L and it decreases to 41.7±39.03 mg/L in December 2014. It reaches 69.3±114.74 mg/L in December 2015. Again a sharp increase was found with the calcium content of 144.1±99.67mg/L in December 2016 and finally attains 112.1±116.12 mg/L of calcium in December 2017. High calcium content of groundwater indicates the weathering process occurring in the study area [5].

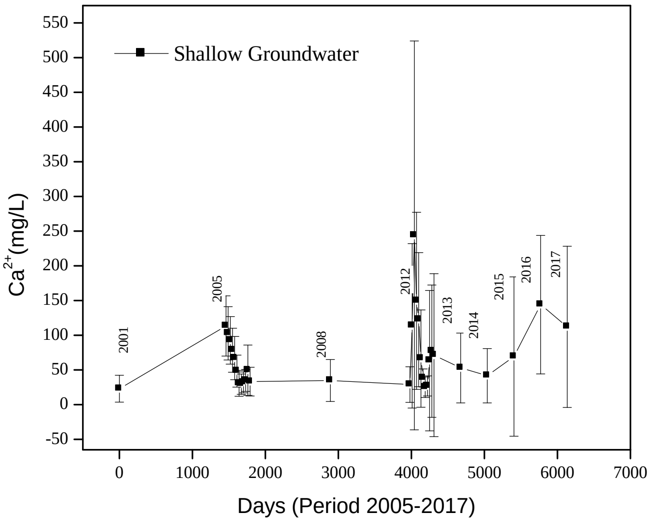

Figure 6.7: Temporal and spatial variation of calcium of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.8 Magnesium (Mg^{2+})

The shallow groundwater exhibits a magnesium content of 5.4 ± 2.23 mg/L during April 2001. However, we can see a gradual increase of magnesium concentration from 2005-2012. Groundwater recorded an annual mean of magnesium 19.4±9.76mg/L during the year 2005 and it is increased to 31.2±48.09 in December 2008. Magnesium reported an annual mean of 53 ± 105.03mg/L during the year 2012. It decreases to 15.3±15.60mg/L during December 2013. But a slight increase was found in December 2014 (24.8±27.48mg/L). Again the concentration decreases to (14.2±14.41mg/L) in December 2015. But in December 2016, a sharp increase was observed (52.5±50.03mg/L). Finally the value reaches

(60.0±69.48mg/L) in December 2017. Source of magnesium in the study area is the weathering of limestone, which releases enough Mg^{2+} ions into groundwater [4].

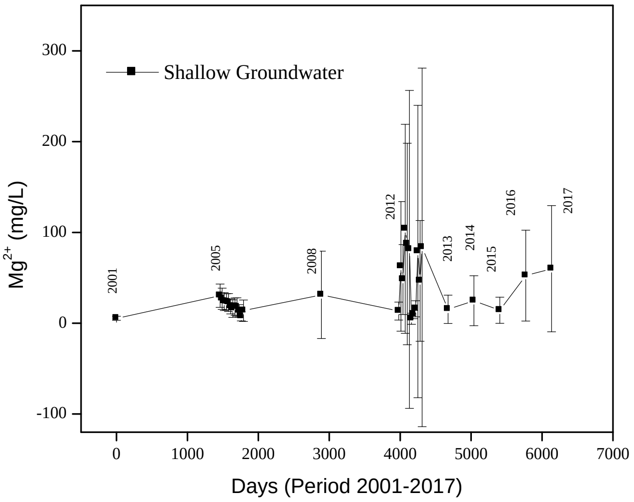

Figure 6.8: Temporal and spatial variation of magnesium of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.9 Sodium (Na^+)

Shallow groundwater sources of the region in 2001 (pre tsunami data) reveal that sodium content had been 30.3±14.55 mg/L. But an increase of sodium concentration in the groundwater can be seen during the year 2005 with an annual average of 1425.5±824.71mg/L, which indicate the instance of inundation by tsunami waves. However, a sharp decrease was observed from 2005 to December 2008 and attains a concentration of 54.7±41.09mg/L (December 2008). Again the concentration was increased to 229.4 ± 358.59mg/L in 2012 (annual mean) and reaches 92.6±76.86mg/L in December 2013. But December 2014, results reported a sodium concentration of 136.8±192.90mg/L, attained a concentration of 246.1±326.29mg/L in December 2015 and after that sodium reaches a low value of 95.7±97.22mg/L in December 2016. But a drastic increases was observed in December 2017 (261.7±297.29mg/L). Salt water intrusion and silicate weathering are the sources of sodium in groundwater of the study area. The NaCl scatter diagram also support this process [5].

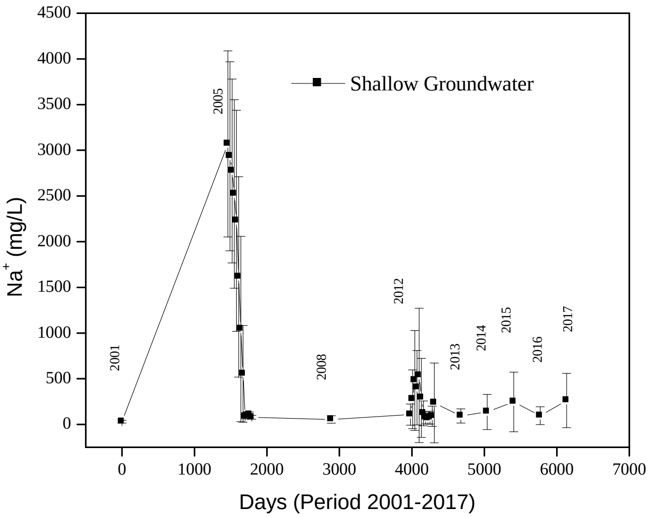

Figure 6.9: Temporal and spatial variation of sodium of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.10 Potassium (K^+)

In 2001, shallow groundwater (SGW) sources exhibits a potassium concentration of 11.9±10.30 mg/L. It was increased to 85.2±52.10mg/L during 2005, indicating the salt water intrusion by Indian Ocean tsunami [2]. Afterwards, the concentration was decreased to 7.0±8.99mg/L (December 2008). In 2012 groundwater possess an annual mean of 16.5 ±

30.73mg/L and it decreases to 7.4±4.63mg/L in December 2013. The concentration was increased gradually to 8.8±9.20mg/L in December 2014. It reached a value of 30.9±50.50 mg/L in December 2015 and a sharp decrease was found during the year December 2016 to 4.9±5.09mg/L. A slight increase was again observed in December 2017 with a potassium content of 16.8±18.71mg/L.

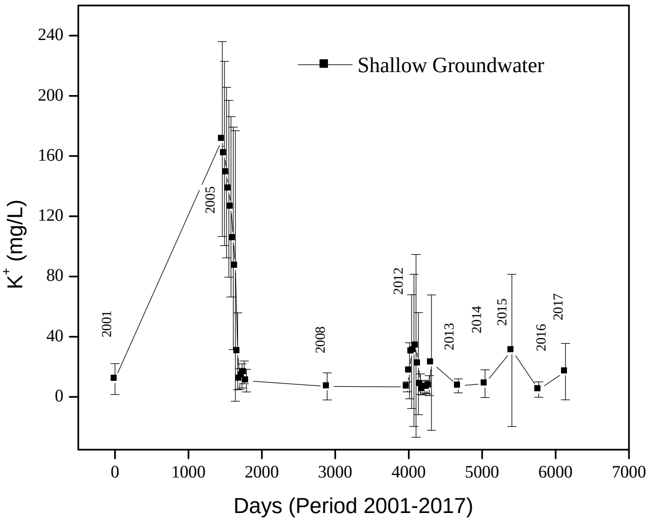

Figure 6.10: Temporal and spatial variation of potassium of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.11 Chloride(Cl^-)

In 2001 data, observed a chloride concentration of 53.3±15.04 mg/L in shallow groundwater sources. But it reaches a very high value in 2005 with an annual average of 1926.1±2144.07mg/L, clearly indicating the salt water intrusion from tsunami event. But the concentration was dropped down in December 2008 to 388.2±669.46mg/L. The concentration was again increased and attains an annual average of 570.8 ± 1049.69mg/L. In December 2013, chloride content decreases to 131.8±137.31 mg/L and then it increases to 205.0±364.12 mg/L in December 2014. Then a sharp decrease was found in December 2015 (344.4±501.17mg/L) and December 2016 (447.3±331.02mg/L). Finally the concentration was increased to 753.6±1013.54mg/L in December 2017. The increased amount of chloride indicates presence of salt water intrusion in the study area [2]. Throughout the study period chloride maintains a concentration within standard permissible limits of BIS [3].

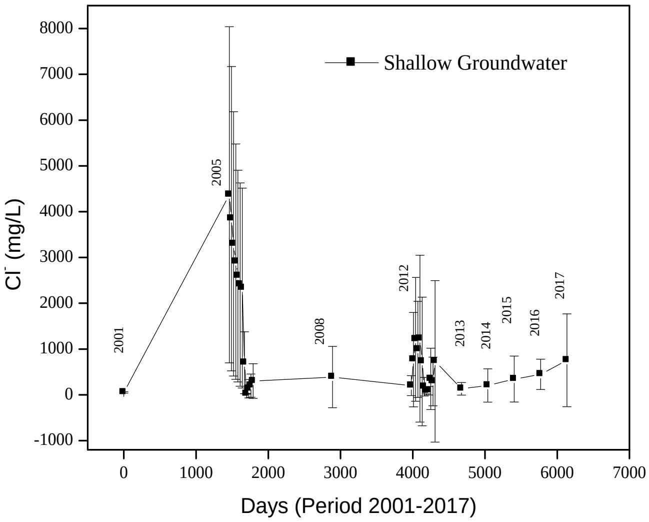

Figure 6.11: Temporal and spatial variation of chloride of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.12 Sulphate (SO_4^{2-})

In 2001, shallow groundwater (SGW) sources reported a sulphate of 25.4 ±19.83 mg/L. Then a trendous increase was observed during the year

2005 (73.8±40.34mg/L). But the concentration was dropped down in December 2008 to 32.3±56.85mg/L. A slight decrease was found in 2012 with an annual mean of 25.9 ± 36.88mg/L. The result of subsequent years analysis are 2.4±4.60mg/L (December 2013), 32.1±27.79 (December 2014), 7.5±13.57mg/L (December 2015), 6.6±8.14mg/L (December 2016) and finally reaches 12.6±19.96 mg/L in December 2017.

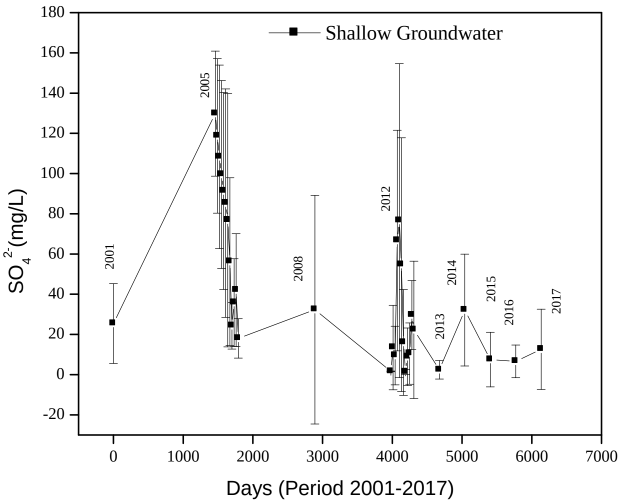

Figure 6.12: Temporal and spatial variation of sulphate of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.13 Nitrate (NO_3^-)

The concentration of nitrate of shallow groundwater recorded an annual mean of 1.0±0.63mg/L during the year 2005 and in December 2008, it becomes 1.0±0.37mg/L. In 2012, groundwater exhibits an annual mean nitrate of 3.2 ± 2.41mg/L of nitrate and the concentration gradually increases in December 2013 onwards and becomes 3.8±2.49 mg/L. Again increased to 4.2±2.49mg/L in December 2014. During Decmber 2015 nitrate was 4.5±2.51 mg/L and it was again increased to 4.8±2.48 mg/L in December 2016. Finally, the nitrate attains a concentration of 5.1±1.53mg/L during December 2017.

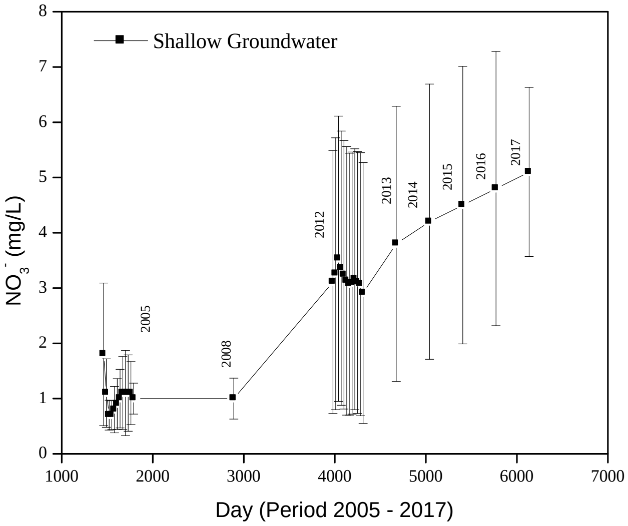

Figure 6.13: Temporal and spatial variation of nitrate of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.14 Phosphate (PO_4^{3-})

Phosphate showed very low concentration throughout the study period. The concentration was almost similar during the study period from 2005 – 2017. Results of study in 2005, exhibits an annual mean of 0.6±0.39mg/l of phosphate in the shallow groundwater sources. But it slightly decreased during December 2008 to 0.2±0.13mg/L. In 2012, phosphate reported an annual average of 0.4 ± 0.4 mg/L and it was slightly increased during December 2013 (0.6±0.55 mg/L). Phosphate concentrations of subsequent years are 0.6±0.55 mg/L in December 2014, 0.2±0.15 in December 2015, 0.5±0.52 in December 2016 and finally attains 0.9±0.64 in December 2017.

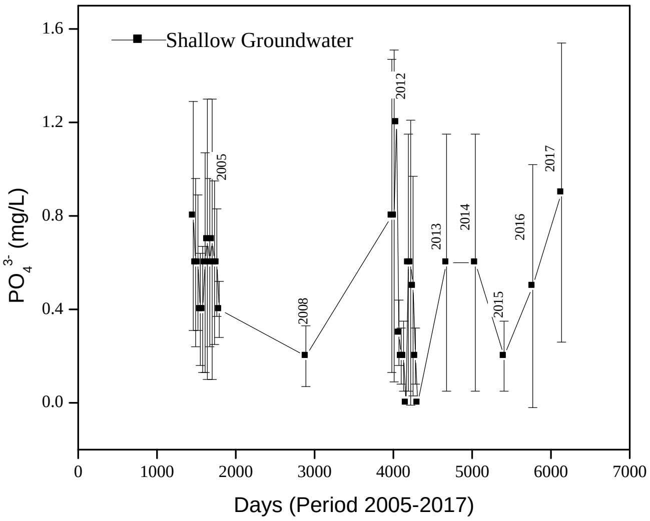

Figure 6.14: Temporal and spatial variation of phosphate of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.15 Total Iron

Total iron concentration of study area exceeds the standard limits of BIS&WHO [3,6] throughout the study periods. It is due to the presence of coastal alluvium in the soil. Groundwater reported an annual mean of 0.1±0.16 mg/L of iron during the year 2005. The iron content remains the same during December 2008 (0.1±0.07mg/L). In 2012, shallow groundwater show an annual mean of 1.2 ± 1.22mg/L and then the concentration was slightly decreased to 1.1±0.72mg/L during the period December 2013. Subsequent years analysis 0.5±0.19mg/L (December 2014), 0.4±0.29mg/L (December 2015), 1.7±0.91mg/L (December 2016) and 1.3±1.71mg/L (December 2017) reveal the presence of iron in the study area.

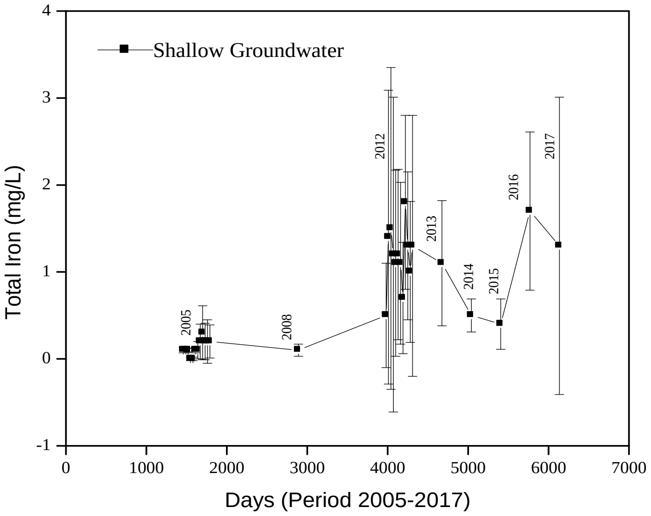

Figure 6.15: Temporal and spatial variation of total iron of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.2.16 Total Dissolved Solids (TDS)

Shallow groundwater of Cherai coast showed a TDS concentration of 4397.7±2998.5 during the year 2005. This increased TDS content was happening as a result of Tsunami event. Then a sharp decrease of TDS was found in December 2008 (694.2±850.3 mg/L). In 2012, the TDS becomes 1603 ± 3355.4 mg/L and again decreased to 953.0±781.1 mg/L in December 2013. A gradual increase was again happening during the year December 2014 (1013.0±1403.4) and December 2015 (1051.4± 1140.7 mg/L). But in December 2016, a decline in the TDS content was noticed (1014.7±1124.4mg/L) and finally reaches 1521.4±1974.1mg/L during December 2017. This high concentration of TDS was produced by the weathering process as well as the saltwater intrusion [7].

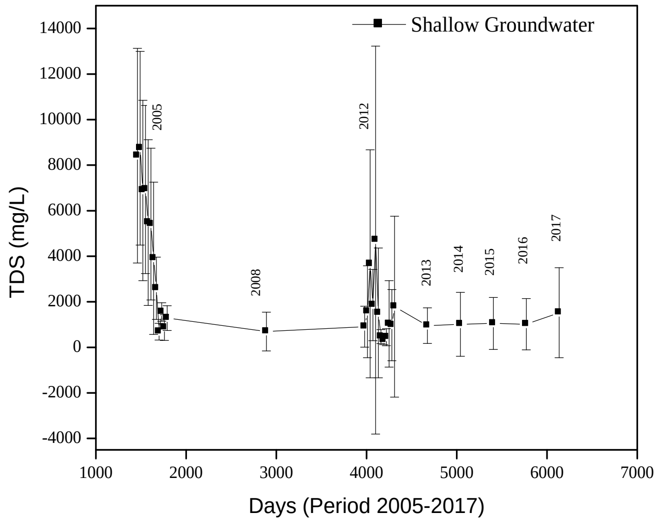

Figure 6.16: Temporal and spatial variation of total dissolved solids (TDS) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3 Irrigation water quality parameters

Irrigation parameters includes sodium adsorption ratio, sodium percent, permeability index, Kelley's ratio, magnesium adsorption ratio, USSL and Wilcox diagrams.

6.3.1 Sodium Absorption Raito (SAR)

Sodium adsorption ratio is an important parameter to measure the irrigation suitability. Irrigation water is classified into four categories based on the SAR value, suggest that excellent class between (0-10), good (10-18), fair (18-26) & poor (>26). During April 2001, groundwater reported a SAR of (2.3), indicates excellent quality for irrigation purposes. But after the tsunami event, SAR showed very high values during January-July 2005 and comes under the permissible class. As a result of monsoonal dilution, the SAR value reduced to 16.6 and the groundwater maintains good quality during August 2005.However, September 2005 onwards the SAR becomes stabilized and then the water belongs to excellent class as shown in the Figure 6.17. During the year 2012, sodium adsorption ratio maintains excellent quality. In December 2012, groundwater reported SAR of 3.0, good for irrigation and then it slightly increases to 3.7 during December 2014.SAR value becomes 6.6 in December 2015 but it again decreases to 1.8 in December 2016. During December 2017 groundwater showed a SAR of 4.2, reveal good for agricultural purposes [8].

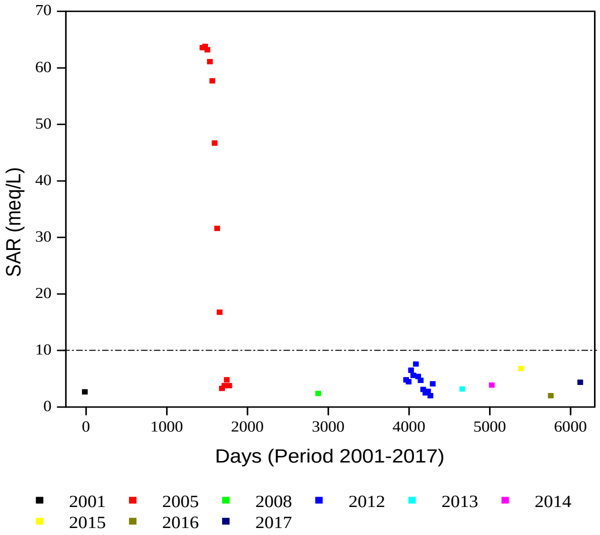

Figure 6.17: Temporal and spatial variation of sodium adsorption ratio (SAR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.1.1 USSL Diagram

During April 2001, groundwater falls under the C2S1 category, indicate water having *low sodium hazard and medium salinity hazard.* But in 2005, groundwater lies in the region of *C1S1 during October*. The remaining months, water comes under the categories of *C2S1*, *C3S1*, *C3S3* and *C3S4*, which showed the saline water intrusion into the aquifer as a result of tsunami. During December 2008, groundwater is having low sodium hazard and medium salinity hazard (*C2S1)*. In 2012, water plots in the regions of *C2S1*, *C3S1*, *C4S1* and *C4S2*, having very low sodium hazard. The December months of subsequent years 2013, 2014, 2015, 2016 and 2017 data reveals that water comes under the category of *C3S1*with low sodium hazard and high salinity hazard [9].

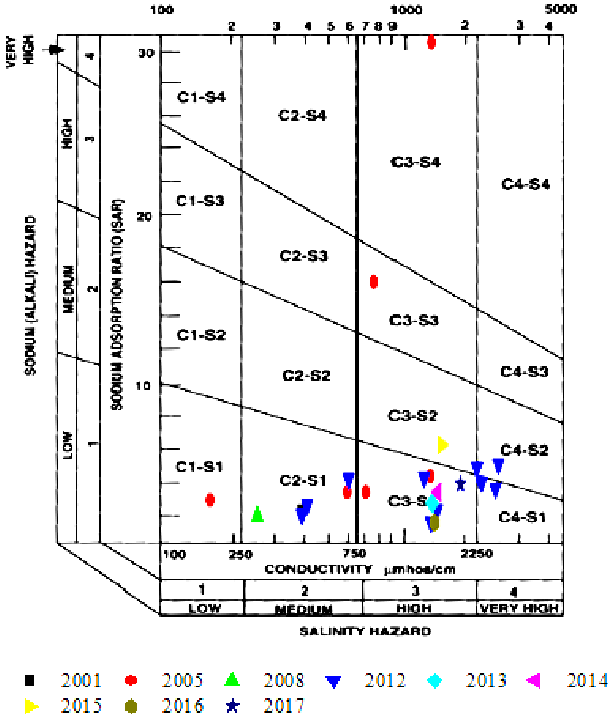

Figure 6.18: USSL diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.2 Sodium Percent (Na%)

Figure 6.19 shows the temporal variation of sodium percentage of shallow groundwater sources. Na % below 40 suggest *good* (G), 40-60 *permissible* (P), 60-80 *doubtful* (D) and above 80 *unsuitable* category (US). Sodium percentage calculated for the shallow groundwater sources reveal that, in 2001 the water belongs to the *permissible category*. In January-July 2005, water is in *unsuitable class*, indicate intrusion of saline water as a result of tsunami [1,2]. Because of monsoonal dilution, the water gets diluted and sodium concentration was decreased and the water reaches *good* for agricultural uses during August 2005. But the water again comes in the class of *permissible* during the months of September & October 2005. During November and December months showed that water becomes *doubtful* for irrigation. During 2008, groundwater comes under *permissible* category. In 2012 till May, water show *permissible category* and after that *permissible category*. Na% showed 61.7 & 60 during the respective months of June & July 2012. From August-October 2012, groundwater occupies in the class of permissible, suitable for irrigation. However in November 2012, Na% becomes 33 having good quality for irrigation use. At the end of December 2012, groundwater recorded a sodium percent of 56.6 and the water quality changed to the permissible category. In 2013 and 2014 the Na% are 50.7 and 43.9 which show again *permissible category*. In December 2015, sodium percent was 69.5, indicates doubtful for irrigation use. A sharp decrease of Na% occurred in December 2016 (25.4) and the irrigation quality becomes *good*. Finally, the quality moved to the class of *permissible* with *a* sodium percent of 49 during December 2017.

Table 6.1: Temporal and spacial variation of sodium adsorption ratio (SAR) and sodium percent (Na%) of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India for the period 2001-2017

Year/Month	SAR	Inference	% Na	Inference
April 2001	2.5	E	56	P
Jan 2005	63.4	P	93.2	US
Feb 2005	63.6	P	93.5	US
Mar 2005	63.0	P	93.8	US
Apr 2005	60.9	P	94.0	US
May 2005	57.5	P	93.8	US
Jun 2005	46.5	P	91.7	US
Jul 2005	31.4	P	82.5	US
Aug 2005	16.6	G	77.0	D
Sep 2005	3.1	E	55.8	P
Oct 2005	3.6	E	59.7	P
Nov 2005	4.6	E	64.6	D
Dec 2005	3.6	E	60.1	D
Dec 2008	2.2	E	46.3	P
Jan 2012	4.6	E	57.1	P
Feb 2012	4.3	E	49.3	P
Mar 2012	6.3	E	51.2	P
Apr 2012	5.4	E	49.9	P
May 2012	7.4	E	57.4	P
Jun 2012	5.2	E	61.7	D
Jul 2012	4.5	E	60.0	D
Aug 2012	2.9	E	54.6	P
Sep 2012	2.3	E	48.2	P
Oct 2012	2.6	E	41.0	P
Nov 2012	1.8	E	33.0	G
Dec 2012	3.9	E	56.6	P
Dec 2013	3.0	E	50.7	P
Dec 2014	3.7	E	43.9	P
Dec 2015	6.6	E	69.5	D
Dec 2016	1.8	E	25.4	G
Dec 2017	4.2	E	49.0	P

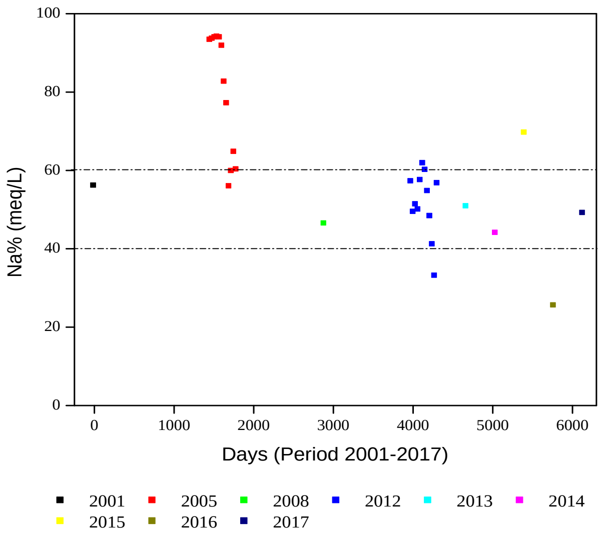

Figure 6.19: Temporal and spatial variation of sodium percent (Na%) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.2.1 Wilcox Diagram

Wilcox diagram indicate that, water comes under *excellent to good* range during the period April 2001. But after the Tsunami incident, water quality become changed and it moved to the *unsuitable* category during the period from January-March 2005. However, water quality was improved after the monsoonal dilution and reached the *good to permissible* category during the period April-August & November 2005. The months of September, October and December 2005 showed *excellent to good quality* of water. The year December 2008 groundwater, also falls under the *good* category. During February, April, June, December 2012 months exhibits, *doubtful to unsuitable* class of water. However, during July-September 2012, quality of water has been enhanced to the *excellent* class (Figure 5.20). During July-September 2012, quality of water has been enhanced to the *excellent* class (Figure 5.20).

But in January, October, December 2012, groundwater becomes *good to permissible* range. However, during February, April, June, December 2012 months exhibits, *doubtful to unsuitable* class of water. In March, May 2012, EC values greater than 3500 µS/cm, falls under the unsuitable category. The data plotted on the *permissible to doubtful* region of Wilcox diagram represents the year December 2015. But the remaining years of December 2014, 2016 & 2017 comes under the *good to permissible* class.

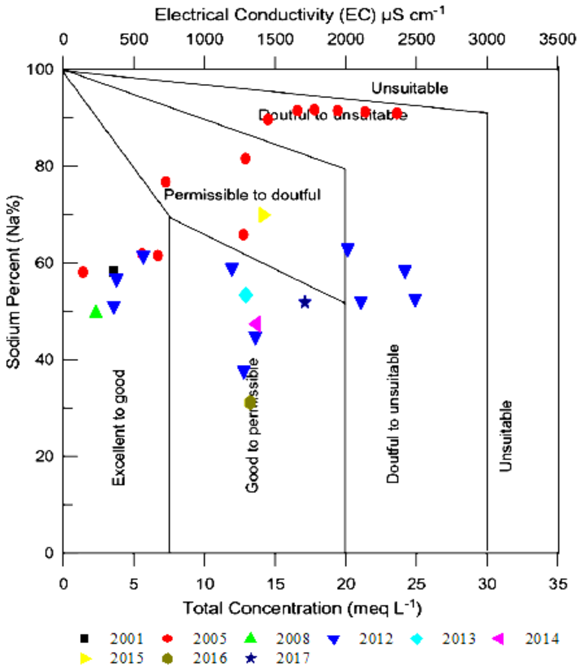

Figure 6.20: Wilcox diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.3 Permeability Index (PI)

The permeability Index is an irrigation water quality parameter, which classified the water into three categories of *class I*, *class II* and *class III*. If the PI value is greater than 25%, indicates there is no permeability problems within the soil and can be used for agricultural uses [10]. During April 2001, groundwater becomes marginally safe for irrigation purposes (class II). Throughout the year 2005, groundwater belongs to the class I. In December 2008, water comes under the class II, indicates suitable for irrigation. Groundwater recorded a PI of 90.5 during month January 2012 and reached in the class I. However during February-May 2012, groundwater showed class II type. Again the permeability values are increased and groundwater remains in the class I from June-September 2012. But October and November months of 2012, water occupied in the position of class II. Water having a PI of 83.2 & 83.1 during the year December 2012 and December 2013 respectively, indicates the suitability. PI was equal to 74.6 during December 2014 and then increases to 95.2 in December 2016. In December 2016 & December 2017, groundwater is considered suitable for agricultural purposes and belongs to the class II.

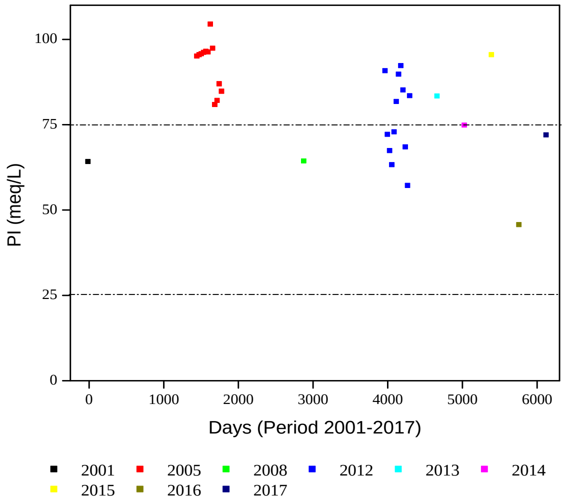

Figure 6.21: Temporal and spatial variation of permeability index (PI) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.4 Kelly’s ratio (KR)

Kelly’s ratio measures of hazard caused by the sodium ions and is considered as an important parameter for the determination of irrigation water quality. If the ratio is less than one, indicate the suitability of groundwater for agricultural purposes [11]. From the Figure 6.22 it is clear that, groundwater possess very high sodium content than Ca and Mg ions in most of the study period. During April 2001, groundwater reported a KI of 2.1 and belongs to the unsuitable class. But after the tsunami incident during the year 2005, very high values of KI are recorded and it decreases to 1.2 during December 2008. But the groundwater remains in the unsuitable class for the entire period except in November 2012, December 2016 and December 2017. During these periods groundwater exhibits a Kelley’s ratio less than one and indicate the irrigation suitability

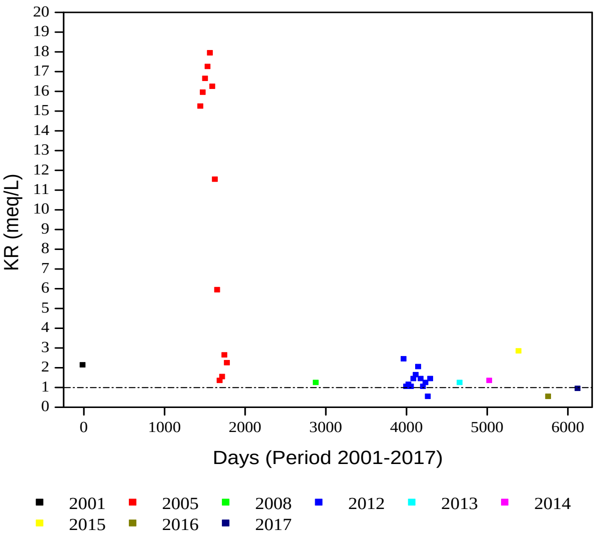

Figure 6.22 Temporal and spatial variation of Kelley’s ratio (KR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.3.5 Magnesium Adsorption Ratio (MAR)

Magnesium adsorption ratio (MAR) determines the hazard caused by Mg ion in groundwater. If the ratio less than 50, water considered to be good for agricultural uses [12]. Figure 6.23 shows the temporal and spatial variation of magnesium adsorption ratio (MAR) of shallow groundwater (SGW) sources along the Cherai coast during the period 2001-2017. In April 2001, MAR becomes 34 and the groundwater possess suitability for irrigation purposes. Throughout the period 2005, groundwater comes under the suitable category. In 2012, groundwater exhibits an MAR value below 50, except in April 2012 and indicates the presence of high amount of magnesium in groundwater due to salt water intrusion. During December 2013 MAR is 21.5 and which decreases to 6.3 in December 2014. MAR was found to be very low in December 2015 (5.4). The subsequent years results are 7.4 in December 2016 & 44.8 in December 2017, suitable for irrigation purposes.

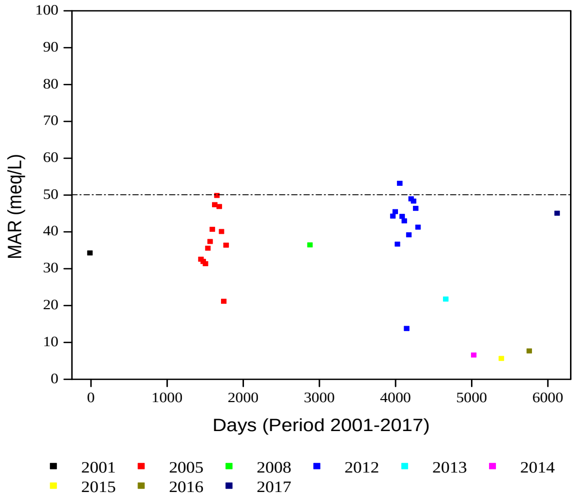

Figure 6.23: Temporal and spatial variation of magnesium adsorption ratio (MAR) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

Table 6.2: Temporal and spacial variation of Kelley's ratio (KR), magnesium adsorption ratio (MAR) and permeability index (PI) of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India for the period 2001-2017

Year/Month	**KR**	**Inference**	**MH**	**Inference**	**PI**	**Inference**
April 2001	2.1	US	34	S	63.9	Class II
Jan 2005	15.2	US	32.3	S	94.8	Class I
Feb 2005	15.9	US	31.7	S	95.2	Class I
Mar 2005	16.6	US	31.1	S	95.5	Class I
Apr 2005	17.2	US	35.3	S	95.9	Class I
May 2005	17.9	US	37.1	S	96.2	Class I
Jun 2005	16.2	US	40.4	S	96.0	Class I
Jul 2005	11.5	US	47.1	S	104.2	Class I
Aug 2005	5.9	US	49.6	S	97.1	Class I
Sep 2005	1.3	US	46.6	S	80.6	Class I
Oct 2005	1.5	US	39.8	S	81.8	Class I
Nov 2005	2.6	US	20.9	S	86.7	Class I
Dec 2005	2.2	US	36.1	S	84.5	Class I
Dec 2008	1.2	US	36.2	S	64.1	Class II
Jan 2012	2.4	US	44.0	S	90.5	Class I
Feb 2012	1.0	US	45.2	S	71.9	Class II
Mar 2012	1.1	US	36.4	S	67.1	Class II
Apr 2012	1.0	US	52.9	US	63.0	Class II
May 2012	1.4	US	43.9	S	72.6	Class II
Jun 2012	1.6	US	42.7	S	81.5	Class I
Jul 2012	2.0	US	13.5	S	89.5	Class I
Aug 2012	1.4	US	38.9	S	92.0	Class I
Sep 2012	1.0	US	48.7	S	84.9	Class I
Oct 2012	1.2	US	48.1	S	68.2	Class II
Nov 2012	0.5	S	46.1	S	56.9	Class II
Dec 2012	1.4	US	41.0	S	83.2	Class I
Dec 2013	1.2	US	21.5	S	83.1	Class I
Dec 2014	1.3	US	6.3	S	74.6	Class II
Dec 2015	2.8	US	5.4	S	95.2	Class I
Dec 2016	0.5	S	7.4	S	45.4	Class II
Dec 2017	0.9	S	44.8	S	71.7	Class II

Table 6.3: Temporal and spatial variation of Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI) of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India for the period 2001-2017

Year/Month	LSI	Inference	RSI	Inference	AI	Inference
Jan 2005	0.6	SFNC	6.5	LSC	12.6	NA
Feb 2005	0.5	SFNC	6.7	LSC	12.5	NA
Mar 2005	0.4	SSFC	6.8	LSC	12.4	NA
Apr 2005	0.1	SSFC	7.3	CS	12.1	NA
May 2005	-0.2	SCNSF	7.7	HC	11.7	MA
Jun 2005	-0.7	SC	8.3	HC	11.4	MA
Jul 2005	-1.0	SC	8.9	HC	10.9	MA
Aug 2005	-0.5	SC	8.3	HC	11.4	MA
Sep 2005	0.1	SSFC	7.7	HC	12.0	NA
Oct 2005	-0.4	SCNSF	8.3	HC	11.5	MA
Nov 2005	-0.6	SC	8.4	HC	11.3	MA
Dec 2005	-1.2	SC	9.3	HC	10.7	MA
Dec 2008	-2.3	IC	11.0	HC	9.6	HA
Jan 2012	-0.4	SCNSF	8.5	HC	11.5	MA
Feb 2012	-0.5	SC	8.0	HC	11.4	MA
Mar 2012	-0.3	SCNSF	7.6	HC	11.6	MA
Apr 2012	-0.1	SCNSF	7.5	HC	11.8	MA
May 2012	-0.1	SCNSF	7.5	HC	11.8	MA
Jun 2012	-0.6	SC	8.4	HC	11.3	MA
Jul 2012	0.0	SSFC	7.8	HC	11.9	MA
Aug 2012	-0.2	SCNSF	8.3	HC	11.6	MA
Sep 2012	-0.4	SCNSF	8.4	HC	11.5	MA
Oct 2012	-0.7	SC	8.5	HC	11.2	MA
Nov 2012	-1.0	SC	8.7	HC	10.9	MA
Dec 2012	-0.9	SC	8.7	HC	11.0	MA
Dec 2013	-0.1	SCNSF	7.8	HC	11.8	MA
Dec 2014	-0.7	SC	8.5	HC	11.3	MA
Dec 2015	-0.2	SCNSF	7.9	HC	11.7	MA
Dec 2016	-0.1	SCNSF	7.4	CS	11.8	MA
Dec 2017	-0.6	SC	8.1	HC	11.4	MA

6.4 Corrosion Indices

6.4.1 Langelier saturation index (LSI)

The shallow groundwater sources of Cherai coast comes under scale forming and non corrosive (SFNC) character in January & February 2005. This may be due to the enhanced content of ions such as sodium, chloride, potassium by salt water intrusion. But March & April 2005, LSI of groundwater becomes *slightly scale forming and corrosive* (SSFC) character. But in May 2005, groundwater having *slightly corrosive but non scale forming* (SCNSF) character. The negative values of LSI indicates, corrosive property of groundwater. From June-August 2005 groundwater comes under the category of serious corrosion (SC). During September 2005, groundwater records a LSI of 0.1 (SSFC) and then it decreases to -0.4 (SCNSF). The water reported significant corrosion nature during the months of November & December 2005. Intolerable corrosion was observed during the year December 2008. Groundwater falls in SCNSF during January 2012 and in February 2012 it becomes SC. However March-May months of 2012 groundwater is having *slightly corrosive but non scale forming* (SCNSF) character. S*erious corrosion* (SC) of groundwater has been noticed in June 2012. Groundwater becomes SSFC in July and then it reaches SCNSF during the months August & September 2012. The LSI move towards *serious corrosion* type during October- December 2012. Very *serious corrosion* (SC) of groundwater has been noticed in December 2008. However, during the year 2012 reported scale forming and non corrossive behaviour of water. The tendency of water is SCNSF during the year December 2013. Again serious corrosion was noticed in December 2014. LSI values suggest that, groundwater becomes SCNSF during December months of the years 2015 & 2016. Finally the LSI of -0.6 indicate having a serious corrosion behaviour during December 2017 [13,14].

6.4.2 Ryznar stability index (RSI)

Groundwater possess a *little scale or corrosive* property during the months January-March 2005. However, the water becomes corrosion significant (CS) character during June, August, October and November months of April 2005. Water is noticed with *heavy corrosion* during periods May-December 2005. December 2008 also observed with *heavy corrosion* of water. Throughout the year 2012, groundwater exhibits heavy corrosion character. Water maintains heavy corrosion (HC) behaviour in the December months of 2013, 2014 & 2015. However in December 2016, behaviour of water changed to CS, indicates the carbonate weathering process. Again the water comes under the category of HC in December 2017 [13].

6.4.3 Aggressiveness index (AI)

Aggressiveness index mainly used to measure corrosion[15]. From the Table 6.3, it is clear that groundwater showed moderately aggressive character throughout the study period. During January-April 2005, groundwater is having a non-aggressive character. But in May-December 2005, groundwater showed moderately aggressive character, except during the month of September 2005. However in December 2008, groundwater becomes highly aggressive (HA). But January 2012 onwards groundwater possess prominent moderately aggressive character.

6.5 Gibb’s Diagrams

Gibb’s diagrams explains that chemical composition of the shallow groundwater sources are controlled by weathering as well as evaporation processes [16]. Evaporation process controls the chemical composition of water during the year 2005 except in September and November 2005. In 2012, groundwater chemistry was controlled by weathering and evaporation processes. Rock-water interaction is responsible for the ionic content of groundwater during the period December 2013 as shown in the Figure 6 24. Weathering of rock forming minerals controls the ion chemistry of water of the study area during the December months of subsequent years 2014, 2015, 2016 & 2017.

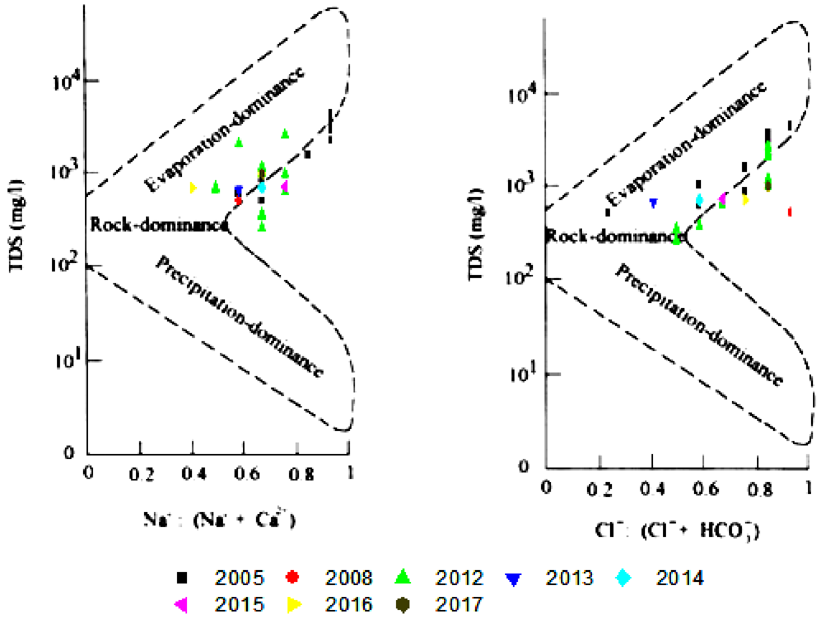

Figure 6.24: Gibb’s diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.6 Hill-Piper-Trilinear Diagram

The water type of the groundwater was assessed by using the piper diagrams. During 2001 April 2001, groundwater possess saline behaviour. In 2005, groundwater noticed a strong saline character with very high sodium and chloride ions, indicates sea water intrusion.

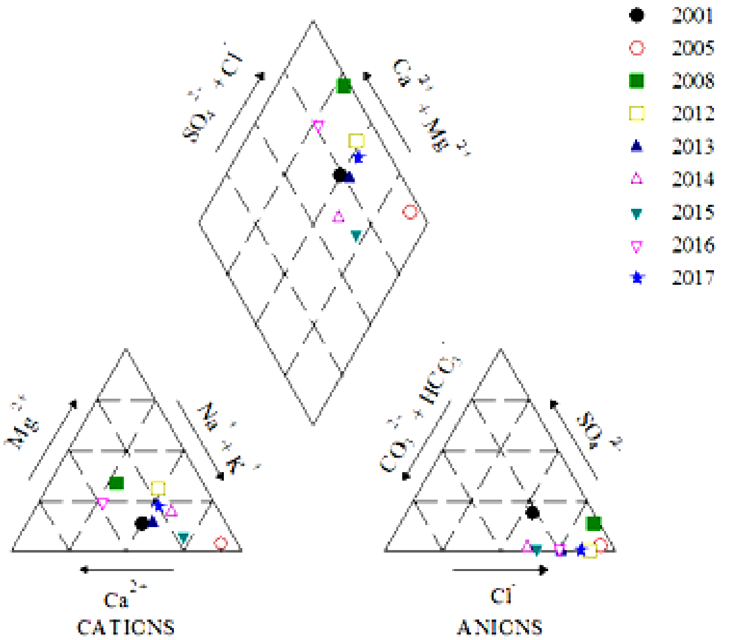

Figure 6.25: Piper diagram of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

Water with dominant permanent hardness characterised by hydrochemical facies of Ca^{2+}-Mg^{2+}-Cl^{-} -SO_4^{2-} type during the year December 2008. In 2012, water type shifted towards the mixed Ca-Mg-Cl region indicates, there is no cation exceeding the 50%. In December 2013, December 2014 and December 2015 groundwater is having prominent saline nature. However, in December 2016, groundwater saline character is shifted to mixed Ca-Mg-Cl type, reveals the dissolution of carbonate minerals. But in December 2017, water type again comes in the saline corner of the diamond, reveals the occurrence of salt water intrusion in the region [17].

6.7 Sodium-Chloride ratios

Sodium-chloride ratio of the groundwater for the period 2001-2017 has been shown in the Figure 6.26. During the year April 2001, reverse ion exchange was the dominant process in the groundwater. The year 2005 showed a prominent ion exchange behaviour except the month of July 2005 [2]. December 2008 also exhibits ion exchange character. In 2012, we can see that, the reverse ion exchange occurred during the months of March-April, October –November 2005, due to the impact of saline water intrusion. December 2014, 2015 & 2017 months reveal the occurrence of reverse ion exchange. However, the reverse ion exchange was again prominent during December 2016, indicates the enhancement of chloride ions in groundwater.

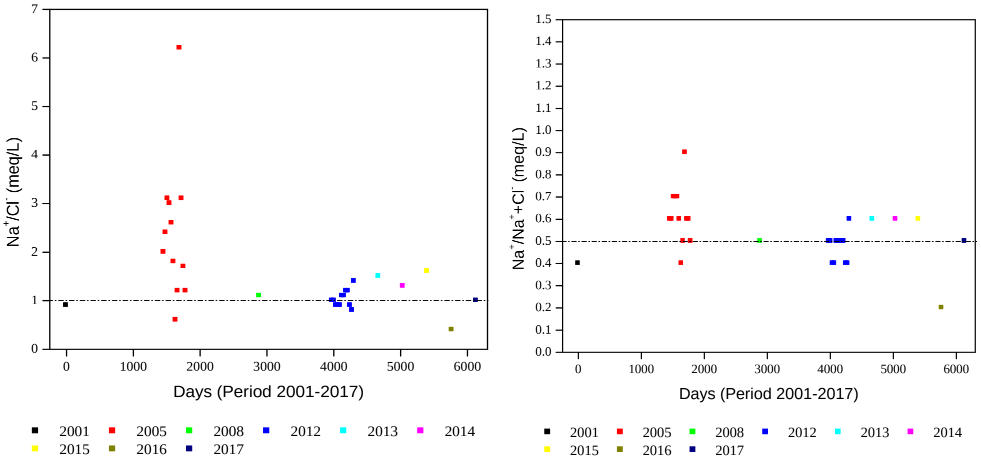

Figure 6.26: Temporal and spatial variation of Na^+/Cl and $Na^+/ Na^+ + Cl^-$ of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

Table 6.4: Temporal and spacial variation of Na^+/Cl and $Na^+/Na^+ + Cl^-$ of shallow groundwater (SGW) sources of Cherai, Ernakulam , Kerala, India for the period 2001-2017

Year/Month	Na/Cl	$Na^+/Na^+ + Cl^-$	Inference
April 2001	0.9	0.4	RIE
Jan 2005	2.0	0.6	IE
Feb 2005	2.4	0.6	IE
Mar 2005	3.1	0.7	IE
Apr 2005	3.0	0.7	IE
May 2005	2.6	0.7	IE
Jun 2005	1.8	0.6	IE
Jul 2005	0.6	0.4	RIE
Aug 2005	1.2	0.5	IE
Sep 2005	6.2	0.9	IE
Oct 2005	3.1	0.6	IE
Nov 2005	1.7	0.6	IE
Dec 2005	1.2	0.5	IE
Dec 2008	1.1	0.5	IE
Jan 2012	1.0	0.5	IE
Feb 2012	1.0	0.5	IE
Mar 2012	0.9	0.4	RIE
Apr 2012	0.9	0.4	RIE
May 2012	0.9	0.5	IE
Jun 2012	1.1	0.5	IE
Jul 2012	1.1	0.5	IE
Aug 2012	1.2	0.5	IE
Sep 2012	1.2	0.5	IE
Oct 2012	0.9	0.4	RIE
Nov 2012	0.8	0.4	RIE
Dec 2012	1.4	0.6	IE
Dec 2013	1.5	0.6	IE
Dec 2014	1.3	0.6	IE
Dec 2015	1.6	0.6	IE
Dec 2016	0.4	0.2	RIE
Dec 2017	1.0	0.5	IE

IE-Ion Exchange RIE-Reverse Ion Exchange

6.8 Water Quality Index (WQI)

Shallow groundwater of the coastal stretch of Kerala showed WQI of 57.6 during the year April 2001, comes under good category. But after the tsunami event, the quality deteriorates very much. During January-February 2005 groundwater become unfit for drinking purposes. However March 2005 onwards, an up gradation can be seen in water quality. From March-May 2005, groundwater appears in very poor category. A slight improvement of quality was again observed and water becomes poor quality. This may be due to the monsoonal dilution [18].

Table 6.5: Temporal and spacial variation of water quality index (WQI) of shallow groundwater (SGW) sources of Cherai coast, Ernakulam, Kerala, India for the period 2001-2017

Year/Month	WQI	Water Quality	Grading
April 2001	57.6	P	B
Jan 2005	112.2	UDP	E
Feb 2005	100.6	UDP	E
Mar 2005	90.6	VP	D
Apr 2005	82.2	VP	D
May 2005	76.9	VP	D
Jun 2005	75.5	P	C
Jul 2005	81.5	VP	D
Aug 2005	96.8	VP	D
Sep 2005	126.6	UDP	E
Oct 2005	107.6	UDP	E
Nov 2005	93.7	VP	D
Dec 2005	77.6	VP	D
Dec 2008	56.3	P	C
Jan 2012	154.4	UDP	E
Feb 2012	350.0	UDP	E
Mar 2012	441.7	UDP	E
Apr 2012	350.2	UDP	E
May 2012	279.9	UDP	E
Jun 2012	341.1	UDP	E
Jul 2012	271.5	UDP	E
Aug 2012	219.3	UDP	E
Sep 2012	513.4	UDP	E
Oct 2012	382.8	UDP	E
Nov 2012	311.2	UDP	E
Dec 2012	279.3	UDP	E
Dec 2013	154.4	UDP	E
Dec 2014	350.0	UDP	E
Dec 2015	441.7	UDP	E
Dec 2016	350.2	UDP	E
Dec 2017	333.8	UDP	E

G-Good P-Poor VP-Very Poor UDP-Unfit for Drinking Purposes

WQI was very poor during the months of July-August 2005. Then it again goes to the UDP category during the period September-October 2005. WQI reported for the months November & December 2005 were 93.7 and 77.6 respectively. During December 2008, WQI decreases to 56.3, becomes poor category. Although 2012 onwards, WQI becomes very high (>100) and comes in the class of UDP.

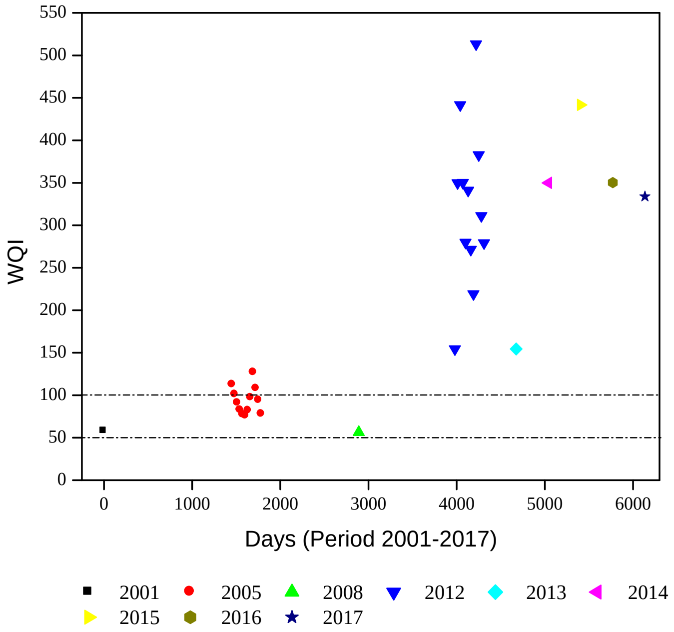

Figure 6.27: Temporal and spatial variation of water quality index (WQI) of shallow groundwater (SGW) sources along the 26th December 2004 Indian Ocean tsunami affected coastal area, Cherai, Ernakulam, Kerala, India for the period 2001-2017

6.8 Analysis of Co-Variance (ANOVA)

ANOVA results conducted to check the variability in the water quality parameters between December month of the years 2008, 2013, 2014, 2015, 2016 and 2017 of shallow groundwater sources discussed below

a) Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Cherai coast during the months of December for years 2008, 2013, 2014, 2015, 2016 and December 2017.

Table 6.6: ANOVA table for the comparison of water quality parameters between December month of the years 2008, 2013,2014,2015,2016 and 2017 of shallow groundwater sources of Cherai coast

Source	**ss**	**df**	**ms**	**F**	**p – value**
Total	7329401.4491	95			
Parameters	6488261.4708	15	432550.7647	49.696	$p < 0.001$
Years	188350.4597	5	37670.0919	4.328	$p < 0.001$
Residual	652789.5186	75	8703.8602		

Inferences

1) Parameters differ significantly over the years ($p < 0.001$). TDS showed significantly higher value followed by Cl^-, and TH.

   Significantly lower values for the parameters are observed for PO_4^{3-}, NO_3^-, SO_4^{2-}, EC, pH, DO and BOD.

2) Years also showed a significant difference between them ($p < 0.001$). 2016 and 2017 showed significantly higher values for the parameters ($p < 0.001$).

3) Significantly lower values for the parameters occur during 2008, 2013, 2014 and 2015.

Table 6.6: Physico Chemical characteristics of shallow groundwater sources of Cherai coast, Ernakulam, Kerala, India during the year 2001, 2005, 2008, 2012, 2013, 2014, 2015, 2016 & 2017

Water Quality Parameter	Apr-01	Annual Mean 2005	Dec-08	Annual mean 2012	Dec-13	Dec-14	Dec-15	Dec-16	Dec-17	WHO 2011	BIS (2012) Permissible limit
pH	7.8±0.76	7.3±0.37	6.5±0.20	7.3 ± 0.38	7.5±0.38	7.1±0.43	7.5±0.20	7.2±0.24	6.9±0.28	6.5-8.5	6.5-8.5
EC (mS/cm)	0.4±0.08	1.5±0.84	0.3±0.18	2.4 ± 5.11	1.4±1.20	1.5±2.16	1.6±1.75	1.5±1.75	1.9±2.57	1.5	
Alkalinity (mg/L)	35.5±47.01	203.2±74.91	20.0±6.32	152.3 ± 87.49	229.8±146.92	173.4±130.09	251.6±182.27	197.5±136.40	183.1±135.55		600
DO (mg/L)		3.0±1.79	2.3±1.71	3.0±1.25	3.4±1.8	2.0±0.8	3.5±1.2	2.1±1.6	2.8±1.38		
BOD (mg/L)		9.7±2.72	1.20	6.8±2.04	7.4±6.29	9.4±5.97	10.4±4.25	14.8±6.43	13.7±8.73		
TH (mg/L)	79.5±49.16	248.8±91.44	201.3±318.37	433.1 ± 653.53	195.4±183.88	206.6±156.91	231.8±279.01	577.2±443.51	528.4±564.24	100	600
Ca^{2+} (mg/L)	23.0±19.34	59.4±28.62	34.9±30.24	85.6 ± 114.53	52.9±50.23	41.7±39.03	69.3±114.74	144.1±99.67	112.1±116.12	75	200
Mg^{2+} (mg/L)	5.4±2.23	19.4±9.76	31.2±48.09	53 ± 105.03	15.3±15.60	24.8±27.48	14.2±14.41	52.5±50.03	60.0±69.48	30	100
Na^+ (mg/L)	30.3±14.55	1425.5±824.71	54.7±41.09	229.4 ± 358.59	92.6±76.86	136.8±192.90	246.1±326.29	95.7±97.22	261.7±297.29		
K^+ (mg/L)	11.9±10.30	85.2±52.10	7.0±8.99	16.5 ± 30.73	7.4±4.63	8.8±9.20	30.9±50.50	4.9±5.09	16.8±18.71		
Cl^- (mg/L)	53.3±15.04	1926.1±2144.07	388.2±669.46	570.8 ± 1049.69	131.8±137.31	205.0±364.12	344.4±501.17	447.3±331.02	753.6±1013.54	250	1000
SO_4^{2-} (mg/L)	25.4±19.83	73.8±40.34	32.3±56.85	25.9 ± 36.88	2.4±4.60	32.1±27.79	7.5±13.57	6.6±8.14	12.6±19.96	250	400
NO_3^- (mg/L)		1.0±0.63	1.0±0.37	3.2 ± 2.41	3.8±2.49	4.2±2.49	4.5±2.51	4.8±2.48	5.1±1.53	50	45
PO_4^{3-} (mg/L)		0.6±0.39	0.2±0.13	0.4 ± 0.4	0.6±0.55	0.6±0.55	0.2±0.15	0.5±0.52	0.9±0.64		
Total Iron (mg/L)		0.1±0.16	0.1±0.07	1.2 ± 1.22	1.1±0.72	0.5±0.19	0.4±0.29	1.7±0.91	1.3±1.71	0.1	0.3
TDS (mg/L)		4397.7±2998.49	694.2±850.27	1603 ± 3355.41	953.0±781.10	1013.0±1403.43	1051.4±1140.65	1014.7±1124.36	1521.4±1974.14		2000

6.9 Conclusion

Spatio-temporal variation of water quality parameters of shallow groundwater sources of Cherai coast is discussed in this chapter. After the tsunami event, SAR showed very high values during January-July 2005 and comes under the permissible class. In December 2012, groundwater reported SAR of 3.0, *good for irrigation* and then it slightly increases to 3.7 during December 2014.SAR value becomes 6.6 in December 2015 but it again decreases to 1.8 in December 2016. During December 2017 groundwater showed a SAR of 4.2, reveal good for agricultural purposes.

In USSL diagram groundwater lies in the region of *C1S1 during October*. The remaining months, water comes under the categories of *C2S1, C3S1, C3S3* and *C3S4,* which showed the saline water intrusion into the aquifer as a result of tsunami. During December 2008, groundwater having low sodium hazard and medium salinity hazard (*C2S1)*. In 2012, water plots in the regions of *C2S1, C3S1, C4S1* and *C4S2*, having very low sodium hazard. The December months of subsequent years 2013, 2014, 2015, 2016 and 2017 data reveals that water comes under the category of *C3S1*with low sodium hazard and high salinity hazard.

Sodium percent in 2001 belongs to the permissible *category*. In January-July 2005, water is in *unsuitable class* and the water reaches *good* for agricultural uses during August 2005. The water again comes in the class of *permissible* during the months of September & October 2005. In 2012 water is in *permissible category* in most of the months. December 2015, sodium percent was 69.5, indicates *doubtful* for irrigation use. Finally, the value was jumped to the class of *permissible* with *a* sodium percent of 49 during December 2017. Groundwater sources falls mostly in good to permissible limit in the year 2005 in Wilcox diagram, but in permissible to doubtful region in the year 2012 and December 2015. But the remaining years of December 2013, 2014, 2016 & 2017 comes under the *good to permissible* class. Most of the groundwater comes in class I and class II of the permeability index during the study period which is suitable for irrigation. Kelly's index is unsuitable for irrigation during the year 2001, 2005 and 2008. The groundwater remains in the unsuitable class for the entire period except in November 2012, December 2016 and December 2017. Magnesium adsorption ratio is <50 throughout the study period indicating the water is suitable for irrigation.

Langelier saturation index in most of the months of 2005 indicates groundwater sources are corrosive in nature due to the enhanced content of ions such as sodium, chloride, potassium by salt water intrusion and very *serious corrosion* (SC) of groundwater has been noticed in December 2008. In the year 2012 water is *slightly corrosive but non scale forming* (SCNSF) character. The tendency of water is SCNSF during the year December 2013. Again serious corrosion was noticed in December 2014 then changed to SCNSF during December 2015 & 2016. Finally during December 2017, LSI having serious corrosion behaviour is noticed during December 2017. Ryznar stability index also reveals that the groundwater sources have a *corrosive behaviour* throughout the study period in the post tsunamic period during the year 2005, December 2008, year 2012, December 2013, 2014, 2015, 2016 and December 2017.Aggressiveness index measured corrosion as *moderately aggressive* throughout the study period.

According to Gibb's diagram groundwater chemistry of the study area is controlled by evaporation process along in most of the months in 2005, whereas both weathering of rocks and evaporation process operated in the year 2012. Weathering of rock forming minerals along controls the ion chemistry of water of the study area during the subsequent years of December 2013, 2014, 2015, 2016 & 2017. From the Hill-Piper trilinear plot overall groundwater in the study area is saline water type.

WQI found to be greater than 100 in most of the period, indicates unfitness of water for direct drinking purpose unless subjected to conventional treatment. The ANOVA results showed that parameters differ significantly over the years ($P < 0.001$). TDS showed significantly higher value followed by Cl^-, and TH. Significantly lower values for the parameters are observed for PO_4^{3-}, NO_3^-, SO_4^{2-}, EC, pH, DO and BOD. Years also showed a significant difference between them ($p < 0.001$). Years 2016 and 2017 showed significantly higher values for the parameters ($p < 0.001$). Significantly lower values for the water quality parameters occur during 2008, 2013, 2014 and 2015.

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Chapter 7

SUMMARY AND CONCLUSION

The study presented in the preceeding chapters descriptively discussed the hydrochemistry and groundwater quality of coastal phreatic aquifers in Andhakaranazhy (Alappuzha) and Cherai (Ernakulam) coasts of Kerala. Groundwater chemistry of the study area is mainly controlled by many natural as well as anthropogenic factors. The region is one of the tsunami devastated and inundated coast of Kerala, during 26th December 2004 Indian Ocean tsunami. The region lies below the mean sea level and groundwater aquifers are mostly phreatic in nature. Salt water intrusion is a major issue prevalent in the study area, hence the fresh groundwater sources are limited in number. This coastal segment elaborately studied the groundwater quality for a period of 2001-2017.

This bound thesis discusses for the variation of physico-chemical parameters, irrigation water quality, corrosion measures, Gibb's diagrams, Hill-Piper plots, ionic ratios and water quality index based on statistical analysis in the respective sections rather exhaustively. Study critically analysed with proper interpretations for selected control well (CW) and shallow groundwater sources (SGW) for Andhakaranazhy and Cherai coasts of Kerala during each month of the year 2012 and also in the subsequent years

2013, 2014, 2015, 2016 & 2017. The overall water quality were determined for a period of 2001-2017 in Andhakaranazhy and Cherai coast.

The research mainly focused (1) To study the groundwater chemistry and monthly variation of major groundwater quality parameters of shallow groundwater sources of the study area Andhakaranazhy (Alappuzha) and Cherai (Ernakulam) during year 2012. (2) To evaluate the drinking water suitability of various sources by comparing with IS &WHO standards and also to classify them using designated best use (DBU) suggested by CPCB, Government of India. (3) To compute the monthly water quality index of groundwater sources by giving adequate weightage to significant water quality parameters. (4) To study in detail the irrigational quality of various groundwater sources (5) To establish the temporal groundwater quality variation profile of a coastal segment of Kerala in Alappuzha and Ernakulam regions over a decade (2001-2017). (6) To analyse the trace element content of shallow groundwater sources. (7) To evaluate the statistical relationship between the water quality parameters using Pearson correlation matrix. (8) To evaluate saturation indices for studying industrial utility of various groundwater sources. (9) To plot Hill-Piper Trilinear diagrams to understand the hydrochemical facies of the study area. (10) To evaluate ionic ratios (sodium-chloride) and to study the major processes occurring in the study area. (11) To plot ionic ratios in Gibb's plot to study the major processes controlling the groundwater quality of the study area.

Hypothesis tested in the study are:*Whether there is any significant difference between mean values of various parameters in control well (CW) at different months of 2012 of Andhakaranazhy coast.* (2) *Whether* *there is any significant difference between mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the each month of year 2012* (3) *Whether there is any significant difference between mean values of various parameters in shallow groundwater sources and control well (CW) strata in each month of year 2012* (4) *Whether there is any significant difference between mean values of water quality index in control well (CW) at different months of 2012 Cherai coast.* (5) *Whether there is any significant difference between mean values of various parameters in shallow groundwater sources of Cherai coast during the each month of year 2012* (6) *Whether there is any significant difference between mean values of various parameters in shallow groundwater sources and control well (CW) strata in each month of year 2012* (7) *Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Andhakaranazhy coast during the months of December for years 2013, 2014, 2015, 2016 and December 2017.* (8) *Whether there is any significant difference between the mean values of various parameters in shallow groundwater sources of Cherai coast during the months of December for years 2013, 2014, 2015, 2016 and December 2017.*

To test the hypothesis, the collected data were subjected to statistical analysis by means of t-Test and Two-Factor ANOVA. Where ever treatment effects are found to be significant, least significant difference (LSD) at 5% level are calculated to identify the significant treatment component. The results concerning each chapter are discussed in the respective chapters.

The study focused on the hydrochemistry and groundwater quality of coastal phreatic aquifers of geographically and ecologically significant coastal sections of Andhakaranazhy (Alappuzha) and Cherai (Ernakulam), Kerala, India. These regions are highly populated and hazard sensitive zone with a number of settlers, mostly fishermen. The availability & utility of groundwater sources are limited, threatened by many factors such as mobilization of natural pollutants (iron) and salt contamination by seawater intrusion, degraded its pristine quality. Sampling at these stations started in January 2012 and continued in each month till December 2012. In the subsequent years, 2013, 2014, 2015, 2016 & 2017 sampling and analysis were done towards the end of the year. Post-tsunami study data available for the year 2005 and those available for year 2001 were compared to, help in generating a database intermittently for a period 2001-2017 along the study area.

Eighteen groundwater sources from selected locations of the two places were considered to identify the variability of groundwater chemistry over the years. Eleven (11) shallow groundwater sources were chosen in Andhakaranazhy coast (8 dug wells, 2 bore wells and 1 open pond). In Cherai coast seven (7) shallow groundwaters were taken for study (consists of 6 dug wells and 1 bore well). The sampling and analysis (APHA; 2005) have been done for a period starting from January-December 2012, also in the December months of successive years 2013, 2014, 2015, 2016 and 2017. The samples were subjected for drinking water quality analysis as per BIS 10500: 2012 and water quality indices were computed. Hill-Piper-Trilinear plots were made to evaluate the water type of the study area using GW chart software. Irrigation suitability is measured by sodium percent (Na %), sodium adsorption ratio (SAR), Kelly's ratio (KR), permeability index (PI), magnesium adsorption ratio (MAR), USSL and Wilcox diagrams. Gibb's plots were made to the chemical composition of groundwater. Corrosion and scaling character of the groundwater is determined by Langelier saturation index (LSI), Ryznar stability index (RSI) and aggressiveness index (AI). These results were compared with the previous year's data April 2001, year 2005 and December 2008. The results will give us an insight into the actual groundwater chemistry of the region.

Overall water quality parameters of the Andhakaranazhy coast evaluated and reported in the chapter 3 are, pH (7.6±0.25), EC (809.4±618.38) mS/cm, Alkalinity (330.2±117.23) mg/L, TH (290.0±108.93) mg/L, DO (4.1±1.95) mg/L, BOD (5.2±2.40) mg/L, Ca^{2+} (83.2± 26.46) mg/L, Mg^{2+} (18.5±11.39) mg/L, TDS (576.3 ± 398.92) mg/L, Na^{+} (119.2±96.21) mg/L, K^{+} (8.3± 8.98) mg/L, Cl^{-} (161.6±169.9) mg/L, SO_4^{2-} (10.2±14.91) mg/L, NO_3^{-} (1.3± 1.41) mg/L, PO_4^{3-} (0.2± 0.18) mg/L & Total Iron (0.8± 0.84) mg/L. Groundwater chemistry of Andhakaranazhy coast revealed that groundwater is having a slightly alkaline behavior, due to the presence of bicarbonate ions. Presence of high concentrations of iron in the groundwater was caused by the recent alluvial deposits of study area. Based on classification of hardness, groundwater comes under *too hard for ordinary domestic purposes*. Irrigation parameters indicate, most of the groundwater is suitable for agricultural uses, but some conventional treatment methods are required. Water sources belongs to the class of *C1S1,C2S1 and C3S1* during the study period revealed by USSL diagrams. However, groundwater maintains *excellent to good* and *good to permissible* category during the year 2012. The abundance of major cations and anions in groundwater are in the order of $HCO_3^{-} > Cl^{-} > SO_4^{2-} > NO_3^{-} >$

PO_4^{3-} and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ respectively. The dissolved carbon present in the groundwater sources under study is mainly derived from inorganic material. Trace elements are well within the safe standard limits. Presence of E. Coli was reported in most of the groundwater sources, hence the water which comes under class C and E as per the classification suggested by CPCB (Centre Pollution Control Board). According to LSI, shallow groundwater possess slightly scale forming & corrosive character and little scale forming behaviour was observed by RSI. However, the groundwater is over saturated with carbonate mineral, mainly limestone and it showed a non-aggressive nature as evidenced by AI (aggressive index). Piper diagram reveals that groundwater sources were fall in Facies I (Ca^{2+}-Mg^{2+}-HCO_3^-) with temporary hardness behaviour, followed by Facies III (Na^+-K^+-Cl^--SO_4^{2-}). The Gibbs diagrams indicate that, the chemical composition of groundwater is mainly contributed by weathering of rock forming minerals. Ion exchange, halite dissolution, dissolution of carbonate mineral, and silicate weathering process are prominent occurring in the study area as shown by ionic ratios. The results of ANOVA indicate that, control well exhibited a significant difference between the parameters ($p < 0.01$). During November and December 2012, showed significantly higher values for the parameters and January, June, July, August, September, and October 2012 registered significantly lower values for the parameters ($p < 0.001$). In shallow groundwater sources, months showed a significant difference between them ($p < 0.01$)., March exhibited significantly higher values for the parameters followed by February and December 2012. Significantly lower values of the parameters are observed during January, June, July , August, September, October and November 2012 (p <

0.01). There is significant difference in the mean WQI of shallow groundwater (SGW) sources and control well (CW) ($p < 0.05$). WQI in SGW is significantly higher than that of CW ($P < 0.05$). Although the overall WQI indicate that, groundwater is not suitable for direct consumption drinking purpose, unless subjected to conventional treatment (pH adjustment and iron removal by simple aeration) followed by disinfection.

The groundwater chemistry of Cherai coast is mainly depended on the parameters such as pH, temperature, total dissolved solids, alkalinity and hardness. The soil type of this coastal stretch is composed of coastal alluvium. This is the main reason for iron contamination in groundwater sources of the study area. Salt water intrusion is a crucial problem when considering the drinking water sources. Most of the groundwater aquifers lie between 2-8 m depth, affected by incursion of saline water very severely. Irrigation water quality parameters showed that most of the groundwater is suitable for agricultural uses but some treatment methods are required. Water comes under the class of *C1S1, C2S1, C3S1, C4S1 and C4S2* indicates the dominance of sea water intrusion. Wilcox diagrams showed groundwater becomes *excellent to good*, *good to permissible* and permissible to doubtful category during the year 2012. The abundance of major cations and anions in the groundwater are in the order of $Cl^- > HCO_3^- > SO_4^{2-} > NO_3^- > PO_4^{3-}$ and $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ respectively. The carbon present in the groundwater sources under study is mainly originated from inorganic source. Trace elements are within the permissible standard limits of BIS. However, the presence of E. Coli was reported in all dug wells, which needs serious attention to protect them from contamination.

Based on CPCB classification, DW1, DW2, DW3 & DW5 comes under the *class C* and DW4 & BW falls in *Class E*. According to LSI, shallow groundwater possess *slightly corrosive but non-scale forming* (SCNSF) character and *heavy corrosion* (HC) behaviour was observed by RSI. However, the groundwater exhibits moderately aggressive nature as evidenced by AI. According to Vescilind (2004) classification of hardness, groundwater becomes *too hard for ordinary domestic purposes*. Hydrochemical facies of groundwater constitutes mainly Na^{+}-K^{+} -Cl^{-} -SO_4^{2-} type followed by Ca^{2+}-Mg^{2+}- Cl^{-} - SO_4^{2-} , mixed *Ca-Mg-Cl* , Ca^{2+}-Na^{+}-HCO_3^{-} and Ca^{2+}-Mg^{2+}-HCO_3^{-} type. Chemical composition of the groundwater was controlled by both weathering and evaporation process evidenced by Gibb's diagrams. Ion exchange, reverse ion exchange, evaporation, weathering of carbonate and silicate mineral are the major processes occurring in the study areas. ANOVA results showed that there is no significant difference between months ($p > 0.05$) of control well. Shallow groundwater showed a very high significant difference ($p < 0.001$). TDS is significantly very high among all the parameters, followed by Cl^{-}, TH and Na^{+}. Eh is having significantly very low value followed by PO_4^{3-}, Fe(t), DO and NO_3^{-}. WQI of Cherai coast is significantly very high in SGW compared to that in CW ($p < 0.001$). WQI explains that, groundwater is not suitable for direct consumption drinking purpose, unless subjected to conventional treatment.

This study summarizes with the following conclusions as regards to the spatio-temporal variation of water quality parameters of shallow groundwater sources of Andhakaranazhy coast are elaborately is discussed in chapter 5 for a period from 2001 to 2017 and the following inferences were obtained.

- The study reveals certain physico-chemical parameters such as alkalinity, total hardness, calcium, sodium, chloride and total iron showed in very high concentration.
- Most of the period groundwater sources indicate the suitability of water for irrigation purpose.
- As per the indices evaluated- LSI, RSI of water is having slightly scale forming and corrossive character.
- AI showed non-aggressive character during the study period.
- Sodium chloride ratio suggests that prominent ion exchange is occurring in the study area.
- Chemical composition of water is suitably explained by Gibb’s diagram, reveals that evaporation and weathering processes control the groundwater chemistry.
- The phreatic groundwater of Andhakaranazhy coastal region is characterized by prominent temporary hardness water type, evidenced by Piper diagrams.
- WQI is found to be greater than 100 in most of the period, indicates water is unfit for drinking purpose unless subjected to convenional pretreatment.
- Parameter evaluated showed a very high significant difference ($p < 0.001$). TDS is significantly the highest observed followed by Alkalinity and TH. Significantly low values were found for the parameters and the following inferences are obtained Fe(t), PO_4^{3-}, DO, EC, pH and BOD.

- Between the years, there is no significant difference ($p>0.05$). In the post tsunamic period, there is not much water quality variations observed specifically during 2008-2017.
- The ANOVA results showed that parameters differ significantly over the years ($p < 0.001$). TDS showed significantly higher value followed by Cl^-, and TH. Significantly lower values for the parameters are observed for PO_4^{3-}, NO_3, SO_4^{2-}, EC, pH, DO and BOD. Years also showed a significant difference between them ($p < 0.001$). 2016 and 2017 showed significantly higher values for the parameters ($p < 0.001$). Significantly lower values for the parameters occur during 2008, 2013, 2014 and 2015.
- Water quality parameters of shallow groundwater sources of Cherai coast reveal that after the tsunami event, SAR showed very high values during January-July 2005 and comes under the permissible class.From 2012 onwards water is good for irrigation since SAR is less than 10.
- In USSL diagram groundwater lies in the region of *C1S1 during October*. The remaining months, water comes under the categories of *C2S1, C3S1, C3S3* and *C3S4,* which showed the saline water intrusion. In December 2008, groundwater having low sodium hazard and medium salinity hazard (*C2S1)*.
- According to measure of corrosion indices water is moderately aggressive as the overall water quality being *slightly corrosive and non-scale forming* (SCNSF) in nature.

- From the Hill-Piper trilinear plot overall groundwater in the study area is saline water type. Gibb’s diagram for groundwater chemistry shows that the study area mostly is controlled by weathering of rock forming minerals.
- Water quality (WQI) water is unfit for direct drinking purpose unless subjected to conventional treatment as most of the period WQI is greater than 100 (WQI>100).
- The ANOVA results showed that parameters differ significantly over the years ($p < 0.001$). TDS have significantly higher value followed by Cl^-, and TH. Significantly lower values are observed for PO_4^{3-}, NO_3^-, SO_4^{2-}, EC, pH, DO and BOD. December 2016 and December 2017 showed significantly higher values for the parameters ($p < 0.001$). Significantly lower values for the water quality parameters occur during 2008, 2013, 2014 and 2015. Years (2008 to 2017) also showed a significant difference between them ($p < 0.001$).

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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., Hydrogeochemistry of Groundwater along a Tsunami Devastated Coastal Segment of Kerala: Arattupuzha Village, Alappuzha, India, *Indian Journal of Geo-Marine Sciences,* (2017) 1765 – 1779

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